

Block

2

INTRODUCTION TO QUANTUM MECHANICS

UNIT 4

Birth of Quantum Physics	7
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UNIT 5

Wave-Particle Duality	37
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UNIT 6

The Uncertainty Principle and its Consequences	67
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UNIT 7

Schrödinger Equation	95
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UNIT 8

Observables and Operators	133
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CONTENTS

Block and Unit Titles	1
Credit page	2
Contents	3
BLOCK 2: INTRODUCTION TO QUANTUM MECHANICS	5
<u>Unit 4 Birth of Quantum Physics</u>	<u>7</u>
4.1 Introduction	8
4.2 Physics at the End of the Nineteenth Century	9
4.3 Black Body Radiation	10
4.3.1 Properties of Black Body Radiation	11
4.3.2 Planck's Law for Black Body Radiation	13
4.3.3 Planck's Quantum Hypothesis	14
4.4 Photoelectric Effect	18
4.4.1 Characteristics of Photoelectric Effect	18
4.4.2 The Quantum Theory of Photoelectric Effect	21
4.4.3 The Momentum of a Photon	24
4.5 Compton Effect	25
4.6 Bohr's Atomic Model	29
4.6.1 Postulates of Bohr's Atomic Model	29
4.6.2 Energy of the Stationary State	30
4.6.3 Bohr's Correspondence Principle	34
4.7 Summary	35
4.8 Terminal Questions	37
4.9 Solutions and Answers	38
<u>Unit 5 Wave-Particle Duality</u>	<u>45</u>
5.1 Introduction	46
5.2 The De Broglie Hypothesis	47
5.2.1 Electron Waves in an Atom	51
5.3 The Davisson- Germer Experiment	52
5.4 Wave-Particle Duality	54
5.5 Matter Waves	55
5.6 Summary	61
5.7 Terminal Questions	62
5.8 Solutions and Answers	62
<u>Unit 6 The Uncertainty Principle and its Consequences</u>	<u>67</u>
6.1 Introduction	68
6.2 The Uncertainty Principle	69
6.2.1 The Uncertainty Principle and Wave-Particle Duality	73
6.2.2 Energy-Time Uncertainty Principle	74
6.3 Some Thought Experiments	76
6.3.1 Heisenberg's Gamma Ray Microscope	76
6.3.2 The Single-Slit Diffraction Experiment	78

6.3.3	The Double-Slit Experiment	80
6.4	Complementarity	82
6.5	Consequences of the Uncertainty Principle	83
6.5.1	The Path of an Object	84
6.5.2	Zero-Point Energy	84
6.5.3	The Size of an Atom	85
6.5.4	Existence of the Electron inside the Nucleus	86
6.5.5	The Angular Momentum of an Object	87
6.6	Summary	88
6.7	Terminal Questions	89
6.8	Solutions and Answers	90
<u>Unit 7 Schrodinger Equation</u>		<u>95</u>
7.1	Introduction	96
7.2	One-dimensional Schrödinger Equation	97
7.3	Probabilistic Interpretation of the Wave Function	102
7.3.1	Phase of the Wave Function	105
7.3.2	Probability Current Density and the Continuity Equation	106
7.3.3	Normalization of the Wave Function	109
7.4	Time Independent Schrödinger Equation	111
7.5	Acceptable Solutions of the Schrödinger Equation	117
7.6	Summary	119
7.7	Terminal Questions	121
7.8	Solutions and Answers	123
<u>Unit 8 Observables and Operators</u>		<u>133</u>
8.1	Introduction	134
8.2	Quantum Mechanical Operators	135
8.2.1	The Parity Operator	138
8.2.2	Properties of Operators	140
8.2.3	Commutators in Operator Algebra	142
8.2.4	Basic Commutator Algebra	143
8.2.5	Linear and Antilinear Operators	145
8.3	Expectation Values	146
8.3.1	Hermitian Operators	149
8.3.2	Eigenfunctions and Eigenvalues	153
8.3.3	Commuting and Non-Commuting Operators	155
8.3.4	Orthonormal Eigenfunctions	156
8.4	Ehrenfest Theorem	159
8.5	Some Postulates of Quantum Mechanics	163
8.6	Summary	164
8.7	Terminal Questions	167
8.8	Solutions and Answers	168
Further Readings		174
Table of Physical Constants		175
List of Blocks and Units: BPHET-141		176
Syllabus: Elements of Modern Physics (BPHET-141)		177

BLOCK 2 : INTRODUCTION TO QUANTUM MECHANICS

In Block 1, you have studied the theory of special relativity, formulated by Einstein in 1905. You have learnt how it generalizes classical physics to include the domain of high velocities and, in the process, radically alters our notions of space and time. In the theory of special relativity, the velocity of light (c) plays a fundamental role; it is the upper limit of the velocity of any material particle. Newtonian mechanics is an accurate approximation to relativistic mechanics in the domain where all relevant particle velocities are much smaller than c . You should note, however, that Einstein's special theory of relativity does not modify the clear distinction between matter and radiation, which is at the root of classical physics. Indeed all pre-quantum physics, relativistic or non-relativistic, is now referred to as classical physics.

During the late nineteenth century and the first quarter of the twentieth century, experimental evidence accumulated about the behaviour of atomic objects (electrons, protons, neutrons, photons, etc.), which required new concepts radically different from those of classical physics. Initially new ideas were introduced in an adhoc fashion. But between the years 1925 and 1927, Schrödinger, Heisenberg and Born evolved a consistent description of the behaviour of matter on a microscopic scale. Their work led to the birth of a new theory known as quantum mechanics.

What is quantum mechanics? To quote Richard Feynman, an outstanding physicist of the twentieth century: "Quantum mechanics is the description of the behaviour of matter in all its details and, in particular, of the happenings on an atomic scale."

Quantum mechanics is a totally new way of interpreting data and predicting the behaviour of microscopic particles based on the idea of an essential discontinuity, the quantum, in the affairs of the world. Compared to the world-view of classical physics, quantum mechanics gives us a radically new view of the world. The discovery of quantum mechanics proceeded along two important but separate tracks. The first track was based on the realization that the exchange of energy between electromagnetic waves and matter takes place in discrete units of energy – they involve quantum jumps. This track began with Max Planck's explanation of black-body radiation spectrum and got a big boost from Neils Bohr's theory of the hydrogen atom. It was ultimately carried to fruition by Werner Heisenberg who formulated the matrix mechanics version of quantum mechanics.

The second track began with Albert Einstein's explanation of the photoelectric effect and his discovery of the wave-particle duality of light. Louis de Broglie generalised the attribute of wave-particle duality to matter. Erwin Schrödinger discovered the wave equation for matter waves and Max Born interpreted the de Broglie-Schrödinger waves as waves of probability. This was the wave mechanics version of quantum mechanics. Finally, it was P A M Dirac who showed that the two versions, matrix mechanics and wave mechanics, are equivalent.

The basic concepts of quantum mechanics (wave-particle duality, uncertainty principle, quantization of physical quantities, etc.) are directly related to the existence of a universal constant, called Planck's constant h . Just as the velocity of light plays a central role in relativity, so does Planck's constant in quantum mechanics. Since Planck's constant is very small, quantum physics is relevant essentially for phenomena at the atomic and subatomic levels.

In 1959, Richard Feynman gave a lecture entitled "**There's Plenty of Room at the Bottom: An Invitation to Enter a New Field of Physics**" in which he considered the possibility of

direct manipulation of individual atoms, denser computer circuitry, and microscopes with tiny resolving power. Just a few decades later, with improvement in material processing and characterization techniques as also computational facilities, the quantum properties of materials are being extensively used in devices; quantum mechanical concepts dominate technology at the nanoscale. In Blocks 2 and 3, we will tell you about how quantum mechanics is used in modern technology, in brief.

In this block, we will introduce the basic concepts of quantum mechanics. We will begin our discussion by briefly presenting, in **Unit 4** entitled **Birth of Quantum Physics**, three important experimental results (of black-body radiation, photoelectric effect and Compton effect) along with the quantum hypothesis of Planck and Einstein's explanation of the photoelectric effect. We also discuss Bohr's atomic model, which was spectacularly successful in explaining the line spectra of hydrogen. We also state Bohr's correspondence principle, which he himself described as the analogy between between classical and quantum mechanics.

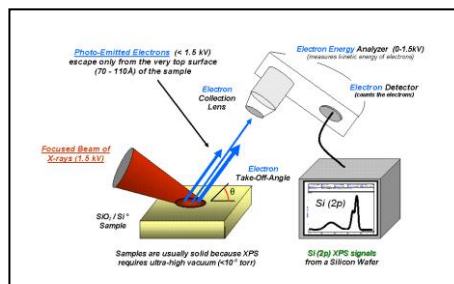
In **Unit 5**, entitled **Wave-Particle Duality**, we describe de Broglie's hypothesis, which introduces the concept that the "dual" or "wave-particle" nature of radiation is a universal characteristic of all matter; it is also a statement about the inherent symmetry of nature. We discuss matter waves, wave-particle duality and the important electron diffraction experiment, which confirmed the existence of matter waves for the first time. In **Unit 6**, entitled **The Uncertainty Principle and its Consequences**, we describe the uncertainty principle, another fundamental principle of quantum mechanics. It is one of the most fundamental differences between classical and quantum physics. It tells us that there is limit to the accuracy with which certain pairs of variables can be measured simultaneously in an experiment. We also describe three important thought experiments, which make it clear that the uncertainty principle is a limitation inherent to quantum physics and not a shortcoming of the measurement apparatus.

The last two units of this block (**Units 7 and 8**) are dedicated to describing the mathematical framework of quantum mechanics. In **Unit 7**, aptly titled **Schrödinger Equation**, we focus on Schrödinger's description of quantum mechanics because the mathematics is familiar to you. The wave nature of particles, first envisaged by de Broglie served as the foundation for the development of the explicit wave equation by Erwin Schrödinger. It describes the evolution of matter waves in space and time. You will also understand what matter waves actually are and learn the properties of an acceptable wave function for physical system. In **Unit 8**, entitled **Observables and Operators**, you learn the language of operators, which describe the dynamical variables for a quantum system. You also learn how to use them and calculate the expectation values of dynamical variables.

The quantum mechanical way of calculating is quite different from the classical ways; you will find that you have to get used to a radically new way of thinking. So, you will also have to learn to think quantum mechanically. If you work through the steps of each derivation and the examples, SAQs and Terminal Questions given in the units, you will understand the concepts better.

We wish you success!

UNIT 4



X-Ray Photoelectron Spectroscopy is a technique based on the photoelectric effect, which is used to identify the elements inside a material.

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BIRTH OF QUANTUM PHYSICS

Structure

- | | | | |
|-----|--|-----|-----------------------------------|
| 4.1 | Introduction | 4.5 | Compton Effect |
| | Expected Learning Outcomes | 4.6 | Bohr's Atomic Model |
| 4.2 | Physics at the end of the Nineteenth Century | | Postulates of Bohr's Atomic Model |
| 4.3 | Black Body Radiation | | Energy of the Stationary State |
| | Properties of Black Body Radiation | | Bohr's Correspondence Principle |
| | Planck's Law for Black Body Radiation | 4.7 | Summary |
| | Planck's Quantum Hypothesis | 4.8 | Terminal Questions |
| 4.4 | Photoelectric Effect | 4.9 | Solutions and Answers |
| | Characteristics of Photoelectric Effect | | |
| | The Quantum Theory of Photoelectric Effect | | |
| | The Momentum of a Photon | | |

STUDY GUIDE

In this unit, you will learn about the major experiments that gave rise to an entirely new understanding of the physical world and a new branch of physics. In the Physics elective courses of the first four semesters you have studied the fundamental principles of mechanics, optics, thermodynamics and electromagnetic theory in great detail. The results of these experiments could not be explained by these classical theories that you have studied. You will understand this unit better if you revise the basic concepts of electromagnetic theory (Block 4, BPHCT 133) and the experiment of black body radiation (Unit 11, BPHCT 135).

“Experiment is the only means of knowledge at our disposal. Everything else is poetry, imagination...”

Max Planck

4.1 INTRODUCTION

In fact, Newtonian mechanics also does not work in the realm of very strong gravity and to understand that, you need the general theory of relativity, which you would study in physics courses at a higher level.

In Block 1 of this course you have studied how **Newtonian mechanics** breaks down when you study systems that move at speeds close to the speed of light. To understand these systems, we apply the special theory of relativity (read the margin remark). In this unit you will learn that Newtonian mechanics is not applicable to microscopic systems, such as atoms and their constituents. Quantum physics is the theory that explains best the behaviour of microscopic objects. We do not observe these effects in our daily life, for the most part.

The ideas introduced in quantum mechanics are far removed from the classical ideas that you have studied so far and may be difficult to imagine. To understand why it was necessary to introduce these ideas, in the first part of this unit, we discuss the results of three important experiments, namely, **black body radiation**, **photoelectric effect** and **Compton Effect**. This will also give you a glimpse into the initial years of the development of quantum physics. In Sec. 4.2, we review our understanding of the physics of natural phenomena at the end of the nineteenth century, which rested on two pillars – the particulate nature of matter and the wave nature of electromagnetic radiation.

In Sec. 4.3, we discuss black body radiation, which you have studied in Unit 11 of the course BPHCT 135 (Thermal Physics and Statistical Mechanics). We revisit the notion of emission and absorption of light in discrete packets or “quanta” of radiation, which emerged from Planck’s theory of black-body radiation. In Sec. 4.4, you will study the photoelectric effect and how it led to the description of light itself as a collection of photons. In Sec. 4.5, you will learn about Compton Effect, which further established the notion of photons as **tiny quanta of energy**. Finally, in Sec. 4.6, we present Bohr’s model of the atom and explain how it led to an understanding of atomic spectra of hydrogen. This was one of the spectacular successes of what is now called the “old” quantum theory. We also discuss Bohr’s Correspondence Principle which talks about the **classical limit of a quantum system**.

In the next unit, you will study about wave-particle duality and the de Broglie hypothesis, which laid the foundation for the mathematical formulation of quantum physics.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ list the properties of the spectral distribution of black body radiation ;
- ❖ explain Planck’s quantum hypothesis;
- ❖ describe the photoelectric effect experiment and its characteristics;
- ❖ describe why the characteristics of photoelectric effect cannot be explained by classical theories;

- ❖ describe how Einstein's hypothesis of the "quanta" of electromagnetic radiation can explain all the observed characteristics of photoelectric effect;
- ❖ describe Compton Effect and how it is explained by the particle nature of radiation,
- ❖ state the postulates of Bohr's atomic model for hydrogen;
- ❖ derive the expression for the energy of the stationary states of hydrogen and describe how Bohr's atomic model can explain its discrete line spectrum; and
- ❖ explain Bohr's correspondence principle.

4.2 PHYSICS AT THE END OF THE NINETEENTH CENTURY

Until the end of the nineteenth century it was believed that all matter, be it solids, liquids or gases, was made up of particles. A particle can be thought of as a quantity of matter. You know that Newtonian mechanics studies the behaviour of these particles by assigning a set of well-defined kinematic variables to each one of them: **position, velocity, momentum and energy**. Each of these dynamical variables can be measured precisely at any instant of time because they follow a set of simple mathematical laws (Newton's laws of motion). All natural phenomena arising from the motion of these particles were believed to be governed by these laws. Even while investigating the thermal properties of material bodies (Kinetic Theory, Block 1, BPHCT 135), heat was assumed to be a consequence of the random motion of the molecules comprising the body. In fact, one of the most important theorems of statistical mechanics (the study of the average behavior of large assemblies of particles undergoing random motion), the "Equipartition Theorem", which you have studied in Unit 2 of BPHCT 135, can also be derived from Newton's laws.

It was thought that these laws could be extended to not just atoms, but also to the subatomic particles. Thomson's discovery of the electron (in 1896) and the discovery that in being deflected by electric and magnetic fields, cathode rays behaved just like tiny lumps of charged matter, seemed to confirm the Newtonian picture.

On the other hand, all radiation was believed to have a wave-like nature, confirmed by experiments on interference and diffraction. Maxwell's electromagnetic theory (1865-1873) showed that light was the visible part of a vast spectrum of electromagnetic waves.

Thus, the physical universe was believed to be made up of two parts: matter made up of particles, that followed Newton's laws and electromagnetic radiation made up of waves that were governed by Maxwell's equations (read the margin remark). The birth of quantum physics essentially eliminated this neat division of the physical world into particles and waves.

These areas are designated as "Classical Mechanics" and "Classical Electrodynamics", respectively.

In the next section, we start by describing the very first experiment that led to the idea that the exchange of radiation with matter takes place in discrete units. Classical thermodynamics and statistical mechanics, which were so successful in understanding the thermal properties of matter, proved to be singularly unsuccessful when it came to explaining the properties of the radiation emitted by heated bodies.

4.3 BLACK BODY RADIATION

In fact, even when objects appear to be cool, they are emitting radiation, mostly in the infrared range. Night vision devices actually capture this infrared radiation to detect objects!

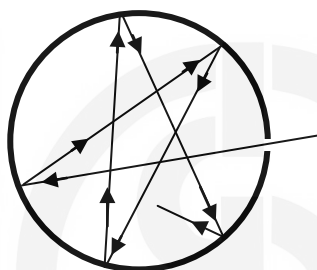


Fig.4.1: A black body enclosure.

The idea of a black body was introduced by **Gustav Kirchhoff** in 1860 :

*"...the supposition that bodies can be imagined which, for infinitely small thicknesses, completely absorb all incident rays, and neither reflect nor transmit any. I shall call such bodies **perfectly black**, or, more briefly, **black bodies**"*

- **Annalen der Physik:** 109, 275-301 (1860)

As you well know, all material bodies above a temperature of absolute zero, radiate heat and light – that is electromagnetic radiation of different wavelengths. You have studied about this in Unit 11 of BPHCT-135.

When the temperature of the heated body is low (say about a 100°C), you have a sensation of warmth when you are near the body. So you can say that some radiation is being emitted which is absorbed by your skin, though it is not visible (read the margin remark). In this case, the emitted electromagnetic radiation is in the infrared region, and has a fairly large wavelength. It produces the sensation of warmth in us. At higher temperatures (of around 600°C , as in the heating element of a typical room heater), a red light is seen. At even higher temperatures, say 2000°C , as in the filament of an electric bulb, a bright white light is seen. So the wavelength of the emitted electromagnetic radiation depends on the temperature of the body (which is why this radiation is sometimes also called thermal radiation). The prominent wavelength of the electromagnetic radiation appears to decrease with increasing temperature of the body while the intensity of the emitted electromagnetic radiation increases with temperature.

In the second half of the nineteenth century, physicists started to study "black body radiation" to understand the properties of thermal radiation. As you know from Unit 11 of BPHCT 135, a black body is an idealized body, which is both a **perfect absorber** and therefore a **perfect emitter of all the electromagnetic radiation incident on it**. It absorbs all the electromagnetic radiation incident on it (without reflecting or transmitting any of it), and emits electromagnetic radiation, which is called the **black body radiation**. The special property of black body radiation is that it depends only on the temperature of the black body and not the material it is made up of. While a perfect black body does not really exist in nature, there are many objects in nature, even stars, that behave approximately like black bodies.

In laboratory experiments, a black body is typically a sealed enclosure with a small hole at the side (Fig. 4.1). The inner walls of the cavity are rough and blackened to ensure that all the electromagnetic radiation entering the cavity through the hole is trapped inside. At a temperature T , when thermodynamic equilibrium is reached, the cavity walls will emit exactly as much electromagnetic radiation as they absorb. This emitted electromagnetic radiation (the black body radiation), coming out of the hole is then analyzed. Keeping the temperature of the cavity fixed, the **energy density of the emitted electromagnetic radiation at each wavelength** (spectral energy density distribution or the spectral distribution) is measured. The result is plotted at different temperatures.

In the next section we briefly list the experimentally observed properties of black body radiation, which you have also studied in Sec. 11.3 of BPHCT 135.

4.3.1 Properties of Black Body Radiation

The typical spectral distribution emitted by a black body at different temperatures is shown in Fig. 4.2.

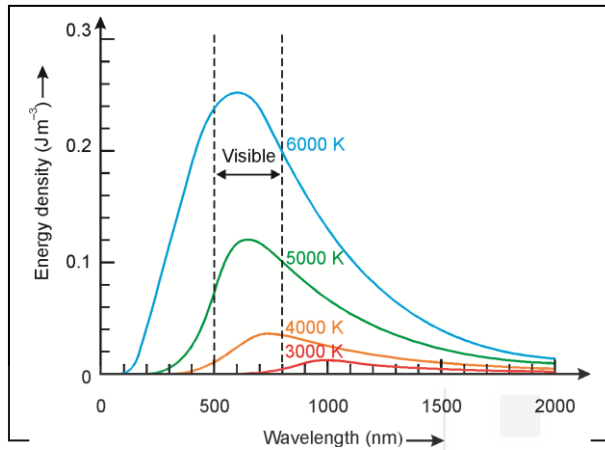


Fig. 4.2: Plot of the spectral energy density of black body radiation with wavelength at different temperatures.

Note from Fig. 4.2 that the black body radiation spectrum has the following properties:

1. The spectrum of a black body is continuous, with some radiation being emitted at all wavelengths.
2. There is a peak in the spectral energy density of the emitted radiation at a particular wavelength.
3. With increasing temperature, the peak wavelength decreases. This follows the Wien's Displacement law (deduced by Wien in 1893 from thermodynamic considerations):

$$\lambda_m T = 2.898 \times 10^{-3} \text{ mK} \quad (4.1)$$

4. The intensity (or flux) at all wavelengths increases as the temperature of the blackbody increases.
5. The total energy being radiated at a given temperature (which is the area under the curve) increases rapidly as the temperature increases. This follows the Stefan-Boltzmann law (deduced empirically by Stefan in 1879 and from thermodynamic considerations by Boltzmann in 1884, Sec. 11.3, Unit 11, BPHCT 135) :

$$E = \sigma T^4 \text{ where } \sigma = 5.672 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4} \quad (4.2)$$

Attempts were made to derive the complex form of the **entire** spectral distribution of black body radiation using the existing theories (thermodynamics, electrodynamics) of the time. In the nineteenth century, the general understanding of the mechanism by which heated bodies emit radiation was the following: heat causes the molecules and atoms in the body to vibrate. It was known from electromagnetic theory that oscillating charges

In late 1890s, precise measurements of the entire black body spectrum, with wavelengths ranging from the ultraviolet to the infrared were made by experimentalists Heinrich Rubens, Ferdinand Kurlbaum, Ernst Pringsheim and Otto Lummer, working at the Imperial Institute of Physics and Technology) in Berlin.

emit electromagnetic radiation and molecules and atoms are complex collections of charges. Therefore, it followed that heated bodies emit electromagnetic radiation of different wavelengths (in the infrared or visible range of wavelengths).

In this picture, a black body cavity at temperature T contains electromagnetic waves which are in thermodynamic equilibrium with the walls of the cavity. These electromagnetic waves continuously exchange energy with the walls of the cavity, or rather with the oscillating charges in the walls of the cavity. In this classical picture, the energy of an oscillator could take any continuous value. So, any amount of energy could be exchanged between the oscillators and the electromagnetic radiation.

Two important laws of black body radiation were derived on the basis of this classical picture of electromagnetic radiation, namely, Wien's Distribution law (1896) and the Rayleigh-Jean's law (1900). We will briefly explain the physical assumptions of these theories so that you can appreciate the extraordinary ideas of Planck.

To derive his law for the spectral energy distribution of black body radiation, Wien assumed that the **radiation is emitted by molecules, whose velocities are governed by the Maxwell-Boltzmann distribution. He also assumed that the wavelength of the radiation emitted by the molecules is a function only of the velocity of the molecule.** He derived the following law for the spectral energy density $u(\lambda, T)$ (the energy per unit volume) in the interval of wavelength $d\lambda$ as:

$$u(\lambda, T)d\lambda = A\lambda^{-5}e^{-a/\lambda T}d\lambda \quad (4.3)$$

where A and a are constants. However, this law could not explain the spectral distribution at long wavelengths.

Rayleigh-Jean's law is based on another approach to the problem: it focused on the behaviour of the electromagnetic waves inside the cavity and not on the behaviour of the oscillating charges in the walls of the cavity. The only assumption was that each of these oscillators has its own characteristic frequency and emits electromagnetic radiation of the same frequency. Since all the radiation incident on the black body is radiated by it, it is as if the entire radiation is reflected from the walls of the cavity, leading to the formation of standing electromagnetic waves. The standing electromagnetic waves must have nodes at the walls of the container. So there is a restriction on the allowed values of the wavelength of the electromagnetic radiation. The number of allowed modes of vibration per unit volume inside the cavity in a range of wavelength λ to $\lambda + d\lambda$ was calculated to be:

$$n(\lambda)d\lambda = \frac{8\pi}{\lambda^4}d\lambda \quad (4.4)$$

Assigning an energy of $k_B T$ ($\frac{1}{2}k_B T$ for the oscillating electric field and

$\frac{1}{2}k_B T$ to the oscillating magnetic field) to each mode of vibration, the spectral energy density in accordance with the law of equipartition of energy is:

$$u(\lambda, T)d\lambda = \frac{8\pi k_B T}{\lambda^4} d\lambda \quad (4.5)$$

While this law gives a good agreement with experimental results at the higher wavelengths, it diverges at the lower wavelengths (called the ultraviolet catastrophe)! Further it also implies that whatever be the temperature of the black body, the total energy emitted by it (which is total area under the curve

$\left(\int_0^\infty u(\lambda) d\lambda \right)$ is always infinite. This stands in contradiction with the law of

conservation of energy (read the margin remark). Let us summarise what we have studied so far.

PROPERTIES OF BLACK BODY RADIATION

The spectral distribution of black body radiation has the following main properties:

- There is a peak in the spectral energy density at a particular wavelength. The peak wavelength decreases with increasing temperature according to the Wien's Displacement law:

$$\lambda_m T = 2.898 \times 10^{-3} \text{ mK} \quad (4.1)$$

- The intensity of the radiation increases with increasing temperature for all wavelengths. The total energy radiated at a given temperature increases rapidly with temperature and follows the Stefan-Boltzmann law:

$$E = \sigma T^4 \text{ where } \sigma = 5.672 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4} \quad (4.2)$$

Two important laws for the spectral energy density $u(\lambda, T)$ of black body radiation in the interval of wavelength $d\lambda$ based on classical considerations are:

- Wien's Law: $u(\lambda, T)d\lambda = A\lambda^{-5} e^{-a/\lambda T} d\lambda \quad (4.3)$

- Rayleigh-Jean's Law: $u(\lambda, T)d\lambda = \frac{8\pi k_B T}{\lambda^4} d\lambda \quad (4.5)$

Neither of these laws was able to explain the black body spectrum over the complete range of wavelengths.

This is the drawback of applying classical statistical mechanics to electromagnetic radiation in the form of waves. Classical statistical mechanics and the ensuing law of equipartition of energy works well for a gas of molecules. This is mainly because, however large the number of molecules in a container, the number is essentially finite. So, assigning a finite energy to each mode of vibration of a molecule cannot lead to infinite energy. On the other hand, the number of possible modes of vibration in electromagnetic waves in the same container is infinite and so is its energy!

4.3.2 Planck's Law for Black Body Radiation

The correct description of the black body radiation curves **over the entire range of wavelengths** comes from Planck's law for the spectral energy distribution of black body radiation. Planck (in October 1900, in a presentation to the German Physical Society) proposed the following empirical function for the energy density, to fit the experimental results for black body radiation:

**Max Planck**

(1858 – 1947) was a German theoretical physicist. He studied physics at the Universities of Munich and Berlin and received his doctorate at the age of 21 and went on to be a Professor at the University of Berlin. He made substantial contributions to physics but is best known for his hypothesis of energy quanta for which he was awarded the **Nobel Prize in Physics in 1918**.

"We consider, however – this is the most essential point of the whole calculation – E to be composed of a very definite number of equal parts and use thereto the constant of nature

$$h = 6.55 \times 10^{-27} \text{ erg} \cdot \text{sec.}$$

This constant multiplied by the common frequency ν of the resonators gives us the energy element ϵ in erg, and dividing E by ϵ we get the number P of energy elements which must be divided over the N resonators."

M. Planck, Verhandl. Dtsch. phys. Ges., 2, 237 (1900)

$$u(\lambda, T) d\lambda = \frac{b\lambda^{-5}}{e^{a/\lambda T} - 1} d\lambda \quad (4.6)$$

where a and b were constants yet to be determined. He then attempted to arrive at a theoretical justification for the law [Eq. (4.6)] which fit the experimental data so well. Note that he continued to assume the classical (purely wave) nature of the electromagnetic radiation in the cavity. Like his predecessors, he also assumed **that the walls of the cavity had multitudes of oscillators of all possible frequencies**. And also that an oscillator with a frequency ν , can only absorb or emit radiation with a frequency ν .

To model the absorption and emission of electromagnetic radiation by these oscillators, he argued that the spectral energy density of the black body radiation over a range of frequency $d\nu$ is nothing but the product of the number of oscillators having a frequency between ν and $\nu + d\nu$, $g(\nu)$ and the average energy $\langle E \rangle$, of an oscillator having a frequency ν :

$$u_\nu d\nu = g(\nu) \langle E \rangle d\nu \quad (4.7a)$$

Or equivalently in terms of the wavelength as:

$$u(\lambda) d\lambda = n(\lambda) \langle E \rangle d\lambda \quad (4.7b)$$

To arrive at his final results (December, 1900), he had to make an assumption that was **totally different from classical ideas**. The following expression is Planck's formula or **Planck's law** for black body radiation:

$$u(\lambda, T) d\lambda = \frac{8\pi hc \lambda^{-5}}{e^{hc/\lambda k_B T} - 1} d\lambda \quad (4.8)$$

He introduced the constant h (Planck's constant, also called the Planck's quantum of action), a universal constant with the value $h = 6.6261 \times 10^{-34} \text{ Js}$. His law also led to the first determination of the value of another universal constant $k_B = 1.3807 \times 10^{-23} \text{ JK}^{-1}$, now called the Boltzmann constant by fitting the law to the existing experimental data on black body radiation.

4.3.3 Planck's Quantum Hypothesis

He put forward the hypothesis that the energy of an oscillator in the wall of the black body enclosure cannot vary continuously but must take on one of the following discrete values (read the margin remark for a quote from his original publication):

$$0, h\nu, 2h\nu, 3h\nu, \dots, nh\nu$$

where ν is the frequency of the oscillator and h , Planck's constant. So, the energy of a **Planck oscillator** is "quantized" and can be written as:

$$E_n = nh\nu, \text{ with } n = 0, 1, 2, 3 \quad (4.9)$$

From this it followed that the electromagnetic radiation inside the cavity could exchange energy with an oscillator in the wall of the cavity only in **discrete amounts** or "**quanta**", and the energy of each quantum is given by:

$$\Delta E = h\nu$$

(4.10)

In later nomenclature, as introduced by Bohr in his atomic model, which you will study in Sec. 4.6, we say that the natural number n is the “**quantum number**” that refers to the “**quantum state**” of the oscillator:

$$\text{Quantum State } n=1 \Rightarrow \text{Energy } E_1 = h\nu$$

$$\text{Quantum State } n=2 \Rightarrow \text{Energy } E_2 = 2h\nu \text{ ...etc}$$

While each oscillator can have infinitely many quantum states (Fig. 4.3), the **minimum** energy difference between these states is $h\nu$. When an oscillator having a frequency ν **absorbs** energy from the electromagnetic radiation, it must do so in units of $h\nu$ and this absorption would send the oscillator to a **higher** quantum state (higher value of n). Similarly, when an oscillator **emits** energy from the electromagnetic radiation, it must also do so in units of $h\nu$ and this **emission** would send the oscillator to the next **lower** quantum state (lower value of n).

While there is no upper limit on the amount of electromagnetic radiation that can be absorbed/emitted, it must be in integral multiples of $h\nu$. Even more importantly, if the energy quantum is not exactly $h\nu$, it is neither absorbed nor emitted.

You may now wonder how these assumptions change the law for the spectral density of black body radiation. In Planck's model, the average energy of a wave with a particular wavelength (frequency) is **not** $k_B T$ as given by the equipartition theorem. Assuming that the probability of occupation of a quantum state n of the oscillator at a temperature T is given by the classical Boltzmann distribution ($e^{-nh\nu/k_B T}$), he calculated **the average energy of a mode of vibration** or **the average energy of an oscillator of energy $h\nu$** to be (read the margin remark):

$$\langle E \rangle = \frac{h\nu}{e^{h\nu/k_B T} - 1} \quad (4.11)$$

Using $\lambda = c/\nu$ we get the following expression for the average energy in terms of the wavelength:

$$\langle E \rangle = \frac{hc\lambda^{-1}}{e^{hc/\lambda k_B T} - 1} \quad (4.12)$$

When this is multiplied by Eq. (4.4), which is number of modes of vibration in a range of wavelength λ to $\lambda + d\lambda$, we can get Eq. (4.8). Planck's law can also be written in terms of the frequency:

$$u(\nu, T) d\nu = \frac{8\pi h\nu^3}{c^3 (e^{h\nu/k_B T} - 1)} d\nu \quad (4.13)$$

Note that this law agrees with the experimental results at both the short and long wavelength limits. You can work out for yourself in Terminal Question 1

$$E_n = nh\nu$$

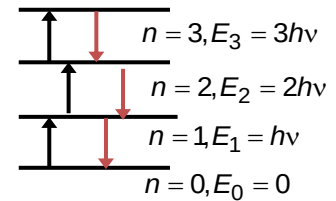


Fig. 4.3: The energy levels of an oscillator of frequency ν . When the oscillator absorbs a unit $h\nu$ of energy, it moves into a **higher quantum state (black arrows). When the oscillator emits a unit $h\nu$ of energy, it moves into a **lower** quantum state (red arrows).**

The average energy of an oscillator of frequency ν is:

$$\begin{aligned} \langle E \rangle &= \frac{\sum_{n=0,1,2,\dots} [nh\nu e^{nh\nu/k_B T}]}{\sum_{n=0,1,2,\dots} [e^{nh\nu/k_B T}]} \\ &= \frac{h\nu}{e^{h\nu/k_B T} - 1} \end{aligned}$$

how Planck's law reduces to Wien's Distribution law and the Rayleigh-Jean's law at short and long wavelengths, respectively.

Let us now work out an example on Planck's hypothesis.

Small values of energies are usually written in units of the electron volt (eV).

$$1\text{eV} = 1.6 \times 10^{-19} \text{ J}$$

$$1\text{meV} = 10^{-3} \text{ eV}$$

$$1\text{MeV} = 10^6 \text{ eV}$$

The value of the Boltzmann constant can be written in units of eVK^{-1} as:

$$k_B = 8.617 \times 10^{-5} \text{ eVK}^{-1}$$

EXAMPLE 4.1 : PLANCK OSCILLATOR

A quantum oscillator in the wall of a black body cavity has frequency $4.00 \times 10^{14} \text{ Hz}$. Calculate

- the energy of the first three quantum states,
- the spacing between the energy levels, and
- the average energy of the oscillator at 3000 K.

SOLUTION ■ The energy of the first three quantum states are calculated using Eq. (4.9) with $\nu = 4 \times 10^{14} \text{ Hz}$ and $n = 1, 2, 3$, respectively.

$$\begin{aligned} \text{i) } E_1 &= h\nu = (6.626 \times 10^{-34} \text{ Js}) \times (4 \times 10^{14} \text{ Hz}) = 26.504 \times 10^{-20} \text{ J} \\ &= \left(\frac{26.504 \times 10^{-20}}{1.6 \times 10^{-19}} \right) \text{ eV} = 1.66 \text{ eV} \text{ (see margin remark)} \end{aligned}$$

$$E_2 = 2h\nu = 2 \times 1.66 \text{ eV} = 3.32 \text{ eV}$$

$$E_3 = 3h\nu = 4.98 \text{ eV}$$

- Using Eq. (4.10) we calculate the energy difference between the states as: $\Delta E = h\nu = 1.66 \text{ eV}$

- Using Eq. (4.11) with $h\nu = 1.66 \text{ eV}$, and the Boltzmann constant $k_B = 8.617 \times 10^{-5} \text{ eVK}^{-1}$, the average energy at is

$$\begin{aligned} \langle E \rangle &= \frac{h\nu}{e^{h\nu/k_B T} - 1} = \frac{1.66 \text{ eV}}{\exp \left[\frac{1.66 \text{ eV}}{8.617 \times 10^{-5} \text{ eVK}^{-1} \times 3000 \text{ K}} \right] - 1} \\ &\approx 2.71 \text{ meV} \end{aligned}$$

For molecules, the typical vibrational frequencies are also in the range of $10^{13} - 10^{14} \text{ Hz}$. Let us now work out the typical energy spacing $\Delta E = h\nu$ for a classical oscillator, for example, a spring-mass system, which you have studied in BPHCT 131.

SAQ 1 - Planck's quantum hypothesis

Calculate the spacing between the energy levels of a spring-mass system for a mass of 5.0 g attached to a spring of spring constant 3000 Nm^{-1} .

From SAQ 1, you can see that the energy difference $\Delta E = h\nu$ between the consecutive energy levels for a classical oscillator is very small. To all intents and purposes, we can assume that the exchange of energy of a classical oscillator is continuous and not discrete. This should reassure you that quantum physics **does not change the way macroscopic objects are described** in classical physics, which you have studied so far.

Rather than assuming anything about the nature of electromagnetic radiation, Planck believed that it was the internal workings of the atoms in the walls of the black body cavity that allowed them to absorb and emit energy in discrete packets. He considered his idea of energy quantization to be, in his own words, “an act of desperation”. In fact, for years afterwards, he tried to fit his quantum ideas into a classical theory and reconciled to it much later (read margin remark)!

“The hypothesis of quanta will never vanish from the world”
Max Planck, 1911.

PLANCK'S LAW

Recap

Planck's law for black body radiation is:

$$u(\lambda, T)d\lambda = \frac{8\pi hc\lambda^{-5}}{e^{hc/\lambda k_B T} - 1} d\lambda \quad (4.8)$$

Planck's quantum hypothesis states that the energy of an oscillator of frequency ν , in the wall of the black body enclosure cannot vary continuously, it must have one of the following discrete values:

$$E_n = nh\nu, \quad \text{with } n = 1, 2, 3 \quad (4.9)$$

where $h = 6.6261 \times 10^{-34}$ Js is Planck's constant.

The exchange of energy between the electromagnetic radiation inside the cavity and an oscillator in the wall of the cavity can take place in **discrete amounts** or “**quanta**”, each quantum having energy:

$$\Delta E = h\nu \quad (4.10)$$

The average energy of a Planck oscillator of energy $h\nu$ at a temperature T is:

$$\langle E \rangle = \frac{h\nu}{e^{h\nu/k_B T} - 1} = \frac{hc\lambda^{-1}}{e^{hc/\lambda k_B T} - 1} \quad (4.11)$$

It was Einstein who realised, in 1905, the inconsistency in Planck's description of oscillators in the walls of a black body having **quantized** energies and the classical **wave** description of electromagnetic radiation in the enclosure of the black body. He surmised that electromagnetic radiation is itself composed of discrete, irreducible amounts of energy or “quanta”. With this he was able to explain the experimental features of photoelectric effect, which you will now study.

4.4 PHOTOELECTRIC EFFECT

It is a strange coincidence that Hertz discovered the photoelectric effect in the same experiments (1886-1887) that confirmed the existence of electromagnetic waves.

In the year 1905, the 26 year old Albert Einstein published four ground breaking papers on three different topics: photoelectric effect, Brownian motion and special relativity, which laid the foundations of modern physics. This year is widely regarded as his Annus Mirabilis (miracle year).

When light of a sufficiently high frequency falls on a metal surface, electrons are emitted. This phenomenon is called the **photoelectric effect** and the electrons that are emitted are called **photoelectrons**. In 1887, Heinrich Hertz first demonstrated that charges are emitted when ultraviolet light is incident on a clean metal surface. The experimental characteristics of photoelectric effect, as established by several scientists, could not be explained by classical electromagnetic theory. Eventually, this led to Einstein's famous 1905 paper (read the margin remark) on this topic which challenged the classical wave picture of light.

Fig. 4.4 shows a schematic diagram of the apparatus that was used in some of these experiments. Note in the figure that a tube contains two electrodes connected to an external circuit. The anode is made up of the metal plate on which light falls. This is also called the photoelectrode. Photoelectrons are emitted when light falls on the metal surface. Some of these electrons have sufficient energy to reach the cathode despite its negative polarity. Such electrons constitute the current (photocurrent) that is measured by the ammeter in the circuit. The potential difference between the electrodes can be increased or decreased. The electrodes are enclosed in an evacuated gas chamber so that the kinetic energy of the photoelectrons is not reduced by collisions with air molecules.

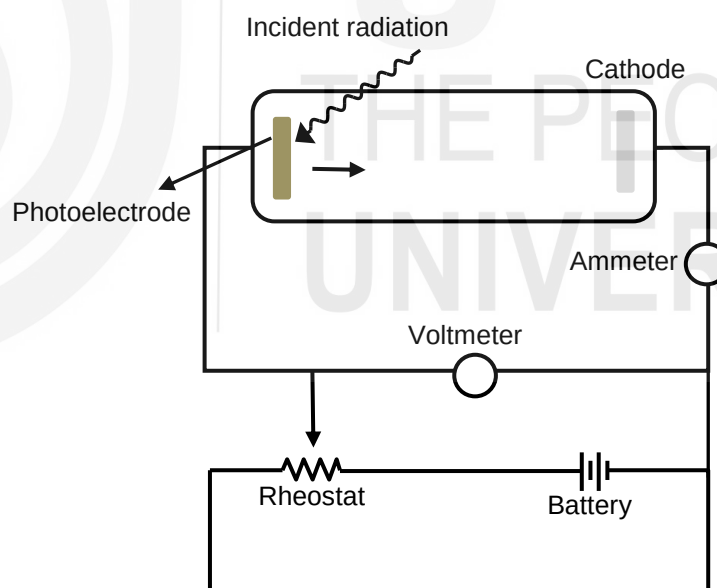


Fig. 4.4: Schematic diagram of the photoelectric effect experiment.

Several measurements were made with this setup, which we now describe. These bring out the characteristics of photoelectric effect that could not be explained by electromagnetic theory.

4.4.1 Characteristics of Photoelectric Effect

We now describe the key observations made in the experiment on the photoelectric effect.

- i) **Instantaneous emission of photoelectrons:** Current in the circuit started flowing as soon as light was incident on the anode. The time lag between shining the light on the metallic anode and the emission of photoelectrons is only about 10^{-9} s. This is true **even when the energy of the incident radiation** is very low.
- ii) **Cut-off frequency:** Photocurrent flowed in the circuit only when the incident light had a **minimum frequency** called the **cut-off frequency or threshold frequency**. If the frequency of incident light was less than that, current would not flow even if the intensity of radiation were increased. It was observed that the value of the cut-off frequency depended on the material of the anode emitting the electrons. It was different for different materials. The cut-off frequencies for two metals are shown in Fig. 4.5.
- iii) **Maximum kinetic energy is independent of the intensity of incident light:** It was observed that for a particular frequency of light, the photoelectrons possessed a maximum kinetic energy (K_{max}). K_{max} increased linearly with frequency (Fig. 4.5). It did not depend on the intensity of light.

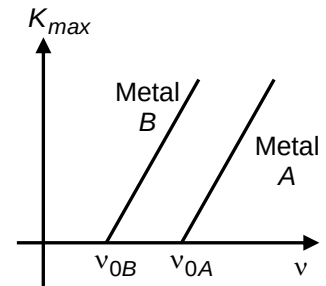


Fig. 4.5: Variation of the maximum kinetic energy of the photoelectrons with frequency for two different metals A and B. The cut-off frequency for the metals are ν_{0A} and ν_{0B} , respectively.

The maximum kinetic energy (K_{max}) was measured by applying a retarding potential between the electrodes. The retarding potential was increased till the photocurrent became zero, and the most energetic photoelectrons could **not** reach the cathode. This potential is known as the **stopping potential** V_S . It is a measure of the maximum kinetic energy:

$$K_{max} = \frac{1}{2} m_e v_{max}^2 = eV_S \quad (4.14)$$

See Fig. 4.6. It is a plot of the typical variation of the photocurrent with the potential difference between the electrodes. Note that the stopping potential V_S is the same for different intensities of light. Therefore, the **maximum kinetic energy K_{max} given by Eq. (4.14) is independent of the intensity** of the incident light.

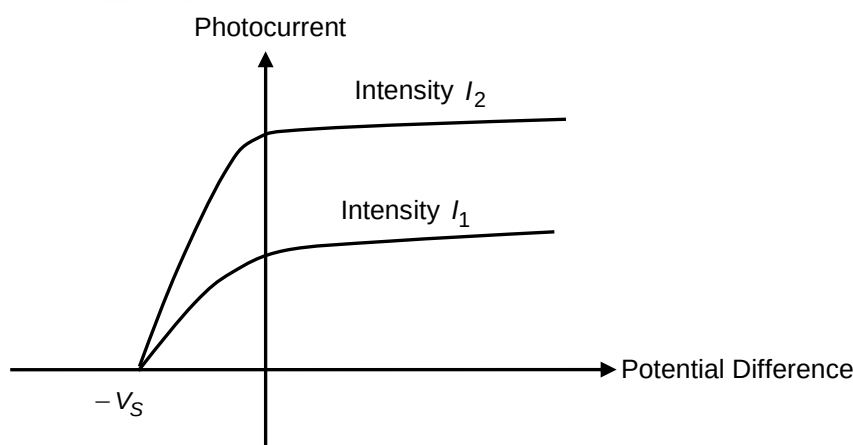


Fig. 4.6: The variation of the photocurrent with the applied potential difference between the electrodes for two different intensities of the incident radiation I_1 and I_2 ($I_2 > I_1$). The stopping potential is independent of the intensity, but the photocurrent increases with the intensity of the radiation.

The electromagnetic theory of light could not explain these experimental observations. Let us see why.

- i) **Instantaneous emission of photoelectrons:** From classical physics, it was known that electrons are not spontaneously emitted from a metal surface. Electrons are bound inside the metal and so a minimum energy is required for their emission from the metal's surface. This binding energy associated with the electron inside a metal is called the **work-function**.

Classically, the transfer of energy from light (the electromagnetic wave) should take time (of the order of a few seconds). There should be a time lapse between the time that the radiation is incident and the electron gathers sufficient energy to be ejected from the electrode.

- ii) **Cut-off frequency:** In the classical picture, the electron absorbs energy continuously from the light wave, irrespective of its frequency. As soon as the electron absorbs sufficient energy to overcome the work function, there should be a photocurrent; electrons should be emitted for light of any frequency having sufficient intensity. There should be no dependence on the frequency of incident light. So, classically, there is no explanation for the existence of a cut-off frequency.

- iii) **Maximum kinetic energy is independent of the intensity of incident light:** Classically, the kinetic energy of the ejected electron should depend only on the intensity of the radiation; it should not depend on the frequency at all. The greater the intensity of the incident radiation, the greater should be the energy absorbed by the electron and its corresponding kinetic energy.

These puzzling characteristics of photoelectric effect that could not be explained by classical electromagnetic theory are summarised below.

CHARACTERISTICS OF PHOTOELECTRIC EFFECT

Photoelectric effect is the phenomenon in which electrons are emitted from a metal surface when electromagnetic radiation, like light, is incident on it. It has the following characteristics:

- When radiation is incident on the photoelectrode, electrons are emitted almost instantaneously (in about 10^{-9} s).
- There is a **minimum cut-off frequency** of the radiation, below which electrons are not emitted from the electrode, no matter how intense the radiation
- Beyond the cut-off frequency, **the maximum kinetic energy of the emitted electrons varies linearly with the frequency of the radiation.**
- The **maximum kinetic energy $K_{\max}$ of the electrons is independent of the intensity** of the radiation.

The characteristic features of photoelectric effect were explained by Einstein in 1905. We will now study his explanation.

4.4.2 The Quantum Theory of Photoelectric Effect

In 1905, Einstein proposed a simple but revolutionary explanation for the photoelectric effect. Recall Planck's postulate from Sec. 4.3: The oscillators in the walls of a black body cavity can emit or absorb radiation in discrete units of energy (quanta). Einstein postulated that the **energy of light is not distributed continuously in space but is carried in discrete packets or (energy) quanta**. In this picture, a beam of monochromatic light of frequency ν is made up of these energy quanta, each of which has an energy $h\nu$:

$$E = h\nu \quad (4.15)$$

The quanta are localized in space (in the way that matter particles are) and can only be emitted or absorbed in **whole** units (you can read his hypothesis from his original paper in the margin remark). Let us see how this postulate explains the properties of photoelectric effect.

According to this postulate, when a light quanta, also called a **photon** (read the margin remark about the naming of light quanta as photons), enters the metal electrode (photoelectrode) – it will give up its **entire energy** ($= h\nu$) to a **single** electron in the electrode. It is not possible for the photon to transfer a part of its energy to the electron and survive as a photon with a reduced energy. Either the photon transfers its entire energy and disappears or it does not transfer any energy at all. The light intensity corresponds to the number of photons incident on unit area of the surface. So increasing the intensity of light increases the number of photons and not the energy of the individual photon, which depends only on its frequency.

The maximum kinetic energy of the electron leaving the surface of the metal is:

$$K_{\max} = h\nu - \phi \quad (4.16)$$

where ϕ is the work function of the metal: It is the minimum energy required to remove an electron from the metal surface. Different metals have different values of the work function as you can see in Table 4.1. Some electrons can leave the metal with a kinetic energy less than $K_{\max}$ because they lose energy in collisions on the way out of the metal.

Let us now write the work function ϕ in terms of a frequency ν_0 as $\phi = h\nu_0$. Then we can rewrite Eq. (4.16) as:

$$K_{\max} = h\nu - h\nu_0 \quad (4.17)$$

When the incident light has a frequency $\nu = \nu_0$, the energy of the photon is $h\nu_0$. So when the photon transfers its energy to the electron, there will be just enough energy to eject the electron from the metal surface but the maximum kinetic energy of the electron will be zero.

And if the frequency of the incident light were less than ν_0 ($\nu < \nu_0$), no individual photon would be able to provide an electron with the energy to be

...one assumes that the energy of light is discontinuously distributed in space. According to the assumption to be contemplated here, when a light ray is spreading from a point, the energy is not distributed continuously over ever-increasing spaces, but consists of a finite number of energy quanta that are localized in points in space, move without dividing, and can be absorbed or generated only as a whole.

Einstein in:
Annalen der Physik
17 (1905) 132-148.

Einstein's paper of 1905 introduced the particle nature of light, which he referred to as "**light quanta**". The word "**photon**" was introduced by the chemist, Gilbert Newton Lewis in a December 18, 1926 letter to the famous science journal, *Nature* to describe a carrier of "radiant energy" – not specifically light, but the name stuck.

Table 4.1: Work Functions of some metals

Element	ϕ (eV)
Cs	1.95
Na	2.28
Mg	3.68
Cd	4.07
Al	4.08
Pb	4.14
Ag	4.73
Ni	5.01
Se	5.11
Pt	6.35

ejected from the metal. So, no matter how intense the incident light is, that is, no matter how many photons are incident on the electrode, electrons are ejected only if the frequency of the incident light is greater than the **cut-off frequency** ν_0 , which is decided by the work function ϕ of the metal. From Eq. (4.17), you can see that $K_{max} > 0$ only when $\nu > \nu_0$ where

$$\nu_0 = \frac{\phi}{h} \quad (4.18)$$

We can also use the relationship between the frequency and wavelength ($\lambda \nu = c$) where c is the speed of light, to introduce the idea of a cut-off wavelength:

$$\lambda_0 = \frac{hc}{\phi} \quad (4.19)$$

So when the incident radiation has a wavelength longer than this **cut-off wavelength**, λ_0 , photoelectric effect will not be observed.

From Eqs. (4.16 and 4.17), it also becomes clear that the maximum kinetic energy of the photoelectrons emitted from a certain metal, K_{max} , depends only on the frequency of the incident radiation through the term $h\nu$. This is because for a particular metal, the work function ϕ is a constant. When the intensity of incident light is increased the **number of photons** incident on the surface increase, and hence the **number of electrons that are ejected**. So increasing the intensity of the incident radiation increases the photocurrent but not K_{max} (or the stopping potential V_S). We can write:

$$K_{max} = eV_S = h\nu - \phi \Rightarrow V_S = \frac{h}{e}\nu - \frac{\phi}{e}$$

or
$$V_S = \frac{h}{e}(\nu - \nu_0) \quad (4.20a)$$

We can also write K_{max} in terms of the wavelength as:

$$K_{max} = eV_S = h\nu - \phi \Rightarrow K_{max} = hc\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right) \quad (4.20b)$$

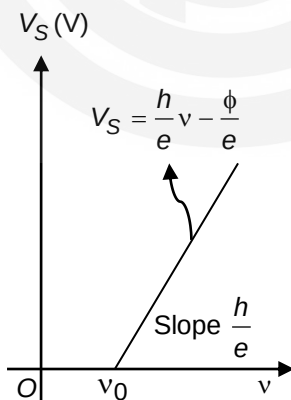


Fig. 4.7: The value of h/e can be calculated from the slope of the plot of the stopping potential V_S with the frequency of the radiation.

So, there is a linear relation between the stopping potential and the frequency of incident radiation, which is also seen experimentally (see Fig. 4.7). The slope of the straight line in Fig. 4.7 is h/e . By calculating the value of the slope from the experimental data of photoelectric effect, the value of h/e can be obtained. When this is multiplied by the value of e , the value of h is obtained. Using data from different experiments on photoelectric effect, Millikan calculated the value of h . The value he calculated was in good agreement with the value obtained from Planck's formula for black body radiation.

That two diverse experiments gave the same value of h is a proof of the fundamental assumption of quantum theory – the particle nature of electromagnetic radiation. **The idea of energy quanta or photons is now extended to the entire electromagnetic spectrum of radiation.** A photon moves with the speed of light and carries an energy

$$E = h\nu = \frac{hc}{\lambda}, \quad \text{where } \lambda \text{ is the wavelength of the radiation.}$$

So, the photon is a localized bundle of energy and not spread over a large area like a classical wave. Therefore, energy transfer between a photon and a single electron is instantaneous when the frequency of light is equal to or above the cut-off frequency. Whatever may be the intensity of the incident light, even if one photon of appropriate energy is incident on the electrode, it will be immediately absorbed by an atom in the metal and the electron will be ejected instantaneously.

Let us now work out an example on photoelectric effect.

EXAMPLE 4.2: PHOTOELECTRIC EFFECT

- The stopping potential observed in a certain experiment on photoelectric effect is 5.0 V. Calculate the maximum kinetic energy and maximum speed of the photoelectrons.
- The cut-off wavelength for copper is 296 nm. Calculate the cut-off frequency, the work function and the maximum kinetic energy of the photoelectrons when ultraviolet light of wavelength 250 nm is incident on a copper photoelectrode.

SOLUTION ■ We use Eqs. (4.14 and 4.17) to solve the problems.

- From Eq. (4.14), the maximum kinetic energy with $V_s = 5.0\text{ V}$ is:

$$K_{\max} = e V_s = 1.6 \times 10^{-19} \text{ C} \times 5.0 \text{ V} = 8.0 \times 10^{-19} \text{ J}$$

You know that the maximum kinetic energy can also be written in terms of the maximum speed of the photoelectrons $v_{\max}$, as:

$$K_{\max} = \frac{1}{2} m_e v_{\max}^2 \quad \Rightarrow \quad v_{\max} = \sqrt{\frac{2K_{\max}}{m_e}} \quad (\text{i})$$

Using Eq. (i) with $K_{\max} = 8.0 \times 10^{-19} \text{ J}$ and the mass of the electron $m_e = 9.109 \times 10^{-31} \text{ kg}$, we get

$$v_{\max} = \sqrt{\frac{2 \times 8.0 \times 10^{-19} \text{ J}}{9.109 \times 10^{-31} \text{ kg}}} = 1.3 \times 10^6 \text{ ms}^{-1}$$

- The cut-off frequency ν_0 is related to the cut-off wavelength λ_0 as:

$$\nu_0 = \frac{c}{\lambda_0} \quad (\text{ii})$$

Using $\lambda_0 = 296 \text{ nm} = 296 \times 10^{-9} \text{ m}$ in Eq. (ii), we get

$$\nu_0 = \frac{3 \times 10^8 \text{ ms}^{-1}}{296 \times 10^{-9} \text{ m}} = 1.01 \times 10^{15} \text{ Hz} \quad (\text{iii})$$

We calculate the work function $\phi = h\nu_0$ with ν_0 from Eq. (iii):

$$\begin{aligned} \phi &= h\nu_0 = (6.626 \times 10^{-34} \text{ Js}) \times (1.01 \times 10^{15} \text{ Hz}) = 6.69 \times 10^{-19} \text{ J} \\ &= 4.18 \text{ eV} \end{aligned}$$

The energy of a photon of wavelength 250 nm is

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ Js}) \times (3 \times 10^8 \text{ ms}^{-1})}{(250 \times 10^{-9} \text{ m})} = .079 \times 10^{-17} \text{ J}$$

$$= 4.94 \text{ eV}$$

So using Eq. (4.19) with $h\nu = E = 4.94 \text{ eV}$ and $\phi = 4.18 \text{ eV}$, we get:

$$K_{\max} = 4.94 \text{ eV} - 4.18 \text{ eV} = 0.76 \text{ eV}$$

You may now like to revise the quantum theory of photoelectric effect.

Recap

QUANTUM THEORY OF PHOTOELECTRIC EFFECT

Einstein postulated that the energy of light is not distributed continuously in space but is carried in discrete packets or (energy) quanta. The energy carried by each quantum of light of frequency ν is given by

$$E = h\nu \quad (4.15)$$

When light of frequency ν is incident on a metal, the maximum possible kinetic energy of the electron leaving its surface is given by:

$$K_{\max} = h\nu - \phi = h\nu - h\nu_0 \quad (4.17)$$

where ϕ is the work function of the metal and ν_0 is the cut-off frequency. In terms of the wavelength of the incident radiation, the maximum kinetic energy of the electrons is:

$$K_{\max} = hc \left(\frac{1}{\lambda} - \frac{1}{\lambda_0} \right) \quad (4.20b)$$

You can now solve the following SAQ.

SAQ 2 - Photoelectric effect

Violet light of wavelength 500 nm is incident on a photoelectrode having a work function of 2.28 eV. Calculate the maximum kinetic energy of ejected electrons and the stopping potential.

There are several practical applications of the photoelectric effect. It is the principle on which solar cells work. Photoemission of electrons is an important technique for investigating the detailed structure of molecules and solids in a method of photoemission spectroscopy. It can be used to determine precisely the valence electron configurations in chemical compounds so that we can understand chemical bonding in a complex compound.

4.4.3 The Momentum of a Photon

So far you have seen that photons are the particles that make up electromagnetic radiation, just as atoms are the constituents of ordinary

matter or electrons, protons, neutrons make up atoms. Yet as you have learnt in Sec. 3.3.2 of Unit 3, the photon is different in the following way:

It always moves in vacuum with the same speed c and it is **massless** (its rest mass $m_0 = 0$). If the rest mass of a particle is zero, how do we determine its momentum or its kinetic energy? In the Newtonian picture, a particle like this cannot even exist!

You have learnt in Sec. 3.3.2 of Unit 3, Block 1 that the relation between the energy and momentum of the photon (or any particle with zero rest mass, massless particle) is given by:

$$E = pc \quad (4.21)$$

which is Eq. (3.34) of Unit 3. You have also learnt that the **linear momentum of a photon** of frequency ν and energy $E = h\nu$, is:

$$p = \frac{E}{c} = \frac{h\nu}{c} \quad (4.22)$$

which is Eq. (3.35) of Unit 3. Using the relation $\lambda\nu = c$, we can also write the linear momentum of the photon in terms of the wavelength λ of the radiation as:

$$p = \frac{E}{c} = \frac{h}{\lambda} \quad (4.23)$$

So like any other particle, the photon also has a linear momentum and it can be described either by its wavelength or by its linear momentum.

Eq. (4.22) is the magnitude of the linear momentum of the photon. In Sec. 17.2 of Unit 17 of the second semester course Electricity and Magnetism (BPHCT 133), you have studied that the direction of propagation of an electromagnetic wave is given by the wave vector $\vec{k}$ where the magnitude of $\vec{k}$ (the wave number) is $k = \frac{2\pi}{\lambda}$. The photon also moves along $\vec{k}$. So, we

write the vector form of the linear momentum of a photon as:

$$\vec{p} = \hbar\vec{k} \quad (4.24)$$

where the constant $\hbar = \frac{h}{2\pi}$ (called “hbar” or “hcross”) is the reduced Planck’s constant. You can check for yourself that the magnitude of the linear momentum is the same in Eqs. (4.23 and 4.24). In 1923, the experiments of Compton gave further proof of the photon hypothesis of Einstein. Let us see how.

4.5 COMPTON EFFECT

You know from school physics that **X-rays, discovered in 1895 by William Roentgen**, are electromagnetic waves with very short wavelengths. Arthur Compton and his collaborators studied the scattering of monochromatic X-rays from carbon targets. A simple schematic diagram of their experimental set up is shown in Fig. 4.8. Monochromatic X-rays are incident on a target and

the intensity of the scattered X-rays is measured at different scattering angles θ :

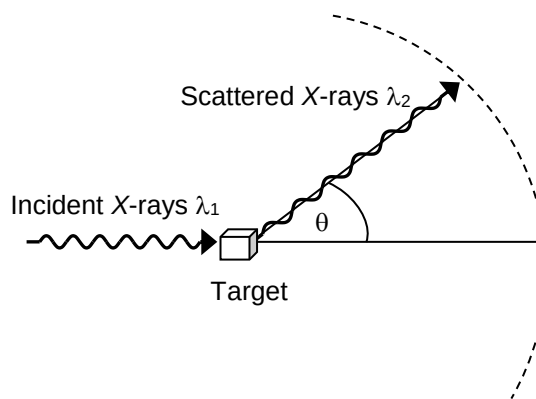


Fig. 4.8: The experimental set up for studying Compton scattering.

It was observed that the scattered X-rays had wavelengths different from those of the incident X-rays. The typical experimental results for the intensity variation with wavelength at different scattering angles are shown in Fig. 4.9.

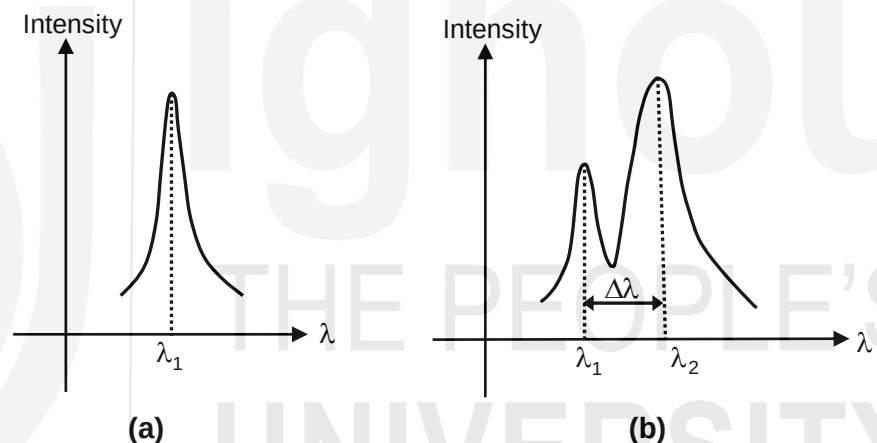


Fig. 4.9: The plot of the intensity of the scattered beam with wavelength λ for a) $\theta = 0$ and b) $\theta > 0$. For $\theta > 0$, two peaks are observed – one is at the wavelength of the incident X-rays (λ_1) and another at a slightly higher wavelength (λ_2).

You can see that at $\theta = 0$ (Fig. 4.9a) the wavelength of the scattered X-rays is identical to that of incident X-rays (λ_1). But for all other angles, two peaks are observed, one at λ_1 and another at a slightly higher wavelength (say, λ_2). The difference in the wavelength ($\lambda_2 - \lambda_1 = \Delta\lambda$), is called the **Compton shift**. At any scattering angle θ , **Compton shift was found to depend only on the scattering angle and not on the intensity of the incident radiation**. Classical electromagnetic theory could not explain why the wavelength of X-rays should change due to scattering from a target.

Compton (1923) explained these results by treating the scattering of X-rays from the target as the **collision** between an electron in the target and a photon in the incident beam. Because of the collision, the recoiling electron would absorb some of the momentum of the photon. If the incident photon has an energy $h\nu_1$ and momentum $\frac{h\nu_1}{c}$, the scattered photon would have a



Arthur Holly Compton (1892 –1962) was an American physicist. He studied the scattering and absorption of gamma rays, which also led to his discovery of the Compton Effect. He was a key figure in the Manhattan Project which developed the first nuclear weapons, and also oversaw the creation of the first nuclear reactor in 1942. He won the **Nobel Prize in Physics in 1927** for his discovery of the Compton effect.

lesser momentum $\frac{h\nu_2}{c}$ ($\nu_2 < \nu_1$) and hence a lower energy $h\nu_2$,

corresponding to a higher wavelength. Compton was able to derive the expression for the Compton shift as a function of the scattering angle. For this, he applied the laws of conservation of energy and momentum to the collision between an isolated electron (to represent the loosely bound outer electrons in an atom) and the photon. Moreover, he used the relativistic expressions for energy and linear momentum and showed that:

$$\lambda_2 - \lambda_1 = \Delta\lambda = \frac{h}{m_e c} (1 - \cos\theta) \quad (4.25)$$

The constant $\frac{h}{m_e c}$ is called the **Compton wavelength of the electron** (read the margin remark). Note the peak at the original wavelength λ_1 , in Figs. 4.9a and b. It is due to the collision of the photon with the tightly bound inner electrons in the atoms of the target. In this process, the entire atom, and not just the electron recoils due to scattering.

In this course we use m_e to denote the mass of an electron

Since the mass of an atom is about 10^4 times the mass of an electron, the shift in wavelength due to the recoil of an atom is negligible. This experiment shows that photons behave like particles with a momentum of $\frac{h\nu}{c}$.

This experiment established the wave-particle duality of electromagnetic radiation. Interactions involving energy exchange between electromagnetic radiation and matter, which you have studied in Secs. 4.2 to 4.4, take place at the atomic level.

In these interactions, electromagnetic radiation shows its “particle”-like nature. In experiments on interference and diffraction, we see the wave-like nature of electromagnetic radiation, as you have studied in BPHCT 137.

Let us now consider an example for calculating the wavelength shift in the Compton effect.

EXAMPLE 4.3: COMPTON EFFECT

X-rays of wavelength 50.0 pm are incident on a target. Calculate the wavelength of the scattered X-rays at the angles of (i) 45° and (ii) 60° .

SOLUTION ■ From Eq. (4.25), we can write the wave length of the scattered radiation as:

$$\lambda_2 = \lambda_1 + \Delta\lambda \quad (i)$$

It is given that $\lambda_1 = 50.0\text{pm}$ (see the margin remark).

(i) Putting $\theta = 45^\circ$ and $\lambda_1 = 50.0\text{pm}$ in Eq. (4.24), we get:

$$\Delta\lambda = \left(\frac{6.626 \times 10^{-34} \text{ Js}}{9.109 \times 10^{-31} \text{ kg} \times 3 \times 10^8 \text{ ms}^{-1}} \right) (1 - \cos 45^\circ)$$

1 pico meter
or

$$1 \text{ pm} = 10^{-12} \text{ m}$$

or
$$\Delta\lambda = (2.42 \times 10^{-12} \text{ m}) \times \left(1 - \frac{1}{\sqrt{2}}\right) = 0.71 \times 10^{-12} \text{ m} = 0.71 \text{ pm}$$

Using Eq.(i), $\lambda_2 = (50.0 + 0.71) \text{ pm} = 50.7 \text{ pm}$

(ii) Putting $\theta = 60^\circ$ and $\lambda_1 = 50.0 \text{ pm}$ in Eq. (4.25), we get

$$\begin{aligned}\Delta\lambda &= (2.42 \times 10^{-12} \text{ m}) \times (1 - \cos 60^\circ) = (2.42 \times 10^{-12} \text{ m}) \times (1 - 0.5) \\ &= 1.21 \times 10^{-12} \text{ m} = 1.21 \text{ pm}\end{aligned}$$

$\therefore \lambda_2 = 50 + \Delta\lambda = (50 + 1.21) \text{ pm} = 51.2 \text{ pm}$

Note that the value of the **Compton wavelength** of the electron is

$$\frac{h}{m_e c} = 2.42 \times 10^{-12} \text{ m} = 2.42 \text{ pm} . \text{ So we can write Eq. (4.25) as:}$$

$$\Delta\lambda = (2.42 \times 10^{-12} \text{ m}) \times (1 - \cos\theta) \quad (\text{ii})$$

Let us now revise the main features of Compton effect.

Recap

COMPTON EFFECT

When monochromatic X-rays are scattered from certain materials, the scattered radiation is found to have wavelengths different from that of the incident X-rays. This is called the **Compton Effect**.

The difference in the wavelength ($\lambda_2 - \lambda_1 = \Delta\lambda$), where λ_1 and λ_2 are the wavelengths of the incident and scattered radiation, respectively, is called the **Compton shift**. At any scattering angle θ , $\Delta\lambda$ **depends only on the scattering angle and not on the intensity of the incident radiation**:

$$\Delta\lambda = \frac{h}{m_e c} (1 - \cos\theta) \quad (4.25)$$

Compton effect is explained by considering the scattering process to be the result of a collision between the photons in the incident X-rays and the weakly bound electrons in the target material. Then laws of conservation of energy and momentum in their relativistic form are applied to the collision.

This experiment demonstrated that photons behave like particles with linear momentum $\frac{h\nu}{c}$.

You may now like to attempt an SAQ on Compton effect.

SAQ 3 - Compton effect

If the Compton shift is equal to one Compton wavelength, what is the angle of scattering? What is the value of θ for which the value of $\Delta\lambda$ is maximum? What is this value of $\Delta\lambda$?

In Sec. 4.3, you have learnt that the electromagnetic radiation from the surface of a heated body has a continuous spectrum. Is the same true for the characteristic radiation emitted by the atoms of an element, known as atomic emission spectra? It was observed in the late 19th century and early 20th century that the atomic emission spectrum had a few discrete wavelengths. See Fig. 4.10. Note that the atomic emission spectrum shown in the figure has a set of discrete colourful lines on a dark background. It is also called the line spectra. These wavelengths were measured with great precision. The wavelengths of the lines in the emission spectrum of an element are characteristic of that element. The classical theories could not explain why the emission spectrum of any element should consist of a few discrete wavelengths. It was felt that any successful model of an atom should be able to explain the atomic emission spectra of elements.

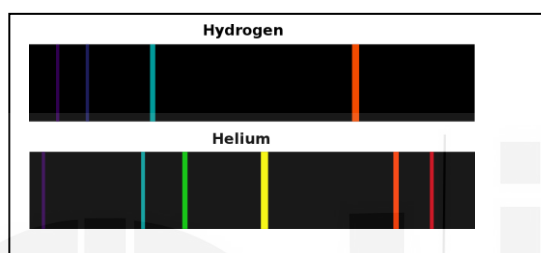


Fig. 4.10: Atomic emission spectrum of hydrogen and helium.

Source: [Ranjithsiji, CC BY-SA 4.0 <https://creativecommons.org/licenses/by-sa/4.0>](https://creativecommons.org/licenses/by-sa/4.0/),
via [Wikimedia Commons](#)

In 1913, Neils Bohr developed a model for the atom, which incorporated some of the features of the quantum theory we have discussed so far.

Historically, this model was an important step in the development of quantum physics, because it was the first model that could explain the line spectrum emitted by hydrogen atoms and the stability of the atom.

You must be familiar with the Bohr model of the hydrogen atom from your senior secondary physics courses. However, we have included the details here for completeness.

4.6 BOHR'S ATOMIC MODEL

The classical crisis with the model of the atom was not dissimilar to the case of black body radiation. Ernest Rutherford had proposed the nuclear model of an atom based on his discovery of the atomic nucleus. In this model, the electrons were supposed to revolve around the nucleus. But since accelerating charges radiate energy, the electrons too must radiate energy. Thus, the electrons would lose energy and eventually spiral into the nucleus. A classical nuclear atom turned out to be unstable! This problem was resolved by Neils Bohr in his atomic model. Let us explain how.

4.6.1 Postulates of Bohr's Atomic Model

Bohr's atomic model accounted for the stability of the atom, by introducing quantum ideas into Rutherford's theory. The model also proved highly

successful in explaining the spectrum of the hydrogen atom. Bohr's atomic model was based on the following four postulates, three of which were radically different from the earlier models:

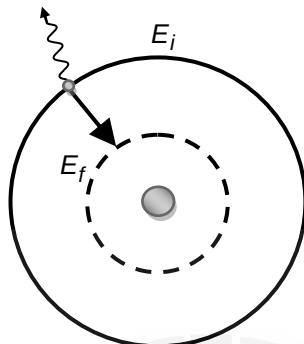
- I. **Electrons in an atom move in circular orbits about the nucleus with the centripetal force provided by the Coulomb attraction between the electron and the nucleus.**
- II. **Of the infinite number of possible circular orbits, only those are allowed for which the value of the orbital angular momentum $|\vec{L}|$ of the electron is an integral multiple of $\hbar = h/2\pi$.** This is Bohr's quantization condition:

$$L = n\hbar \quad \text{where } n = 1, 2, 3, \dots \quad (4.26)$$

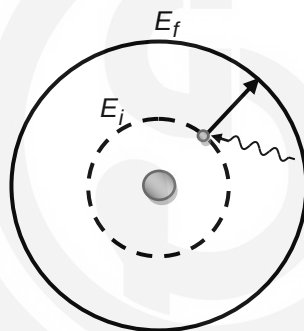
In Eq. (4.26), n is called the quantum number. If the radius of the n^{th} (circular) orbit of the electron in the atom is r_n and the speed of the electron is v_n , the angular momentum quantization condition is:

$$L = m_e v_n r_n = n\hbar \quad \text{where } n = 1, 2, 3, \dots \quad (4.27)$$

You should note that Bohr preferred quantization of angular momentum instead of energy as was done by Planck, in order to introduce h (the quantum of action) in his theory.



(a)



(b)

Fig. 4.11: a) Emission and b) absorption of photons.

- III. **An electron moving in an allowed orbit does not radiate any energy.**

These states of constant energies are called **stationary states**. Note that the electron is not stationary in a stationary state; it is moving. This postulate takes care of the problem of Rutherford's nuclear model of the atom, in which the electron would continuously lose energy and fall into the nucleus.

- IV. **Energy is emitted (or absorbed) from an atom only when its electron makes a transition from one allowed orbit of energy E_i to another allowed orbit of energy E_f .**

The frequency of the emitted (or absorbed) radiation is, given by Einstein's frequency condition (see Fig 4.11):

$$h\nu = E_i - E_f \quad (\text{emission } E_i > E_f) \quad (4.28a)$$

$$= E_f - E_i \quad (\text{absorption } E_f > E_i) \quad (4.28b)$$

Let us now derive the expression for the radius of the orbit and the energy of the electron in the n^{th} stationary state.

4.6.2 Energy of the Stationary State

Consider an atom in which a single electron is revolving around the nucleus in (one of the allowed) circular orbits of radius r_n with a speed v_n . If the atomic number is Z , then the charge on the nucleus is $+Ze$. Assuming that the mass of the nucleus is much greater than the mass of the electron, we can say that the nucleus is fixed in its place and only the electron is moving.

Using postulate I we equate the centripetal force [LHS of Eq. (4.29)] to the Coulomb force of attraction [RHS of Eq. (4.29)] between the positively charged nucleus and the electron having charge $-e$. So, we get:

$$\frac{m_e v_n^2}{r_n} = \frac{1}{4\pi\epsilon_0} \left(\frac{Ze^2}{r_n^2} \right) \quad (4.29)$$

From the angular momentum quantization relation of Eq. (4.27), we can write:

$$v_n = \frac{n\hbar}{m_e r_n} \quad (4.30)$$

Substituting for v_n from Eq. (4.30) in Eq. (4.29), we can derive an expression for the radius of the n^{th} orbit:

$$\frac{m_e}{r_n} \left(\frac{n\hbar}{m_e r_n} \right)^2 = \frac{1}{4\pi\epsilon_0} \left(\frac{Ze^2}{r_n^2} \right) \text{ where } n = 1, 2, 3, \dots$$

$$\Rightarrow r_n = \frac{n^2 h^2 \epsilon_0}{Ze^2 m_e \pi} \quad (4.31)$$

Notice that the radius of the allowed orbit is proportional to the square of the quantum number n .

Substituting the expression of r_n from Eq. (4.31) in Eq. (4.30), we can obtain the speed of the electron in the n^{th} orbit:

$$v_n = \frac{Ze^2}{2nh\epsilon_0} \text{ where } n = 1, 2, 3, \dots \quad (4.32)$$

The total energy of the electron the n^{th} orbit is the sum of its kinetic and potential energies:

$$E_n = \frac{1}{2} m_e v_n^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_n} \quad (4.33)$$

Substituting for r_n and v_n from Eqs. (4.31 and 4.32) in Eq. (4.33), we get:

$$E_n = -\frac{Z^2 e^4 m_e}{8\epsilon_0^2 h^2} \frac{1}{n^2} \text{ where } n = 1, 2, 3, \dots \quad (4.34)$$

So the energy of the electron in the n^{th} orbit or n^{th} stationary state is proportional to the inverse square of n . If we denote the energy of the stationary state with quantum number $n = 1$ by $-E_0$, then we have:

$$E_0 = -\frac{Z^2 e^4 m_e}{8\epsilon_0^2 h^2} \quad (4.35)$$

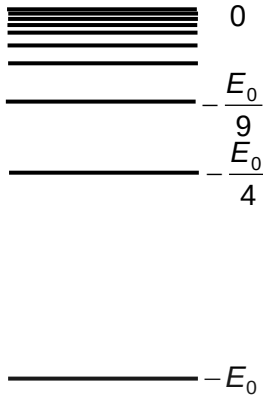
The energies corresponding to $n = 2, 3, 4, \dots$ are $-E_0/4, -E_0/9, -E_0/16, \dots$ and so on.

Note from Eq. (4.34) that energy can have only certain discrete values corresponding to $n = 1, 2, 3, \dots$ In other words, the total energy of the electron

is quantized and this is a consequence of the quantization of the angular momentum (postulate II).

We can write Eq. (4.34) as:

$$E_n = -\frac{R_H Z^2}{n^2} \quad (4.36)$$



As you will calculate in SAQ 4, the value of R_H is 2.18×10^{-18} J (or 13.6 eV).

We can represent the energy states of an electron in an energy level diagram, in which each line represents a stationary state with increasing values of n .

Fig. 4.12 shows the energy level diagram for the Hydrogen atom ($Z = 1$). The ($n = 1$) state has the lowest energy and is, therefore, the most stable. This is also called the **ground state**. The energy increases (becomes less negative) with increasing values of n . These are the **excited states**. There can be infinite energy states but $E_{n \rightarrow \infty} = 0$. When the electron makes a transition between energy states, energy is emitted or absorbed. However since the energy levels are discrete, the emitted or absorbed energy corresponds only to specific frequencies (or wavelengths).

Fig. 4.12: Schematic of the energy-level diagram for the Bohr Atomic Model.

SAQ 4 - Energy in Bohr's atomic model

Derive the expression for E_n (Eq. 4.34) and calculate the value of

$$R_H = \frac{e^4 m_e}{8 \epsilon_0^2 h^2}.$$

According to Bohr's fourth postulate, the frequency ν_{mn} of the emitted (or absorbed) radiation when the electron makes a transition from the n^{th} state to m^{th} state is given by:

$$\nu_{mn} = \frac{(E_n - E_m)}{h} = \frac{R_H Z^2}{h} \left(\frac{1}{m^2} - \frac{1}{n^2} \right) \quad (4.37)$$

The result can also be written in terms of the wavelength of the emitted light:

$$\frac{1}{\lambda_{mn}} = \frac{(E_n - E_m)}{hc} = \frac{R_H Z^2}{hc} \left(\frac{1}{m^2} - \frac{1}{n^2} \right) \quad (4.38)$$

The results of these calculations agree remarkably well with the frequency spectrum of the hydrogen atom. Immediately after Bohr's atomic theory was published, Franck and Hertz performed experiments which demonstrated the existence of discrete energy states. Let us revise Bohr's atomic model.

Recap

BOHR'S ATOMIC MODEL

According to Bohr's atomic model,

- An electron in an atom moves around the nucleus in a circular orbit.
- An electron can only move in an orbit in which its orbital angular momentum is an integral multiple of $\hbar$: $L = m_e v_n r_n = n\hbar$, $n = 1, 2, 3, \dots$

- An electron moving in an allowed orbit does not radiate electromagnetic energy, so its total energy is a constant.
- Energy is emitted (or absorbed) from an atom only when its electron makes a transition from one allowed orbit of energy to another.
- The energy of an electron in the n^{th} orbit (n^{th} stationary state) is:

$$E_n = -\frac{Z^2 e^4 m_e}{8 \epsilon_0^2 h^2} \frac{1}{n^2} \quad \text{where } n = 1, 2, 3, \dots \quad (4.34)$$

where Z is the atomic number. The radius of the n^{th} orbit is:

$$r_n = \frac{n^2 h^2 \epsilon_0}{Z e^2 m_e \pi} \quad \text{where } n = 1, 2, 3, \dots \quad (4.31)$$

The frequency ν_{mn} of the emitted (or absorbed) radiation when the electron makes a transition from the n^{th} state to m^{th} state is given by:

$$\nu_{mn} = \frac{(E_n - E_m)}{h} = \frac{R_H Z^2}{h} \left(\frac{1}{m^2} - \frac{1}{n^2} \right), \quad (4.37)$$

where $R_H = 2.18 \times 10^{-18} \text{ J}$

Let us now apply Bohr's atomic model to calculate wavelengths.

EXAMPLE 4.4: BOHR'S ATOMIC MODEL

Using the Bohr model, calculate the wavelength of the lines corresponding to the following two transitions for the hydrogen atom ($Z = 1$):

- $n = 3 \rightarrow m = 2$ and
- $n = 4 \rightarrow m = 2$

SOLUTION ■ We use Eq. (4.38) with $Z = 1$:

$$\frac{1}{\lambda_{mn}} = \frac{R_H}{hc} \left(\frac{1}{m^2} - \frac{1}{n^2} \right) \quad (i)$$

Let us first determine the value of the constant $\frac{R_H}{hc}$, which has the unit of m^{-1} . With $R_H = 13.6 \text{ eV} = 2.18 \times 10^{-18} \text{ J}$, we get:

$$\frac{R_H}{hc} = \frac{2.18 \times 10^{-18} \text{ J}}{(6.626 \times 10^{-34} \text{ Js})(3.0 \times 10^8 \text{ ms}^{-1})} = 0.11 \times 10^8 \text{ m}^{-1}$$

So,
$$\frac{1}{\lambda_{mn}} = 0.11 \times 10^8 \text{ m}^{-1} \left(\frac{1}{m^2} - \frac{1}{n^2} \right) \quad (ii)$$



Niels Bohr (1885 – 1962) was a Danish physicist who in a career spanning fifty seven years, starting 1905, was a central figure in the development of quantum mechanics. He introduced the idea of a quantum state in his model of the atom in 1913. He was awarded the **Nobel Prize in Physics in 1922** "for his services in the investigation of the structure of atoms and of the radiation emanating from them"

a) With $m = 2$ and $n = 3$ in Eq. (ii), we get:

$$\frac{1}{\lambda_{mn}} = (0.11 \times 10^8 \text{ m}^{-1}) \left(\frac{1}{4} - \frac{1}{9} \right) \Rightarrow \lambda_{mn} = 654 \text{ nm}$$

b) With $m = 2$ and $n = 4$ in Eq. (ii), we get:

$$\frac{1}{\lambda_{mn}} = (0.11 \times 10^8 \text{ m}^{-1}) \left(\frac{1}{4} - \frac{1}{16} \right) \Rightarrow \lambda_{mn} = 485 \text{ nm}$$

You should appreciate that the four postulates of Bohr's atomic model are a hybrid of classical and non-classical physics. In the first postulate the electron is a particle that is acted upon by the Coulomb force and its motion obeys Newton's law of motion. But the postulates of the quantization of angular momentum and stationary states are non-classical, as is the last postulate. According to postulate III, electrons in stationary orbits do not radiate energy, so they do follow the classical electromagnetic theory, which says that an accelerated charged particle should emit radiation.

The non-classical postulates draw upon the ideas of both Planck and Einstein. Bohr applied

- i) the notion of quantized energy levels to the electrons orbiting the nucleus inside the atom in stationary states; and
- ii) the concept of the photon to derive the frequency of the emitted radiation as the electron makes a transition between two stationary states.

However radical these ideas were, you can notice that there was still an attempt to retain a link with the classical physics. You know that at high temperatures or at low frequencies, the black body radiation formula given by Planck reduces to the classical Rayleigh-Jeans formula. Based on these ideas Bohr gave the Correspondence Principle in 1923.

4.6.3 Bohr's Correspondence Principle

The idea underlying this principle is as follows:

The principles of quantum physics must yield the same results as those of classical physics in situations for which classical physics is valid.

According to the correspondence principle:

- a) Quantum theory should give the same results for the behaviour of any physical system as classical physics, in the limit in which the quantum numbers specifying the state of the system become very large.
- b) A selection rule holds true over the entire range of the quantum number concerned. Hence, at large quantum numbers, if any selection rule is required to obtain correspondence between classical and quantum physics then the same selection rule holds at low quantum numbers also.

The topics covered in this unit demonstrate how quantum physics developed to explain experimental results which could not be done by the existing classical theories of the time. Thus, a new physics was born, which is now known as “old quantum theory”. In spite of its many successes, this (old) quantum theory was felt to be inadequate in some respects.

While the theory of atomic spectra correctly explained the atomic transitions leading to the spectral lines of the hydrogen atom, *it could not explain the optical spectral of more complex atoms*. Even more critical was that the old quantum theory, with its amalgamation of classical ideas and quantum assumptions, lacked a solid theoretical foundation.

Quantum theory was developed by Louis de Broglie, Werner Heisenberg and Erwin Schrödinger into a new mechanics, now known as **quantum mechanics**. You will learn about their contributions in the remaining four units of this block.

We now summarise the concepts you have studied in this unit.

4.7 SUMMARY

Concept	Description
Planck's law for black body radiation and Planck's quantum hypothesis	■ Planck's law for black body radiation is: $u(\lambda, T)d\lambda = \frac{8\pi hc\lambda^{-5}}{e^{\frac{hc}{\lambda k_B T}} - 1} d\lambda$ Planck's quantum hypothesis states that the energy of an oscillator of frequency ν, in the wall of the black body enclosure cannot vary continuously, it must have one of the following discrete values: $E_n = nh\nu, \quad \text{with } n = 0, 1, 2, 3$ where $h = 6.626 \times 10^{-34}$ Js is Planck's constant. The exchange of energy between the electromagnetic radiation inside the cavity and an oscillator in the wall of the cavity can take place in discrete amounts or “quanta”, each quantum having energy: $\Delta E = h\nu$ The average energy of a Planck oscillator of energy $h\nu$ at a temperature T is: $\langle E \rangle = \frac{h\nu}{e^{\frac{h\nu}{k_B T}} - 1} = \frac{hc\lambda^{-1}}{e^{\frac{hc}{\lambda k_B T}} - 1}$
Quantum theory of photoelectric effect and linear momentum of a photon	■ Photoelectric effect is the phenomenon in which electrons are emitted from a metal surface when electromagnetic radiation, like light, is incident on it. The quantum theory of photoelectric effect given by Einstein postulates that the energy of light is not distributed continuously in space but is carried in discrete packets or (energy) quanta.

The energy carried by each quantum of light of frequency ν , is given by

$$E = h\nu$$

When light of frequency ν or wavelength λ is incident on a metal, the maximum possible kinetic energy of the electron leaving its surface is given by:

$$K_{max} = h\nu - \phi = h\nu - h\nu_0 = hc\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)$$

where ϕ is the work function of the metal, ν_0 , the cut-off frequency and λ_0 , the cut-off wavelength.

The linear momentum of the photon is given by:

$$\vec{p} = \hbar\vec{k} \quad \text{and} \quad p = \frac{E}{c} = \frac{h\nu}{c} = \frac{h}{\lambda}$$

Compton effect

- When monochromatic X-rays are scattered from certain materials, the scattered radiation is found to have wavelengths different from that of the incident X-rays. This is called the **Compton Effect**.

The difference in the wavelength ($\lambda_2 - \lambda_1 = \Delta\lambda$), where λ_1 and λ_2 are the wavelengths of the incident and scattered radiation, respectively, is called the **Compton shift**. At any scattering angle θ , $\Delta\lambda$ **depends only on the scattering angle and not on the intensity of the incident radiation**:

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

Compton effect is explained by considering the scattering process to be the result of a collision between the photons in the incident X-rays and the weakly bound electrons in the target material. Then laws of conservation of energy and momentum in their relativistic form are applied to the collision. This experiment demonstrated that photons behave like particles with linear momentum $\frac{h\nu}{c}$.

Bohr's atomic model

- According to **Bohr's atomic model**,
 - An electron in an atom moves around the nucleus in a circular orbit.
 - An electron can only move in an orbit in which its orbital angular momentum is an integral multiple of $\hbar$: $L = m_e v_n r_n = n\hbar$, $n = 1, 2, 3, \dots$
 - An electron moving in an allowed orbit does not radiate electromagnetic energy, so its total energy is a constant.
 - Energy is emitted (or absorbed) from an atom only when its electron makes a transition from one allowed orbit of energy to another.
 - The energy of an electron in the n^{th} orbit (n^{th} stationary state) is:

$$E_n = -\frac{Z^2 e^4 m_e}{8 \epsilon_0^2 h^2} \frac{1}{n^2} \quad \text{where } n = 1, 2, 3, \dots$$

and Z is the atomic number. The radius of the n^{th} orbit is:

$$r_n = \frac{n^2 h^2 \epsilon_0}{Z e^2 m_e \pi} \quad \text{where } n = 1, 2, 3, \dots$$

The frequency ν_{mn} of the emitted (or absorbed) radiation when the electron makes a transition from the n^{th} state to m^{th} state is given by:

$$\nu_{mn} = \frac{(E_n - E_m)}{h} = \frac{R_\infty Z^2}{h} \left(\frac{1}{m^2} - \frac{1}{n^2} \right),$$

where $R_\infty = 2.18 \times 10^{-18} \text{ J}$

**Bohr's
correspondence
principle**

■ According to **Bohr's correspondence principle**,

- Quantum theory should give the same results for the behaviour of any physical system as classical physics, in the limit in which the quantum numbers specifying the state of the system become very large.
- A selection rule holds true over the entire range of the quantum number concerned. Hence, at large quantum numbers, if any selection rule is required to obtain correspondence between classical and quantum physics then the same selection rule holds at low quantum numbers also.

4.8 TERMINAL QUESTIONS

1. Derive the short and long wavelength limits of Planck's law of black body radiation.
2. Calculate the average energy of a Planck's oscillator which has an energy (i) $h\nu = 0.10k_B T$ and (ii) $h\nu = 10k_B T$ at temperature T . Which of these is closer to the classical value of the average energy of an oscillator at this temperature?
3. Calculate the (i) wavelength and (ii) linear momentum of a gamma ray photon which has energy 6.0 MeV.
4. The work function for Aluminium is 4.20 eV. Calculate the cut-off frequency. What is the maximum kinetic energy of the photoelectrons and the stopping potential when the electrode is illuminated with light of frequency $12.0 \times 10^{14} \text{ Hz}$?
5. Light of frequency $7.0 \times 10^{14} \text{ Hz}$ is incident on a metal surface. Electrons with a maximum speed of $5.0 \times 10^5 \text{ m s}^{-1}$ are ejected from the surface. Calculate the cut-off frequency.

6. Determine the linear momentum and energy of a photon which has a wavelength of 620 nm.
7. A 380 nm violet light ejects photoelectrons with a maximum kinetic energy of 1.31 eV from a photoelectrode. What is the work function of the material of the photoelectrode?
8. Determine the wavelengths of the photons scattered at (i) 60° (ii) 90° and (iii) 180° when X-rays of wavelength 15.0 pm are scattered from a target.
9. Calculate the radius of the orbit and the energy for the first three stationary states of the hydrogen atom.
10. Calculate the radius and energies of the first three stationary states of the: (i) He^+ ion ($Z=2$) (ii) Li^{2+} ion ($Z=3$)
11. An H- δ line in the emission spectrum of hydrogen has wavelength 4101.7 Å. It corresponds to the transition between the states $n = 6$ to a state m . Determine m .
12. Calculate the energy of the photon that is absorbed when the hydrogen atom makes a transition from the $n = 1$ state to the $n = 3$ state.

4.9 SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. The natural frequency of a spring-mass system is $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$. We use $k = 3000 \text{ Nm}^{-1}$ and $m = 5.0 \text{ g} = .005 \text{ kg}$ to get

$$\nu = \frac{1}{2\pi} \sqrt{\frac{3000 \text{ Nm}^{-1}}{.005 \text{ kg}}} = 123 \text{ Hz}$$

From Eq. (4.10), the spacing between the energy levels is:

$$\Delta E = h\nu = 6.626 \times 10^{-34} \text{ Js} \times 123 \text{ Hz} = 8.14 \times 10^{-32} \text{ J}$$

2. We calculate the energy E of a photon of light with wavelength $\lambda = 500 \text{ nm} = 5 \times 10^{-7} \text{ m}$ following the steps of Example 4.2a.

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ Js}) \times (3 \times 10^8 \text{ ms}^{-1})}{(5 \times 10^{-7} \text{ m})} = 3.976 \times 10^{-19} \text{ J} = 2.48 \text{ eV}$$

Using Eq. (4.16) for the maximum kinetic energy with

$$h\nu = \frac{hc}{\lambda} = 2.48 \text{ eV} \text{ and } \phi = 2.28 \text{ eV} \text{ we get}$$

$$K_{\max} = 2.48 \text{ eV} - 2.28 \text{ eV} = 0.20 \text{ eV}$$

3. In Eq. (ii) of Example 4.3, we have derived:

$$\Delta\lambda = (2.42 \times 10^{-12} \text{ m}) \times (1 - \cos\theta) \quad (\text{i})$$

When $\Delta\lambda$ is $2.42 \times 10^{-12} \text{ m}$, we must have $1 - \cos\theta = 1$ in Eq. (i), hence $\theta = 90^\circ$ ($\cos 90^\circ = 0$).

The value of $\Delta\lambda$ is maximum when the value of $\cos\theta$ is minimum, which is at $\theta = 180^\circ$. At $\theta = 180^\circ$, $\Delta\lambda = 4.84 \times 10^{-12} \text{ m} = 4.84 \text{ pm}$ ($\because \cos 180^\circ = -1$).

So irrespective of the wavelength or intensity of the incident radiation

$$0 \leq \Delta\lambda \leq 4.84 \text{ pm for } 0 \leq \theta \leq 180^\circ.$$

4. From Eqs. (4.31 and 4.32), we have $r_n = \frac{n^2 h^2 \epsilon_0}{Ze^2 m_e \pi}$ and $v_n = \frac{Ze^2}{2n h \epsilon_0}$.

The kinetic energy of the electron is

$$\frac{1}{2} m_e v_n^2 = \frac{1}{2} m_e \left(\frac{Ze^2}{2n h \epsilon_0} \right)^2 = \frac{1}{8} \frac{m_e Z^2 e^4}{n^2 h^2 \epsilon_0^2} \quad (\text{i})$$

The potential energy of the electron is

$$-\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_n} = -\frac{Z^2 e^4 m_e}{4n^2 h^2 \epsilon_0^2}$$

And the total energy (Eq. 4.33) is,

$$\begin{aligned} E_n &= \frac{1}{2} m_e v_n^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_n} = \frac{1}{8} \frac{m_e Z^2 e^4}{n^2 h^2 \epsilon_0^2} - \frac{Z^2 e^4 m_e}{4n^2 h^2 \epsilon_0^2} \\ &= -\frac{Z^2 e^4 m_e}{8h^2 \epsilon_0^2} \left(\frac{1}{n^2} \right) \end{aligned}$$

We evaluate $R_H = \frac{e^4 m_e}{8h^2 \epsilon_0^2}$ with $\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$ from Table

of Physical constants:

$$\begin{aligned} R_H &= \frac{(1.6 \times 10^{-19} \text{ C})^4 \times (9.109 \times 10^{-31} \text{ kg})}{8 \times (6.626 \times 10^{-34} \text{ Js})^2 \times (8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})^2} \\ &= 2.18 \times 10^{-18} \text{ J} = 13.6 \text{ eV} \end{aligned}$$

Terminal Questions

1. From Eq. (4.8), the spectral energy density is:

$$u(\lambda, T) = \frac{8\pi hc \lambda^{-5}}{e^{\frac{hc}{\lambda k_B T}} - 1} \quad (\text{i})$$

For very large values of λ , $\frac{hc}{\lambda k_B T}$ is very small $\left(\frac{hc}{\lambda k_B T} \ll 1 \right)$.

We can expand the exponential in Eq. (i) as:

$$e^x = 1 + x + x^2 + \dots \quad \text{where } x = \frac{hc}{\lambda k_B T}$$

$$\Rightarrow e^x - 1 \approx (1 + x + x^2 + \dots) - 1 \approx x = \frac{hc}{\lambda k_B T}$$

Therefore, Eq. (i) can be written as:

$$u(\lambda, T) = \frac{8\pi hc \lambda^{-5}}{\left(\frac{hc}{\lambda k_B T}\right)} \Rightarrow u(\lambda, T) = 8\pi \lambda^{-4} k_B T \quad (\text{ii})$$

This is the Rayleigh Jean's law [Eq. (4.5)]. For small λ , $\exp\left(\frac{hc}{\lambda k_B T}\right)$ is large and we can write:

$$e^{\frac{hc}{\lambda k_B T}} - 1 \approx e^{\frac{hc}{\lambda k_B T}} \quad (\text{iii})$$

$$\text{And } u(\lambda, T) = 8\pi hc \lambda^{-5} e^{-\frac{hc}{\lambda k_B T}} \quad (\text{iv})$$

This is Wien's law (Eq. 4.3).

2. The average energy of a Planck oscillator of frequency ν is calculated using Eq. (4.11).

(i) For $\nu = 0.10 k_B T$

$$\langle E \rangle = \frac{0.10 k_B T}{e^{\frac{(0.10 k_B T)}{k_B T}} - 1} = \frac{0.10 k_B T}{e^{0.10} - 1} = 0.95 k_B T \approx 1.0 k_B T$$

(ii) For $\nu = 10 k_B T$

$$\langle E \rangle = \frac{10 k_B T}{e^{\frac{(10 k_B T)}{k_B T}} - 1} = \frac{10 k_B T}{e^{10} - 1} \approx (4.5 \times 10^{-4}) k_B T$$

So the average energy of the oscillator is closer to its classical value ($k_B T$) at low frequencies (long wavelengths) which is why the Rayleigh-Jeans Law works only at long wavelengths.

3. The energy E of a photon is related to its wavelength λ by the relation

$$E = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{E} \quad (\text{i})$$

We use Eq. (i) with $E = 6.0 \text{ MeV} = 6.0 \times 1.6 \times 10^{-13} \text{ J} = 9.6 \times 10^{-13} \text{ J}$

$$\lambda = \frac{(6.626 \times 10^{-34} \text{ Js}) \times (3.0 \times 10^8 \text{ ms}^{-1})}{(9.6 \times 10^{-13} \text{ J})} = 2.1 \times 10^{-13} \text{ m}$$

We calculate the momentum p of the photon using Eq. (4.22) with $E = 9.6 \times 10^{-13} \text{ J}$. So,

$$p = \frac{9.6 \times 10^{-13} \text{ J}}{3.0 \times 10^8 \text{ ms}^{-1}} = 3.2 \times 10^{-21} \text{ kgms}^{-1}$$

You can also calculate the momentum using Eq. (4.23) with

$$\lambda = 2.1 \times 10^{-13} \text{ m. So,}$$

$$p = \frac{h}{\lambda} = \frac{6.626 \times 10^{-34} \text{ Js}}{2.1 \times 10^{-13} \text{ m}} = 3.2 \times 10^{-21} \text{ kgms}^{-1}$$

4. We use Eq. (4.18) with $\phi = 4.20 \text{ eV} = 4.20 \times 1.6 \times 10^{-19} \text{ J} = 6.72 \times 10^{-19} \text{ J}$.
So,

$$\nu_0 = \frac{6.72 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ Js}} = 1.014 \times 10^{15} \text{ Hz} = 10.1 \times 10^{14} \text{ Hz}$$

Using Eq. (4.17) for $K_{\max}$ with $\nu = 12.0 \times 10^{14} \text{ Hz}$ and $\nu_0 = 10.1 \times 10^{14} \text{ Hz}$

$$\begin{aligned} K_{\max} &= (6.626 \times 10^{-34} \text{ Js}) \times (12.0 \times 10^{14} \text{ Hz} - 10.1 \times 10^{14} \text{ Hz}) \\ &= (6.626 \times 10^{-34} \text{ Js}) \times (1.90 \times 10^{14} \text{ Hz}) = 12.6 \times 10^{-20} \text{ J} \\ &= 0.788 \text{ eV} \end{aligned}$$

5. The maximum kinetic energy is calculated using Eq. (4.14) with $\nu_{\max} = 5.0 \times 10^5 \text{ ms}^{-1}$. So,

$$K_{\max} = \frac{1}{2} \times (9.109 \times 10^{-31} \text{ kg}) \times (5.0 \times 10^5 \text{ ms}^{-1})^2 = 11.39 \times 10^{-20} \text{ J} \quad (\text{i})$$

The energy of a photon of light of frequency is $E_{ph} = h\nu$ with $\nu = 7.0 \times 10^{14} \text{ Hz}$. Therefore,

$$E_{ph} = (6.626 \times 10^{-34} \text{ Js}) (7.0 \times 10^{14} \text{ Hz}) = 46.38 \times 10^{-20} \text{ J} \quad (\text{ii})$$

Using Eq. (4.16) we write $K_{\max} = E_{ph} - \phi \Rightarrow \phi = E_{ph} - K_{\max}$.

Using the values of $K_{\max}$ and E_{ph} from Eq. (i) and (ii), respectively, we get:

$$\phi = 46.38 \times 10^{-20} \text{ J} - 11.39 \times 10^{-20} \text{ J} = 34.99 \times 10^{-20} \text{ J}$$

Using Eq. (4.18), the cut-off frequency ν_0 is:

$$\nu_0 = \frac{(34.99 \times 10^{-20} \text{ J})}{(6.626 \times 10^{-34} \text{ Js})} = 5.3 \times 10^{14} \text{ Hz}$$

6. With $\lambda = 620 \text{ nm}$ we get

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ Js}) \times (3.0 \times 10^8 \text{ ms}^{-1})}{620 \times 10^{-9} \text{ m}} = 3.20 \times 10^{-19} \text{ J} \quad (\text{i})$$

Using this value of E in Eq. (4.22), we get

$$p = \frac{E}{c} = \frac{3.20 \times 10^{-19} \text{ J}}{(3.0 \times 10^8 \text{ ms}^{-1})} = 1.07 \times 10^{-27} \text{ kgms}^{-1}.$$

7. Energy of photon of wavelength 380 nm is:

$$E = \frac{hc}{\lambda} = 3.27 \text{ eV}$$

Using Eq. (4.20b) with $\frac{hc}{\lambda} = 3.27 \text{ eV}$ and $K_{\max} = 1.31 \text{ eV}$ we get

$$\phi = \frac{hc}{\lambda} - K_{\max} \Rightarrow \phi = 3.27 \text{ eV} - 1.31 \text{ eV} = 1.96 \text{ eV}$$

8. We use $\Delta\lambda = 2.42(1 - \cos\theta) \text{ pm}$ and $\lambda_2 = \lambda_1 + \Delta\lambda$ with $\lambda_1 = 15.0 \text{ pm}$

- (i) For $\theta = 60^\circ$

$$\Delta\lambda = 2.42(1 - \cos 60^\circ) \text{ pm} = 2.42(1 - 0.5) \text{ pm} = 1.21 \text{ pm}$$

$$\text{And } \lambda_2 = \lambda_1 + \Delta\lambda = (15.0 + 1.21) \text{ pm} = 16.2 \text{ pm}$$

- (ii) For $\theta = 90^\circ$

$$\Delta\lambda = 2.42(1 - \cos 90^\circ) \text{ pm} = 2.42 \text{ pm}$$

$$\Rightarrow \lambda_2 = (15 + 2.42) \text{ pm} = 17.4 \text{ pm}$$

- (iii) For $\theta = 180^\circ$

$$\Delta\lambda = 2.42(1 - \cos 180^\circ) \text{ pm} = 4.84 \text{ pm}$$

$$\Rightarrow \lambda_2 = (15 + 4.84) \text{ pm} = 19.8 \text{ pm}$$

9. For hydrogen $Z = 1$, so using Eq. (4.31) we can write the expression for r_n as :

$$r_n = \frac{h^2 \epsilon_0}{e^2 m_e \pi} (n^2)$$

Let us first calculate the value of $\frac{h^2 \epsilon_0}{e^2 m_e \pi}$, which has the unit of length.

$$\begin{aligned} \frac{h^2 \epsilon_0}{e^2 m_e \pi} &= \frac{(6.626 \times 10^{-34} \text{ Js})^2 \times (8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})}{(1.6 \times 10^{-19} \text{ C})^2 \times (9.109 \times 10^{-31} \text{ kg}) \times 3.14} \\ &= 5.3 \times 10^{-11} \text{ m} = 0.53 \text{ \AA} \end{aligned}$$

Thus, $r_n = 0.53 \times n^2 \text{ \AA}$

For the first three states,

$$r_1 = 0.53 \times (1)^2 = 0.53 \text{ \AA} ; r_2 = 0.53 \times (2)^2 = 2.12 \text{ \AA} ; r_3 = 0.53 \times (3)^2 = 4.77 \text{ \AA}$$

The energy of the first three stationary states of hydrogen are obtained by substituting $Z = 1$, $R_H = 13.6 \text{ eV}$ and $n = 1, 2, 3$ in Eq. (4.36):

$$\text{So, } E_n = -\frac{13.6}{n^2} \text{ eV}$$

$$E_1 = -\frac{13.6}{(1)^2} \text{ eV} = -13.6 \text{ eV} ;$$

$$E_2 = -\frac{13.6}{(2)^2} \text{ eV} = -3.4 \text{ eV} ;$$

$$E_3 = -\frac{13.6}{(3)^2} \text{ eV} = -1.51 \text{ eV}$$

10. From Eqs. (4.31) and (4.36), $r_n = \frac{h^2 \epsilon_0}{e^2 m_e \pi} \left(\frac{n^2}{Z} \right)$ and $E_n = -R_H \left(\frac{Z^2}{n^2} \right)$

From TQ9 we know that $\frac{h^2 \epsilon_0}{e^2 m_e \pi} = 0.53 \times 10^{-10} \text{ m} = 0.530 \text{ \AA}$, so

$$r_n = 0.530 \times \frac{n^2}{Z} \text{ \AA} \quad (\text{i})$$

And $E_n = -(13.6 \text{ eV}) \frac{Z^2}{n^2} \quad (\text{ii})$

We use Eq. (i) and (ii) to determine the radius and energy of the stationary states

i) For He^+ , $Z = 2$ and

$$r_n = \left(\frac{0.530}{2} \right) \times n^2 = 0.265 \times n^2 \text{ \AA} \quad (\text{iii})$$

$$\therefore r_1 = 0.265 \text{ \AA} ; r_2 = (0.265 \times 4) = 1.06 \text{ \AA} ; r_3 = (0.265 \times 9) = 2.39 \text{ \AA}$$

$$E_n = -13.6 \text{ eV} \times 4 \times \frac{1}{n^2} = -\frac{54.4}{n^2} \text{ eV} \quad (\text{iv})$$

$$\therefore E_1 = -54.4 \text{ eV} ; E_2 = -\frac{54.4}{4} \text{ eV} = -13.6 \text{ eV} ; E_3 = -\frac{54.4}{9} \text{ eV} = -6.04 \text{ eV}$$

ii) For Li^+ , $Z = 3$ and

$$r_n = \left(\frac{0.530}{3} \right) \times n^2 = 0.177 \times n^2 \text{ \AA} \quad (\text{v})$$

$$\text{So } r_1 = 0.177 \text{ \AA} ; r_2 = 0.708 \text{ \AA} ; r_3 = 1.59 \text{ \AA}$$

$$\text{And } E_n = -(13.6 \times 9) \text{ eV} \times \frac{1}{n^2} = -\frac{122.4}{n^2} \text{ eV} \quad (\text{vi})$$

$$\therefore E_1 = -122.4 \text{ eV} ; E_2 = -30.6 \text{ eV} ; E_3 = -13.6 \text{ eV}$$

11. We use Eq. (4.38) with $\lambda = 4101.7 = 4101.7 \times 10^{-10} \text{ m}$, $Z = 1$ (for hydrogen atom), $n = 6$ and $\frac{R_H}{hc} = 0.11 \times 10^8 \text{ m}^{-1}$ as calculated in Example 4.5. So,

$$\frac{1}{\lambda_{mn}} = (0.11 \times 10^8 \text{ m}^{-1}) \times \left(\frac{1}{m^2} - \frac{1}{6^2} \right)$$

$$\Rightarrow \frac{1}{m^2} - \frac{1}{6^2} = \frac{1}{(4101.7 \times 10^{-10} \text{ m} \times 0.11 \times 10^8 \text{ m}^{-1})}$$

$$\Rightarrow \frac{1}{m^2} = .25 \Rightarrow m^2 = 4 \text{ or } m = 2$$

And the H- δ line corresponds to a transition $n = 6 \rightarrow m = 2$.

12. Using Eq. (4.37) with $Z = 1$ and $n = 3, m = 1$, we can write

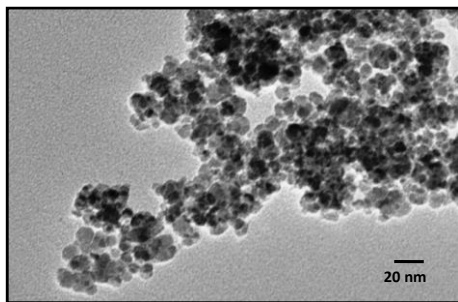
$$E_n - E_m = R_H \left(\frac{1}{1^2} - \frac{1}{3^2} \right) = R_H \left(\frac{8}{9} \right)$$

with $R_H = 2.18 \times 10^{-18} \text{ J} = -13.6 \text{ eV}$

$\therefore$ The energy absorbed is $= \left(13.6 \times \frac{8}{9} \right) \text{ eV} = 12.1 \text{ eV}$



UNIT 5



The image of a material using a Transmission Electron Microscope (TEM), which works on the principle of electron diffraction and has a resolution of ~ 0.2 nm.

Source: PhD Thesis, Ms. Richa Jain, IGNOU (2021)

WAVE-PARTICLE DUALITY

Structure

- | | | | |
|-----|--------------------------------|-----|-----------------------|
| 5.1 | Introduction | 5.4 | Wave-Particle Duality |
| | Expected Learning Outcomes | 5.5 | Matter Waves |
| 5.2 | The De Broglie Hypothesis | 5.6 | Summary |
| | Electron Waves in an Atom | 5.7 | Terminal Questions |
| 5.3 | The Davisson-Germer Experiment | 5.8 | Solutions and Answers |

STUDY GUIDE

In this unit, you will learn about the de Broglie hypothesis, wave-particle duality, matter waves and their discovery. The concepts introduced in this unit are fundamental to your basic understanding of quantum physics. Recall that in the last unit you have studied how certain ideas were introduced to explain experimental results, which could not be explained by classical mechanics and electromagnetic theory. In this unit, you will study the next few steps, which were born of an intuitive understanding of nature. While the mathematics of the unit is fairly simple, you must pay attention to the new ideas to understand how quantum physics came to be one of the most complete theories of the natural world.

“Discoveries in physics are made when the time for making them is ripe, and not before...”

Clinton Davisson

5.1 INTRODUCTION

"it is on this concept of the duality of waves and corpuscles in Nature, expressed in a more or less abstract form, that the whole recent development of theoretical physics has been founded and that all future development of this science will apparently have to be founded"

De Broglie,
Nobel Lecture (1929)

In Unit 4, you have studied the important experiments and theories that led to the birth of quantum physics. To explain black body radiation, Planck postulated that the oscillators in the walls of a black body cavity have discrete energy levels and **emit** electromagnetic radiation of frequency ν in units of energy equal to $h\nu$, where h is Planck's constant. In his explanation of the photoelectric effect, Einstein proposed that all radiant energy is **made up of** discrete bundles or *quanta* of energy, each having an energy $h\nu$. The Compton scattering experiment gave further proof of the particle nature of light. It became clear that under different experimental conditions, light could behave either as a wave or as a particle, and possessed a sort of inherent **"duality"**. Bohr's atomic model, in which the states of an electron in an atom were quantized, was successful in explaining atomic spectra.

In spite of its many successes, the (old) quantum theory was felt to be inadequate in some respects. For example, while the theory of atomic spectra, correctly explained the atomic transitions leading to the spectral lines of the hydrogen atom, it could not explain the relative intensity of these lines. In the early 1920s, theoretical physicists developed a more systematic quantum theory, which came to known as "quantum mechanics". You will learn in this block that there are two main approaches to the mathematical formulation of quantum mechanics. One of these mathematical formulations was built on the foundations of the **de Broglie hypothesis**.

In 1923, Louis de Broglie proposed, as part of his doctoral dissertation, that the **"dual" or "wave-particle" nature of radiation is actually a characteristic of all matter**. This is known as the de Broglie hypothesis, which we discuss in Sec. 5.2. We also introduce the concept of **"matter wave"**. In Sec. 5.3, we discuss the Davisson-Germer experiment that first confirmed the existence of matter waves. In Sec. 5.4, we explain the concept of **wave-particle duality**, which is one of the fundamental principles of quantum mechanics. In Sec. 5.5, we describe the characteristics of matter waves and relate those to the motion of a particle. You will learn about an interesting consequence of representing a particle by a wave packet. We find that the position and momentum of the particle cannot be measured to any desired accuracy at the same time (simultaneously). This is known as **Heisenberg's Uncertainty Principle** about which you will study in the next unit.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ state the de Broglie hypothesis and explain the concept of wave-particle duality;
- ❖ calculate the de Broglie wavelength of a particle in motion;
- ❖ explain the concepts of matter wave and wave packet; and
- ❖ derive the relation between the group velocity and the particle velocity.

5.2 THE DE BROGLIE HYPOTHESIS

In 1923, in a series of notes presented to the Academy of Sciences, Paris a young graduate student, Louis de Broglie, postulated that just as electromagnetic radiation has the characteristics of both waves and particles, **all forms of matter should also have both particle and wave properties.** This is known as the **de Broglie Hypothesis**. In de Broglie's own words:

"...for both matter and radiations, light in particular, it is necessary to introduce the corpuscle concept and the wave concept at the same time. In other words the existence of corpuscles accompanied by waves has to be assumed in all cases." **Louis de Broglie, Nobel Lecture, 1929**

His justification for this postulate rested on the argument that nature loves symmetry and so the two entities that make up the physical world, matter and electromagnetic radiation, must be symmetrical. If radiation has the characteristics of waves and particles, a particle (of matter) too must have the characteristics of both particles and waves.

He further developed this idea of "the wave nature of matter" in his doctoral thesis, which was presented on November 25, 1924. Just as photons are associated with every electromagnetic wave, he suggested that every material particle must be associated with a wave, which is called a **matter wave**. He presented the following expression for the **wavelength** λ of the matter wave associated with a free particle having **linear momentum** p :

$$\lambda = \frac{h}{p} \quad (5.1)$$

This wavelength λ is called the **de Broglie wavelength** of the particle. Note from Eq. (5.1) that the **wavelength of the wave associated with a particle of matter in motion is inversely proportional to the particle's momentum, and the constant of proportionality is just the Planck constant.**

Eq. (5.1) is a complete statement of the **wave-particle duality**.

A particle with linear momentum p can exhibit wave-like properties and the wavelength of the associated matter waves is h/p . Recall from Sec. 4.4.3 of Unit 4, that the converse is also true. So, an electromagnetic wave of wavelength λ has particle-like properties and the linear momentum associated with the particle is h/λ [Eq. (4.23)].

The **total energy of the particle** is related to the frequency of the wave associated with it by the relation:

$$v = \frac{E}{h} \quad (5.2)$$

Do you note that Eq. (5.1) is the same as Eq. (4.23) of Unit 4, which was the expression for the linear momentum of the photon, and Eq. (5.2) also gives the energy of the photon as in Eq. (4.15)? So, in Eqs. (5.1 and 5.2), you can see that the **wave aspects** (defined by the wavelength and frequency) and **particle aspects** (defined by its energy and linear momentum) **for a material**



Louis Victor de Broglie (1892-1987) belonged to an aristocratic French family and he had a rather unusual scientific career. His elder brother Maurice de Broglie was an outstanding experimental physicist but Louis started out as a student of medieval history at the Sorbonne in France. He shifted to the study of physics only after a stint of six years in the French Army during World War I, in the field radio-communications unit. His interest then shifted to electromagnetic waves and the philosophical physics problems of the time. His hypothesis of wave particle duality was a watershed for the development of quantum mechanics. De Broglie was awarded **the Nobel Prize in Physics in 1929** for the discovery of the wave nature of the electron.

“Since corpuscles and waves cannot be independent because, according to Bohr’s expression, they constitute two complementary forces of reality, it must be possible to establish a certain parallelism between the motion of a corpuscle and the propagation of the associated wave.”

– Louis de Broglie (1929) in his Nobel Lecture

In 1926, the Austrian physicist Erwin Schrödinger published four papers in which the wave nature of particles was treated explicitly with wave equations. The physical interpretation of the wave function was given by Max Born in the same year.

particle are related in exactly the same way as they are for photons and electromagnetic radiation. This is what de Broglie had set out to do (read the margin remark).

Although we refer to the wave associated with a moving particle as a matter wave, you must understand that matter waves are **NOT** particles of matter oscillating in space. De Broglie himself did not say anything about the physical nature of this matter wave. We will discuss wave-particle duality and matter waves in detail in Secs. 5.4 and 5.5, respectively.

This novel idea of matter waves did not receive much attention in the scientific community, mainly because there was no experimental evidence to support them. However, when Einstein received a copy of Louis de Broglie’s doctoral thesis, he recognized at once the importance of the revolutionary ideas put forth in it. He recommended the thesis to Erwin Schrödinger, who then went on to expand the idea of the wave associated with a moving particle. He deduced a complete theory with the celebrated **Schrödinger equation** to explain the behaviour of these waves.

To understand why experimental proof for the existence of matter waves took so long in coming, you should work through Examples 5.1 and 5.2.

EXAMPLE 5.1 : DE BROGLIE WAVELENGTH

Calculate the de Broglie wavelength for a cricket ball travelling at a speed of 50 ms^{-1} given that its mass is 150 g .

SOLUTION ■ We use Eq. (5.1) to determine the de Broglie wavelength for the cricket ball.

With $m = 150 \text{ g} = 0.15 \text{ kg}$ and $v = 50 \text{ ms}^{-1}$, we get

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ Js}}{(0.150 \text{ kg}) \times (50.0 \text{ ms}^{-1})} = 0.88 \times 10^{-34} \text{ m}$$

Note that the wavelength of the cricket ball of Example 5.1 is $\sim 10^{-34} \text{ m}$. Now recall how you observe the wave nature of light – you carry out experiments on interference and diffraction of light keeping slit sizes of the order of the wavelengths (e.g., thin wire). Now if you wanted to observe the “wave-like” properties of the ball in Example 5.1, you would need a slit of the order of 10^{-34} m for it to exhibit either interference or diffraction. This is smaller than the size of any known object (smaller even than atomic sizes). So, is it possible to have slits of such widths? At present, this seems rather out of question. This is why we do not observe the wave nature of the cricket ball experimentally or around us. This is true of all macroscopic objects.

But does this mean that macroscopic objects do not have wave-like properties? No. It only means that a macroscopic object does have a wave associated with it, but **the wavelength is so small that it cannot be measured**. So, we describe **macroscopic objects as particles in all**

situations. Therefore, we continue to study the motion of macroscopic objects using the laws of classical mechanics.

REMEMBER: The de Broglie hypothesis **does not change** the classical description developed by Newton for the motion of macroscopic objects. You may like to know: Why, then, do we even talk about the wave nature of matter? When does it become important in actual observations and experiments?

To understand that, let us calculate the de Broglie wavelength of a really tiny particle like an electron. Let us work out another example.

EXAMPLE 5.2: DE BROGLIE WAVELENGTH

Calculate the de Broglie wavelength of an electron accelerated from rest through a potential difference of 100 V.

SOLUTION ■ We use the expressions of kinetic energy in terms of the potential and linear momentum along with Eq. (5.1).

The kinetic energy, K , of the electron is equal to the work done in accelerating the electron through a potential difference $V = 100\text{ V}$. So, we write

$$K = \frac{1}{2} m_e v^2 = eV \quad (\text{i})$$

where m_e is the mass of the electron and v , its speed.

$$\therefore m_e v^2 = 2eV \Rightarrow m_e v = \sqrt{2m_e eV} \quad (\text{ii})$$

Therefore, the linear momentum of the electron is

$$p = m_e v = \sqrt{2m_e eV} \quad (\text{iii})$$

Substituting for p from Eq. (iii) in Eq. (5.1), we get the expression for the de Broglie wavelength of the electron as:

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m_e eV}} \quad (\text{iv})$$

Substituting the values of h, e, m_e and V in Eq. (iv) we get:

$$\begin{aligned} \lambda &= \frac{6.626 \times 10^{-34} \text{ Js}}{\sqrt{2 \times (9.109 \times 10^{-31} \text{ kg}) (1.6 \times 10^{-19} \text{ C}) \times (100 \text{ V})}} \\ &= 1.227 \times 10^{-10} \text{ m} = 1.23 \text{ \AA} \end{aligned}$$

Did you note that that the de Broglie wavelength of the electron in Example 5.2 is much smaller than that of the cricket ball (Example 5.1)? In fact, the wavelength of the electron in this case ($\sim 1.2 \times 10^{-10} \text{ m}$) lies in the range of the wavelengths for X-rays (10^{-8} m to 10^{-12} m). The electron wavelength is also of the order of the typical spacing between atoms in a crystal. In that case, the electron waves should undergo diffraction by a crystal

just like X-rays! In fact, this is how the existence of matter waves was first confirmed, in electron diffractions experiments which you will read about in Sec. 5.3.

In general, when a particle of mass m carrying a charge q is accelerated from rest through a potential difference V , its de Broglie wavelength is given by the relation:

$$\lambda = \frac{h}{\sqrt{2mqV}} \quad (5.3)$$

We can calculate the de Broglie wavelength of a particle of mass m , if we know its kinetic energy (K). Since we know that $K = \frac{p^2}{2m}$, we can write $p = \sqrt{2mK}$, and the de Broglie wavelength of the particle is:

$$\lambda = \frac{h}{\sqrt{2mK}} \quad (5.4)$$

Let us revise the de Broglie hypothesis before you study further.

Recap

DE BROGLIE HYPOTHESIS

De Broglie hypothesis states that

Just as electromagnetic radiation has the characteristics of both waves and particles, **all forms of matter should also have both particle and wave properties.**

The wavelength of the matter wave associated with a particle having linear momentum p is:

$$\lambda = \frac{h}{p} \quad (5.1)$$

The frequency of the matter wave is:

$$\nu = \frac{E}{h} \quad (5.2)$$

where E is the energy of the particle.

The de Broglie wavelength of a particle of mass m carrying charge q , and accelerated from rest through a potential difference V , is given by:

$$\lambda = \frac{h}{\sqrt{2mqV}} \quad (5.3)$$

The de Broglie wavelength of a particle of mass m having kinetic energy K is given by:

$$\lambda = \frac{h}{\sqrt{2mK}} \quad (5.4)$$

You may now like to solve a few problems.

SAQ 1 - Calculating de Broglie wavelength

- Calculate the de Broglie wavelength of i) a proton and ii) an alpha particle, each having kinetic energy 4.0 keV. The mass of an alpha particle is 6.644×10^{-27} kg.
- The average kinetic energy of a molecule of an ideal gas at a temperature T is $\frac{3}{2} k_B T$. Using this relation, calculate the average de Broglie wavelength of a gas of oxygen molecules at room temperature (300 K). Take the mass of the oxygen molecule to be 5.31×10^{-26} kg.

Before you learn about the experimental proof of the existence of matter waves, we would like to present a simple application of Eq. (5.1). De Broglie applied the idea of matter wave to the motion of electrons in atoms and was able to provide an explanation for Bohr's quantization rules for the stability of atomic orbits. Let us see how.

5.2.1 Electron Waves in an Atom

Being a lover of music, De Broglie decided to look upon the atom as a musical instrument. You have learnt about musical notes in Unit 3 of the fourth semester course Wave and Optics (BPHCT 137). You know that a musical instrument can have only a particular basic tone and related overtones. For example, when a guitar string is plucked, the vibrations of the string set up standing waves. But only those standing waves are allowed which have nodes at both ends. Because of this, only particular wavelengths are allowed (see Fig. 5.1).

De Broglie then suggested that the electron is moving in an orbit inside the atom, accompanied by its matter wave or electron wave. He **stipulated** that for the stability of the orbit, the length of the orbit should be such that only an integer number of wavelengths of the electron waves fit into it.

So, for the first atomic orbital (see Eq. 4.30), which has radius r_1 , we should have $2\pi r_1 = \lambda$ (λ is the de Broglie wavelength of the electron wave in the orbital). For the second atomic orbital, which has radius r_2 , we should have $2\pi r_2 = \lambda$, and so on. In general, we can write that in an allowed atomic orbital which has radius r_n , the following condition must be satisfied:

$$2\pi r_n = n\lambda, \quad \text{for } n = 1, 2, 3, \dots \quad (5.5)$$

So only certain discrete values of r_n are possible (see Fig. 5.2). Assuming that the wavelength of the electron wave is [Eq. (5.1)]:

$$\lambda = \frac{h}{p} = \frac{h}{m_e v} \quad (5.6)$$

we can write, from Eq. (5.5),

$$2\pi r_n = n\lambda = n \left(\frac{h}{m_e v} \right) \quad (5.7)$$

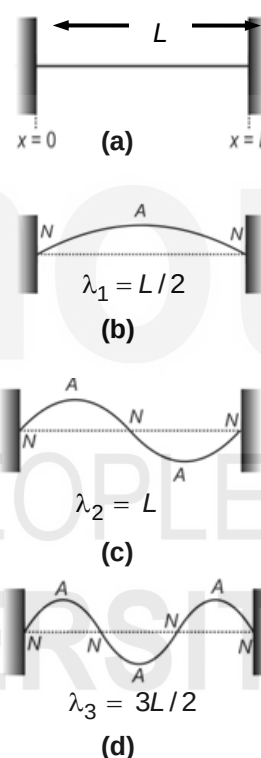


Fig. 5.1: Standing waves on a guitar string of length L with nodes (N) and antinodes (A) marked.

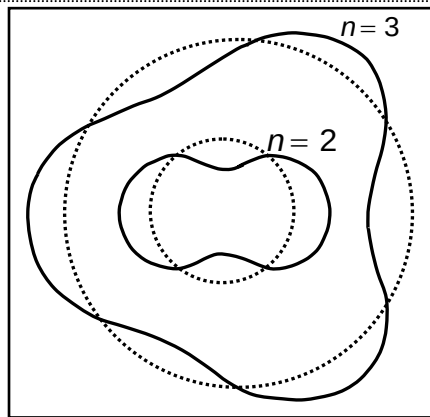


Fig. 5.2: De Broglie waves in atomic orbitals.

Rearranging the terms of Eq. (5.7), we get back the familiar angular momentum quantization condition for the stationary orbits of the electron in the atom of Bohr's atomic model:

$$m_e v r_n = n \left(\frac{h}{2\pi} \right) = n\hbar \quad (5.8)$$

So, now we have a physical interpretation of the angular momentum quantization condition, as a condition for having standing waves of electrons in the atomic orbit. Let us now discuss the electron diffraction experiment that gave us the first proof of the existence of the matter waves proposed by de Broglie.



G. Davisson and L. H. Germer worked at the Bell Telephone Laboratories in the United States of America. In the year 1925, they designed and built a vacuum apparatus to study the energies of electrons scattered by a metal surface. They were quite unaware of the work of de Broglie and his idea of an electron wave. That this experiment eventually led to a confirmation of the existence of matter waves, was happy chance at its best! Davisson and G. P. Thomson received the **Nobel Prize in Physics in 1936** for their experimental discovery of the diffraction of

5.3 THE DAVISSON-GERMER EXPERIMENT

The Davisson-Germer experiment led to the first experimental confirmation of the existence of matter waves and a measurement of the electron wavelength. In Fig. 5.3 you can see a schematic diagram of the experimental set up.

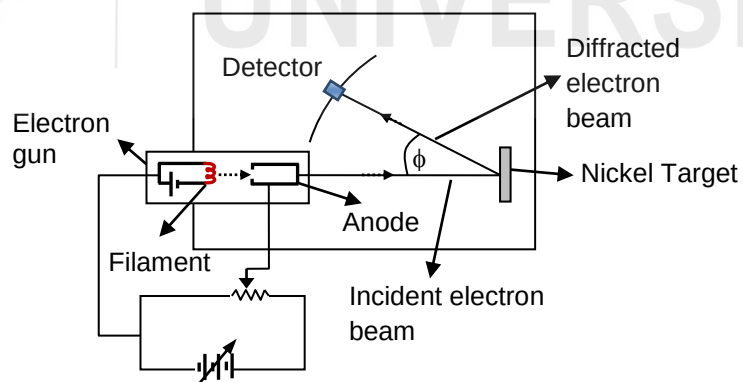


Fig. 5.3: The experimental setup for the electron diffraction experiment.

A well-collimated beam of electrons, produced by an electron gun was allowed to be incident on a poly crystalline nickel sample normal to its surface. In an electron gun, thermal electrons emitted by a heated filament are accelerated through a potential difference V . The kinetic energy K (and the velocity v) of the electrons can be adjusted by adjusting the potential difference V since

$$K = \frac{1}{2} m_e v^2 = eV$$

The entire apparatus was enclosed in an evacuated chamber to prevent the collision of electrons with air molecules. Electrons are scattered in different directions from the Nickel surface. The intensity of the scattered electrons could be measured as a function of the scattering angle ϕ by a sensitive detector. Initially a smooth variation of the intensity of the beam with ϕ was observed (as is seen for $V=40\text{V}$ and $V=68\text{V}$ in Fig. 5.4)

For a fixed energy, the intensity was found to decrease with ϕ . In course of their experiment an oxide coating got deposited on the nickel sample due to an accidental break in their vacuum system. To remove the oxide layer, Davisson and Germer heated the nickel sample in a hydrogen atmosphere.

When they continued the scattering experiments with this reduced sample, the results were very different. A distinct variation of intensity with scattering angle was observed (see second to sixth figures in Fig. 5.4). Based on their original work, for electrons with kinetic energy of 54 eV, a maximum was observed in the scattered intensity at $\phi = 50^\circ$ (Nobel Lecture, 1936). When the kinetic energy of the electrons was appreciably higher or lower than 54 eV, as you can see in Fig 5.4, the maximum was found to disappear!

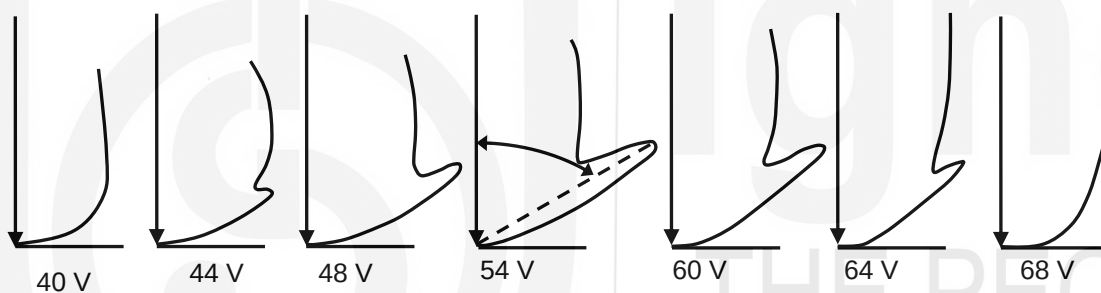


Fig. 5.4: Experimental results at different accelerating voltages.

It turned out that heating the polycrystalline nickel sample had led to formation of large regions of single crystals. The regular extended arrays of atoms in the single crystal regions then behave like a diffraction grating, and electron diffraction takes place from the interference of electron waves, in the same way that X-ray diffraction takes place in a crystal.

Recognizing the importance of this discovery, Davisson and Germer thoroughly investigated electron scattering from large single crystals. They were able to prove in 1927, that electrons indeed undergo diffraction and the electron wavelength is $\lambda = \frac{h}{m_e v}$. This value of the electron wavelength was

calculated from the experiments by applying the conditions of constructive interference.

It agrees with the value of the electron wavelength λ_e calculated from the de Broglie relation (Eq. 5.7): $\lambda_e = \frac{h}{\sqrt{2m_e eV}}$

They experimented with different orientations of the target and different kinetic energies of the electron and were able to confirm the relation between the electron wavelength and linear momentum in each (nineteen) of these.

In an electron microscope, a beam of high energy electrons from an electron gun is focused into a thin coherent beam using a condenser lens. This beam is used to study the specimen and a two dimensional shadow pattern is created on a screen, depending on the varying degrees of transmission through the sample. The TEM remains an indispensable tool for material characterization to this date and while over the years there has been a huge improvement in the performance of a TEM, the working principle remains the same.

Ernst Ruska received the **Nobel Prize in Physics in 1986** for the design of the first electron microscope.

Within a few months of this experiment, British physicist G. P Thomson also observed electron diffraction by passing a beam of high energy electrons through a very thin film. The wave properties of neutral atoms and molecules were demonstrated by Eastermann, Frisch and Stern, by observing the diffraction of hydrogen and helium through a lithium fluoride crystal.

In recent times, diffraction studies have been carried for molecules as large as fullerene molecule (C_{60}); and even a molecule comprising over one hundred atoms, $C_{48}H_{26}F_{24}N_8O_8$, which you may have thought was too large to exhibit wave nature! Experiments on wave particle duality are carried out with even larger molecules. So, it is quite possible that some day you would see at what size of an object there is a transition from the world of everyday physics where classical laws hold into the quantum realm.

The Davisson- Germer experiment shows us that electrons behave like waves. The experiment also shows that we can actually control the wavelength by adjusting the potential difference through which the electrons are accelerated.

Since the electron wavelength is so much less than that of visible light, it was thought than an “electron microscope” would have a much higher resolution than an ordinary microscope. The first such transmission electron microscope (TEM) was built in 1931 by Max Knoll and Ernst Ruska (read the margin remark). You may like to attempt an SAQ before studying further.

SAQ 2 - Neutron diffraction

The neutron diffraction experiment was carried out for the first time in 1945. Calculate the linear momentum and energy of a neutron which would have a wavelength of the order of a typical atomic spacing $\sim 2.0 \text{ \AA}$.

5.4 WAVE-PARTICLE DUALITY

So far in this unit, we have talked a lot about the wave nature of matter. We have seen that when a beam of electrons (and indeed many other particles, albeit very small ones) passes through a crystal or a thin metal film, we get a diffraction pattern. But you have also studied in physics courses so far that the electron is a tiny negatively charged particle. When these negatively charged particles flow in a circuit they create an electric current. So, it is clear that depending on the experiment being carried out, the electron could behave either as a particle or as a wave.

What about electromagnetic radiation? The wave nature of light has been known for a very long time. Yet, in the previous unit you saw that light shows its particle nature in its interactions with matter, in photoelectric effect and in Compton effect.

In fact, there is enough evidence to show that light behaves both as a particle and a wave, and so do electrons, sub atomic particles, atoms and molecules. It would seem that this “wave-particle” duality is, therefore a universal phenomenon. However, the effects of wave-particle duality are appreciable

only in the microscopic world! In the everyday world of our experiences, the classical laws hold. This is because Planck's constant h is a tiny number though finite. Note from Eq. (5.1) that Planck's constant establishes the relation between the particle and wave aspects of a wave and between the wave and particle aspects of a material particle (Eq. 5.1).

So, wave-particle duality is a basic tenet of quantum theory even though it is one of the most intriguing and mind-boggling ideas of modern physics.

Wave-particle duality ascribes two seemingly contradictory traits to a single object.

In fact the idea of "wave-particle duality" was called "**one real mystery of quantum mechanics**" by the famous physicist Richard Feynman. You may wonder: How does it actually happen? Does a particle actually change its nature depending on the experiment being carried out on it – behaving like a particle at times and like a wave at other times? Or is it always **simultaneously** a particle and a wave – just that we see wave-like properties in some experiments and its particle-like properties in others? Can we show that something can actually behave simultaneously like a particle and a wave, and clinch this debate? The standard interpretation of quantum mechanics (arrived at in 1925 in Copenhagen, capital of Denmark) says that we can never observe both the wave and particle aspects of a quantum system simultaneously. This is the idea of complementarity that we will discuss in Unit 6.

However, after decades of speculation on this subject, in 2012, a team of physicists from the University of Bristol (in the United Kingdom) were able to design an experiment in which the particle and wave behaviour of light could be investigated at the same time. They were able to show that the photon behaves simultaneously as a particle and a wave (as reported in *Science* 02 Nov 2012: Vol. 338, Issue 6107, pp. 634-637, DOI: 10.1126/science.122671).

A particle is localized in space, a wave is not. So, in the world of microscopic particles where wave-particle duality is significant, we can no longer work with the **classical** description of the particle. Instead we need a description of the particle which is consistent with the de Broglie hypothesis. So far we have been talking only about the wavelength and frequency of the matter wave associated with a particle. We can call this microscopic particle a **quantum** particle because quantum effects are significant. What more can we say about this matter wave?

Clearly if the motion of a quantum particle is governed by the propagation of the matter wave associated with it, it is necessary to establish a relation between the properties of the wave and the particle it describes. Let us now discuss the matter wave in detail.

5.5 MATTER WAVES

You have learnt that the de Broglie wavelength of a particle having linear momentum p is $\lambda = \frac{h}{p}$. So, if the motion of a quantum particle is governed

by the propagation of the matter wave associated with it, we must know how the matter wave propagates and what kind of a wave it is.

You have studied about mechanical waves and electromagnetic waves in Block 1 of BPHCT 137. You know that every wave is described by two things:

- a function of spatial coordinates (x,y,z) and time, the “**wave function**”, and
- a differential equation in spatial and time coordinates, the “**wave equation**”, which tells us how the wave function evolves in space and time.

So let us start by introducing a **wave function** $\psi(x,y,z,t)$ to represent the matter wave.

Recall what you have studied about waves in Unit 1 of the course Waves and Optics (BPHCT 137). The classical one-dimensional wave equation is:

$$\frac{d^2y}{dt^2} = \frac{1}{v^2} \frac{d^2y}{dx^2} \quad (5.9)$$

And it defines a travelling wave given by:

$$y = A \sin(kx - \omega t) \quad (5.10)$$

where A is the amplitude of the wave. The angular frequency ω and the wave number k are related to the wavelength λ and the frequency ν of the wave by the relations:

$$\omega = 2\pi\nu \quad \text{and} \quad k = \frac{2\pi}{\lambda} \quad (5.11)$$

The velocity “ v ” of the wave, also called its **phase velocity**, is $v_p = \nu\lambda$.

Now consider a particle that has linear momentum p and total energy E , and is moving along the x -direction. Let us assume that the matter wave associated with the particle is given by:

$$\psi(x,t) = A \sin(kx - \omega t) = A \sin 2\pi \left(\frac{x}{\lambda} - \nu t \right) \quad (5.12)$$

where λ is the de Broglie wavelength and λ and ν in Eq. (5.12) are defined by the Eqs. (5.1 and 5.2), respectively (see Fig. 5.5).

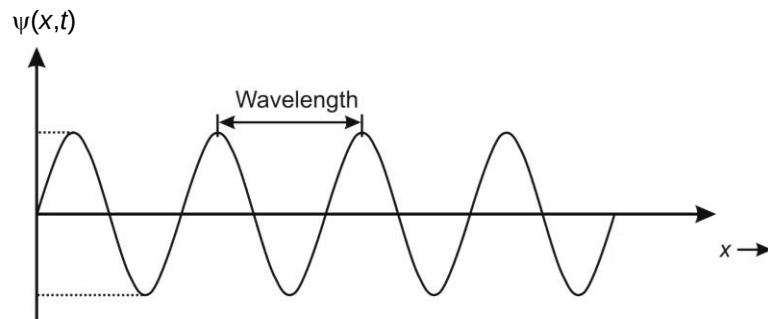


Fig. 5.5: The matter wave as a sine wave of fixed wavelength.

If the net force being exerted on the particle is zero (i.e., it is a free particle), then the momentum of the particle does not change with time and so the de Broglie wavelength λ is a constant.

Using the de Broglie relation [Eq. (5.1)] in Eq. (5.12), we can relate the wave number k for the matter wave to the momentum p of the particle:

$$\frac{2\pi}{k} = \frac{h}{p} \Rightarrow p = \left(\frac{h}{2\pi} \right) k \quad \text{or} \quad p = \hbar k \quad (5.13)$$

You will notice that Eq. (5.13) gives us exactly the same relationship between the momentum and wave number for a matter wave that we had obtained for the photon (Eq. 4.24). Extending Eq. (5.13) to the three-dimensional space, we can write the relation between the momentum vector $\vec{p}$ and the wave vector $\vec{k}$ for a matter wave as:

$$\vec{p} = \hbar \vec{k} \quad (5.14)$$

The wave vector, as you know, gives the direction of propagation of a wave. So, **the momentum (and hence the velocity) of the particle is always parallel to the direction of the propagation of the matter wave** associated with it!

Using the relation between the angular frequency ω and the frequency ν , $\omega = 2\pi\nu$ in Eq. (5.2) we get the total energy of the particle as:

$$E = h\nu = h \left(\frac{\omega}{2\pi} \right) = \hbar\omega \quad (5.15)$$

Further, for a classical free particle we know that $E = \frac{p^2}{2m}$. So, using

Eqs. (5.13) and (5.15), we can write:

$$E = \hbar\omega = \frac{p^2}{2m} = \frac{(\hbar k)^2}{2m} \Rightarrow \omega = \frac{\hbar k^2}{2m} \quad (5.16)$$

This gives us the relation between the angular frequency and wave number of the matter wave. A relation between the angular frequency ω and the wave number k is called a **dispersion relation**. Notice that $\omega \propto k^2$ for a matter wave, whereas $\omega \propto k$ for the light wave

The phase velocity of a wave is:

$$v_p = \frac{\omega}{k} \quad (5.17)$$

From the dispersion relation for the matter wave [Eq. (5.16)], we can write the phase velocity of the matter wave as:

$$v_p = \frac{\omega}{k} = \frac{\hbar k}{2m} = \frac{p}{2m} \quad (5.18)$$

So, you have learnt that if you represent the matter wave associated with a particle of mass m moving with a momentum p ($=mv$) as a travelling sine wave given by Eq. (5.12), the phase velocity of this matter wave is **one-half of the classical velocity** (v) of the particle.

There is another aspect to be considered when you associate the moving particle with a wave of the kind shown in Fig. 5.5. Notice that the wave is

spread out uniformly in space. Now ask yourself this question: Where is the particle? Can you locate it in a particular position? Obviously, you cannot!

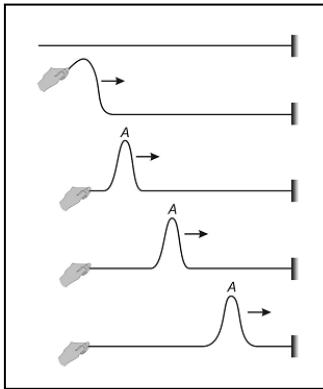


Fig. 5.6: A wave pulse.

It can be anywhere in the region in which the wave propagates. So although the particle has a definite momentum, it appears that the particle does not have a definite location in space. So can it really represent a particle? This also has implications about which we will study in detail in Unit 6.

If a matter wave has to represent a particle, it should be **spatially associated with the particle in such a way that the amplitude of the wave is non-zero only in the neighbourhood of the particle**. So, the matter wave should not look like the wave in Fig 5.5. Rather it should look like the pulse that is generated when you flip one end of a long string, as shown in Fig 5.6. Unlike a wave, **pulses** or **wave groups** as they are called, have both a starting point and an ending point, and are therefore **localized** over a region of space. You have studied about this in Unit 2 of BPHCT 137.

A wave group is formed by the superposition of waves of different wavelengths (frequencies). The amplitudes and phases of these waves are such that when they are superposed, there is a net amplitude over a very small region; outside that region, the net amplitude is zero.

Consider a simple situation in which two waves with slightly different wavelengths are superimposed. The nature of the resultant wave is quite different from either of the individual waves (Sec. 2.5, Unit 2, BPHCT 137).

Consider the following two waves:

$$\psi_1(x, t) = A \sin(kx - \omega t); \quad \psi_2(x, t) = A \sin[(k + \Delta k)x - (\omega + \Delta \omega)t] \quad (5.19)$$

The resultant wave (shown in Fig. 5.7) is: $\psi = \psi_1 + \psi_2$

$$\text{or} \quad \psi(x, t) = 2A \cos\left[\left(\frac{\Delta k}{2}\right)x - \left(\frac{\Delta \omega}{2}\right)t\right] \sin(kx - \omega t) \quad (5.20)$$

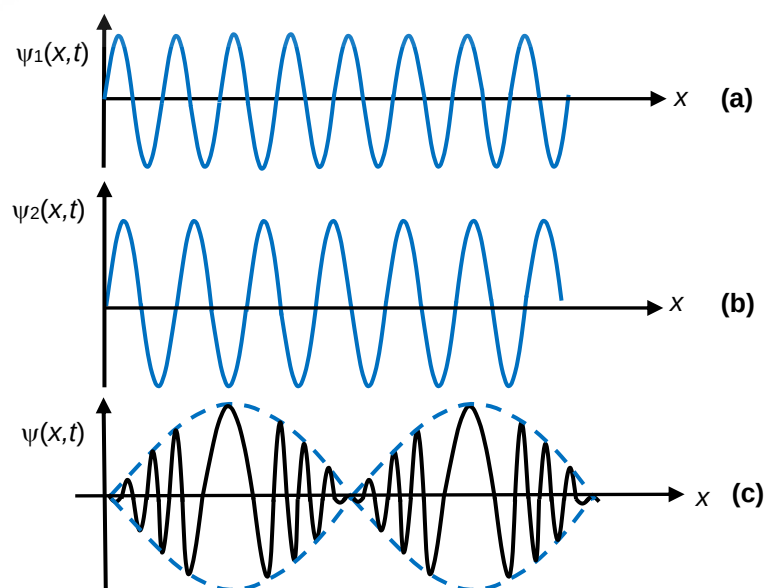


Fig. 5.7: Superposition of two waves of the same amplitude but slightly different frequencies: **a)** $\psi_1(x, t)$; **b)** $\psi_2(x, t)$; **c)** $\psi(x, t) = \psi_1(x, t) + \psi_2(x, t)$.

You can see that the resultant wave ψ has a broad envelope equal to

$2A \cos \left[\left(\frac{\Delta k}{2} \right) x - \left(\frac{\Delta \omega}{2} \right) t \right]$ (shown by the dashed line in Fig. 5.7c) which modulates the sine wave $\sin(kx - \omega t)$. This is still not really a pulse, but an infinite wave.

To construct a pulse, you have to superimpose a very large number of waves having a continuous distribution of wavelengths distributed about a central wavelength λ . Such a pulse is called a “**wave-packet**” and is shown in Fig 5.8.

Although the wave packet shown in Fig. 5.8 is a wave, it is localized in space. It has finite amplitude over a region (Δx), and is actually zero everywhere else. Clearly, it exhibits both the particle and wave aspects. This is why we represent a microscopic particle not by wave but by a wave packet.

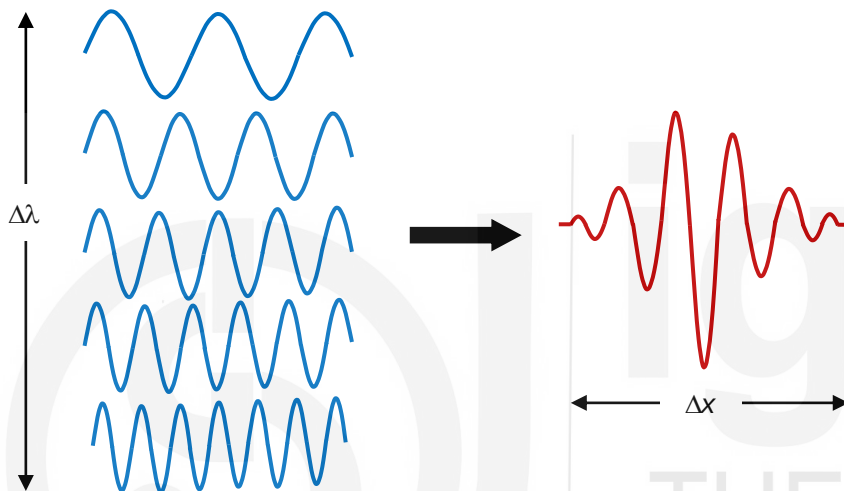


Fig. 5.8: The superposition of a group of waves with a spread of wavelength $\Delta\lambda$ about a central wavelength λ , leads to the formation of a wave packet, which has a finite size Δx .

The central wavelength of the wave packet is the de Broglie wavelength of the particle.

WAVE PACKET

A wave packet is a group of waves with slightly different wavelengths and frequencies interfering with one another in such a manner that the amplitude of the group (i.e., the envelope) is non-zero only in the neighbourhood of the particle.

How do we determine the velocity of this wave packet? After all, it is supposed to describe a particle moving with a certain velocity!

We have talked about the phase velocity of a wave, earlier in this section.

Phase velocity is the velocity of a wave of a single wavelength.

But a wave packet consists of waves of different wavelengths, each wavelength corresponding to a different momentum. From Eq. (5.18), you know that the velocity of each of these waves will be different.

But as you have studied in Unit 2 of BPHCT 137, the envelope of a wave group (the dashed line in Fig. 5.7) moves with a different velocity, which is called the **group velocity**: $v_g = \frac{d\omega}{dk}$.

Using Eq. (5.16) for the dispersion relation for a matter wave, we can write down the group velocity of the matter wave as:

$$v_g = \frac{d\omega}{dk} = \frac{d}{dk} \left(\frac{\hbar k^2}{2m} \right) = \frac{\hbar k}{m} = \frac{p}{m} = v \quad (5.21)$$

So the group velocity of the wave packet is just the velocity of the particle (Fig 5.9).

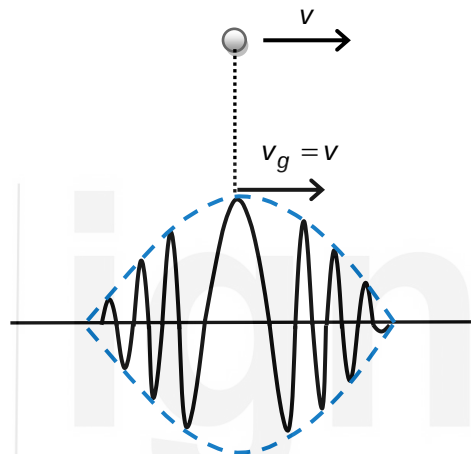


Fig. 5.9: The matter wave for a particle of mass m is a wave packet.

MATTER WAVE

A particle is represented by a group of waves called a wave packet. The group velocity of the wave packet is equal to the velocity of the particle.

So far, you have studied that a particle cannot be represented by a single wave, but rather a group of waves is required to represent it. From Eq. (5.1), we can write

$$\frac{\Delta\lambda}{\lambda} = -\frac{\Delta p}{p} \quad (5.22)$$

and $\Delta\lambda = 0 \Rightarrow \Delta p = 0$

The difference $\Delta\lambda$ is finite because we cannot use a single wave to describe a spatially localized particle. Eq. (5.21) tells us that **if $\Delta\lambda$ is finite, Δp is also finite.**

This suggests that there is a **fundamental limit to the accuracy with which we can measure a particle's position and linear momentum at the same time.** In the next unit, we will discuss this idea.

Let us now summarise what you have learnt in this unit.

5.6 SUMMARY

Concept	Description
The De Broglie hypothesis	■ The de Broglie hypothesis states that just as electromagnetic radiation has the characteristics of both waves and particles, all forms of matter should also have both particle and wave properties. The wavelength of the matter wave associated with a particle which has a linear momentum p is: $\lambda = \frac{h}{p}$ The frequency of the matter wave is: $\nu = \frac{E}{h}$ where E is the energy of the particle. The de Broglie wavelength of a particle of mass m carrying charge q, and accelerated from rest through a potential difference V, is given by: $\lambda = \frac{h}{\sqrt{2mqV}}$ The de Broglie wavelength of a particle of mass m having kinetic energy K is given by: $\lambda = \frac{h}{\sqrt{2mK}}$ The Davisson-Germer experiment was the first experimental confirmation of the de Broglie hypothesis and the existence of matter waves.
Wave-particle duality	■ Wave-particle duality ascribes two seemingly contradictory traits of the particle and the wave to a single entity. So, electromagnetic radiation and microscopic particles like the electrons, sub atomic particles, atoms and molecules behave both as a particle and a wave. This is a universal phenomenon. However, the effects of wave-particle duality are appreciable only in the microscopic world.
Matter waves	■ Matter waves are associated with microscopic particles for which wave-particle duality is significant. The motion of a quantum particle is governed by the propagation of the matter wave associated with it. The matter wave associated with a particle is not a single wave but a wave packet. Thus, a particle is represented by a group of waves called a wave packet, which is a group of waves with slightly different wavelengths and frequencies interfering with one another in such a manner that the amplitude of the group (the envelope) is non-zero only in the neighbourhood of the particle. The group velocity of the wave packet is equal to the velocity of the particle.

5.7 TERMINAL QUESTIONS

1. Calculate the de Broglie wavelength of (i) a 10 eV electron, and (ii) a 1.0 MeV neutron.
2. An increase of 150 eV in the energy of an electron reduces its de Broglie wavelength to half of its earlier value. Calculate the initial de Broglie wavelength.
3. What is the potential through which a proton must be accelerated so that its de Broglie wavelength is $2.0 \text{ \AA}$?
4. Determine the de Broglie wavelength of an electron in the first Bohr orbit.
5. An electron has a de Broglie wavelength equal to that of a photon of red light having wavelength 620 nm. (i) Calculate the energy of the electron. (ii) What would its de Broglie wavelength be if the energy of the electron were equal to the energy of this photon?
6. Calculate the average de Broglie wavelength for a gas of fullerene (C_{60}) molecules heated to a temperature of 900 K. The mass of a fullerene molecule is approximately 720 amu ($1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$).
7. In an electron microscope, electrons are accelerated through a voltage of 200 keV. Calculate the electron's de Broglie wavelength (assume that the electron is non-relativistic).
8. A thermal neutron with a speed v corresponding to the average thermal energy $\frac{3}{2} k_B T$ at temperature $T = 300 \text{ K}$ is incident on a crystal. Will a diffraction pattern be observed? Explain.
9. A photon and an electron each have energy of $6.0 \times 10^3 \text{ eV}$. What are their wavelengths? Which of these would you use to probe atomic structures?
10. Calculate the de Broglie wavelength of a ^{87}Rb (Rubidium) atom that has been laser cooled to $120 \text{ \mu K}$ (the mass of a Rubidium atom is $1.419 \times 10^{-25} \text{ kg}$).

5.8 SOLUTIONS AND ANSWERS

Self-Assessment Questions

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$$

$$\begin{aligned} 1 \text{ keV} &= 10^3 \text{ eV} \\ &= 1.6 \times 10^{-16} \text{ J} \end{aligned}$$

1. a) We use Eq. (5.4) for calculating λ with

$$K = 4.0 \text{ keV} = 4.0 \times 10^3 \text{ eV} = 6.4 \times 10^{-16} \text{ J} \text{ (see the margin remark).}$$

- i) Substituting $m = m_p = 1.673 \times 10^{-27} \text{ kg}$, we get:

$$\lambda = \frac{6.626 \times 10^{-34} \text{ Js}}{\sqrt{2 \times (1.673 \times 10^{-27} \text{ kg}) \times (6.4 \times 10^{-16} \text{ J})}} = 4.5 \times 10^{-13} \text{ m}$$

ii) Substituting $m = m_{\alpha} = 6.664 \times 10^{-27} \text{ kg}$, we get:

$$\lambda = \frac{6.626 \times 10^{-34} \text{ Js}}{\sqrt{2 \times (6.664 \times 10^{-27} \text{ kg}) \times (6.4 \times 10^{-16} \text{ J})}} = 2.3 \times 10^{-13} \text{ m}$$

b) We use Eq. (5.4) with $m = 5.312 \times 10^{-26} \text{ kg}$ and :

$$K = \frac{3}{2} k_B T = \frac{3}{2} \times (1.380 \times 10^{-23} \text{ JK}^{-1}) \times 300 \text{ K} = 6.21 \times 10^{-21} \text{ J}$$

$$\therefore \lambda = \frac{6.626 \times 10^{-34} \text{ Js}}{\sqrt{2 \times (5.31 \times 10^{-26} \text{ kg}) \times (6.21 \times 10^{-21} \text{ J})}} = 2.6 \times 10^{-11} \text{ m}$$

2. The de Broglie wavelength of the neutron is $2.0 \text{ \AA}$. So, $\lambda = 2 \times 10^{-10} \text{ m}$.

From Eq. (5.1), we get the linear momentum p as:

$$p = \frac{h}{\lambda} = \frac{6.626 \times 10^{-34} \text{ Js}}{2 \times 10^{-10} \text{ m}} = 3.313 \times 10^{-24} \text{ kg ms}^{-1}$$

The energy of this neutron would be $E = \frac{p^2}{2m_n}$ where

$$m_n = 1.675 \times 10^{-27} \text{ kg}.$$

$$E = \frac{(3.313 \times 10^{-24} \text{ kg ms}^{-1})^2}{2 \times (1.675 \times 10^{-27} \text{ kg})} = 3.276 \times 10^{-21} \text{ J} \approx 2.0 \times 10^{-2} \text{ eV}$$

Terminal Questions

1. We use Eq. (5.4) for calculating λ

i) Substituting $m = m_e = 9.109 \times 10^{-31} \text{ kg}$ and

$K = 10 \text{ eV} = 1.6 \times 10^{-18} \text{ J}$ we get:

$$\begin{aligned} \lambda &= \frac{6.626 \times 10^{-34} \text{ Js}}{\sqrt{2 \times (9.109 \times 10^{-31} \text{ kg}) \times (1.6 \times 10^{-18} \text{ J})}} \\ &= 3.9 \times 10^{-10} \text{ m} = 3.9 \text{ \AA} \end{aligned}$$

ii) Substituting $m = m_n = 1.675 \times 10^{-27} \text{ kg}$ and

$K = 1.0 \text{ MeV} = 1.6 \times 10^{-13} \text{ J}$:

$$\lambda = \frac{6.626 \times 10^{-34} \text{ Js}}{\sqrt{2 \times (1.675 \times 10^{-27} \text{ kg}) \times (1.6 \times 10^{-13} \text{ J})}} = 2.9 \times 10^{-14} \text{ m}$$

2. Let the initial de Broglie wavelength of the electron be λ_1 corresponding to an energy K_1 . From Eq. (5.4) we can write:

$$\lambda_1 = \frac{h}{\sqrt{2m_e K_1}} \quad (i)$$

When the energy is increased to $K_2 = K_1 + 150 \text{ eV}$ the de Broglie wavelength of the electron is $\lambda_2 = \lambda_1/2$, so we have

$$\lambda_2 = \frac{h}{\sqrt{2m_e K_2}} \Rightarrow \frac{\lambda_1}{2} = \frac{h}{\sqrt{2m_e (K_1 + 150 \text{ eV})}} \quad (ii)$$

Dividing Eq. (i) by Eq. (ii) we get:

$$\sqrt{\frac{(K_1 + 150 \text{ eV})}{K_1}} = 2 \Rightarrow K_1 = 50 \text{ eV} \quad (iii)$$

Substituting for K_1 in Eq. (i) we get:

$$\lambda = \frac{6.626 \times 10^{-34} \text{ Js}}{\sqrt{2 \times (9.109 \times 10^{-31} \text{ kg}) \times (50 \times 1.6 \times 10^{-19} \text{ J})}} = 1.7 \times 10^{-10} \text{ m} = 1.7 \text{ \AA}$$

3. From Eq. (5.3), we write the relation between the de Broglie wavelength λ , of a charged particle of mass m and charge q and the potential V through which it is accelerated as:

$$V = \frac{h^2}{2mq\lambda^2} \quad (i)$$

Substituting $m = m_p = 1.673 \times 10^{-27} \text{ kg}$, $\lambda = 2.0 \times 10^{-10} \text{ m}$ and $q = 1.6 \times 10^{-19} \text{ C}$ in Eq. (i), we get

$$V = \frac{(6.626 \times 10^{-34} \text{ Js})^2}{2 \times (1.673 \times 10^{-27} \text{ kg}) \times (1.6 \times 10^{-19} \text{ C}) \times (2.0 \times 10^{-10} \text{ m})^2} = 2.0 \times 10^{-2} \text{ V}$$

4. We use Eq. (5.4) for calculating λ .

Substituting $m = m_e = 9.109 \times 10^{-31} \text{ kg}$ and the energy of the electron in the first Bohr orbit, which is $K = 13.6 \text{ eV} = 2.18 \times 10^{-18} \text{ J}$, we get:

$$\lambda = \frac{6.626 \times 10^{-34} \text{ Js}}{\sqrt{2 \times (9.109 \times 10^{-31} \text{ kg}) \times (2.18 \times 10^{-18} \text{ J})}} = 3.33 \times 10^{-10} \text{ m} = 3.33 \text{ \AA}$$

5. (i) Using Eq. (5.1), we can write the kinetic energy of the electron as:

$$K = \frac{p^2}{2m_e} = \frac{h^2}{2\lambda^2 m_e} \quad (i)$$

Using $\lambda = 620\text{nm} = 620 \times 10^{-9}\text{m} = 6.2 \times 10^{-7}\text{m}$ in Eq. (i), the kinetic energy of the electron is:

$$K = \frac{(6.626 \times 10^{-34}\text{ Js})^2}{2 \times (6.20 \times 10^{-7}\text{ m})^2 \times (9.109 \times 10^{-31}\text{ kg})}$$

$$= 6.27 \times 10^{-25}\text{ J}$$

ii) The energy of a photon which has a wavelength $\lambda = 6.2 \times 10^{-7}\text{m}$ is

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\text{ Js} \times 3 \times 10^8\text{ ms}^{-1}}{6.2 \times 10^{-7}\text{ m}} = 3.2 \times 10^{-19}\text{ J}$$

The de Broglie wavelength of the electron, if its energy is equal to the energy of a photon of wavelength $\lambda = 6.2 \times 10^{-7}\text{m}$, can be calculated using Eq. (5.4) with $K = 3.2 \times 10^{-19}\text{ J}$:

$$\lambda = \frac{6.626 \times 10^{-34}\text{ Js}}{\sqrt{2 \times (9.109 \times 10^{-31}\text{ kg}) \times (3.2 \times 10^{-19}\text{ J})}} = 8.7 \times 10^{-10}\text{ m} = 8.7\text{ \AA}$$

6. The mass of the fullerene (C_{60}) molecule is:

$$m_F = 720\text{ amu} = 720 \times 1.66 \times 10^{-27}\text{ kg} = 1.20 \times 10^{-24}\text{ kg}$$

The kinetic energy of the C_{60} molecule at 900 K is:

$$K = \frac{3}{2}k_B T = \frac{3}{2} \times (1.38 \times 10^{-23}\text{ JK}^{-1}) \times (900\text{ K}) = 1.863 \times 10^{-20}\text{ J}$$

Using Eq. (5.4) with $K = 1.863 \times 10^{-20}\text{ J}$ and $m = m_F$ we get,

$$\lambda = \frac{6.626 \times 10^{-34}\text{ Js}}{\sqrt{2 \times (1.204 \times 10^{-24}\text{ kg}) \times (1.863 \times 10^{-20}\text{ J})}} = 3.13 \times 10^{-12}\text{ m} = 3.13\text{ pm}$$

7. We use Eq. (5.4) with $m = m_e$, $q = e$ and $V = 200\text{keV} = 2.0 \times 10^5\text{ V}$:

$$\lambda = \frac{6.626 \times 10^{-34}\text{ Js}}{\sqrt{2 \times (9.109 \times 10^{-31}\text{ kg}) \times (1.6 \times 10^{-19}\text{ C}) \times (2.0 \times 10^5\text{ V})}}$$

$$= 2.75 \times 10^{-12}\text{ m} = 2.75\text{ pm}$$

8. The kinetic energy corresponding to 300 K is (calculated in SAQ1b):

$$K = \frac{3}{2}k_B(300\text{ K}) = 6.21 \times 10^{-21}\text{ J} \quad (\text{i})$$

The de Broglie wavelength for a neutron with this energy K can be calculated from Eq. (5.4) with $m = m_n$:

$$\lambda = \frac{h}{\sqrt{2m_n K}} = \frac{6.626 \times 10^{-34} \text{ Js}}{\sqrt{2 \times (1.675 \times 10^{-27} \text{ kg}) \times (6.21 \times 10^{-21} \text{ J})}}$$

$$= 1.45 \times 10^{-10} \text{ m} \approx 1.45 \text{ \AA}$$

Neutron diffraction will take place because the de Broglie wavelength of the neutron $\approx$ lattice spacings in the crystal.

9. The energy $E = 6.0 \times 10^3 \text{ eV} = 6.0 \times 1.6 \times 10^{-19} \times 10^3 \text{ J} = 9.6 \times 10^{-16} \text{ J}$

From Eq. (4.23), the wavelength of the photon is:

$$\Rightarrow \lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ Js}) \times (3 \times 10^8 \text{ ms}^{-1})}{9.6 \times 10^{-16} \text{ J}}$$

$$= 2.1 \times 10^{-10} \text{ m} = 2.1 \text{ \AA}$$

To calculate the de Broglie of an electron with this energy E we use Eq. (5.4) with $K = E$,

$$\lambda_e = \frac{h}{\sqrt{2m_e E}} = \frac{6.626 \times 10^{-34} \text{ Js}}{\sqrt{2 \times (9.109 \times 10^{-31} \text{ kg}) \times (9.6 \times 10^{-16} \text{ J})}}$$

$$= 1.584 \times 10^{-11} \text{ m} = 0.16 \text{ \AA}$$

So, electrons can be used to probe atomic structures, because λ_e is of the order of atomic sizes.

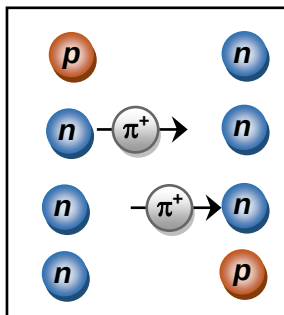
10. The kinetic energy K at a temperature of $T = 120 \mu\text{K} = 120 \times 10^{-6} \text{ K}$ is

$$K = \frac{3}{2} k_B T = \frac{3}{2} \times (1.38 \times 10^{-23} \text{ JK}^{-1}) \times (120 \times 10^{-6} \text{ K})$$

$$= 2.484 \times 10^{-27} \text{ J}$$

Using $m = 1.419 \times 10^{-25} \text{ kg}$ and the value of K in Eq. (5.4), we get:

$$\lambda = \frac{6.626 \times 10^{-34} \text{ Js}}{\sqrt{2 \times (1.419 \times 10^{-25} \text{ kg}) \times (2.484 \times 10^{-27} \text{ J})}} = 2.5 \times 10^{-8} \text{ m} = 25 \text{ nm}$$



The strong nuclear force between a pair of nucleons is transmitted by the creation and exchange of a pion. This process violates the laws of conservation of energy and momentum, yet it is possible because of the uncertainty principle.

THE UNCERTAINTY PRINCIPLE AND ITS CONSEQUENCES

Structure

- | | |
|--|---|
| <p>6.1 Introduction
Expected Learning Outcomes</p> <p>6.2 The Uncertainty Principle
The Uncertainty Principle and Wave-Particle Duality
Energy-Time Uncertainty Principle</p> <p>6.3 Some Thought Experiments
Heisenberg's Gamma Ray Microscope
The Single-Slit Diffraction Experiment
The Double-Slit Experiment</p> <p>6.4 Complementarity</p> | <p>6.5 Consequences of the Uncertainty Principle
The Path of an Object
Zero-Point Energy
The Size of an Atom
Existence of the Electron inside the Nucleus
The Angular Momentum of an Object</p> <p>6.6 Summary</p> <p>6.7 Terminal Questions</p> <p>6.8 Solutions and Answers</p> |
|--|---|

STUDY GUIDE

In the previous unit, we have started developing the fundamental ideas of quantum theory and discussed the concept of wave-particle duality. You have learnt about the wave nature of matter and the matter wave. In this unit, you will study another important concept of quantum theory: the uncertainty principle. You will see that it has practical consequences in the study of atomic and sub-atomic systems. While the uncertainty principle cannot be derived, you will learn about some thought experiments, which confirm the limits set by this principle. Please read through carefully to understand the experiments. You must also work out the numerical problems so that you understand the importance of this principle.

“We have to remember that what we observe is not nature in itself but nature exposed to our method of questioning.”

Werner Heisenberg

6.1 INTRODUCTION

In Unit 5, you have studied that wave-particle duality is the inherent characteristic of all radiation and matter. You have also learnt that each moving particle is associated with a wave and the wavelength, the de Broglie wavelength, is related to the linear momentum of the particle. The wave nature of matter was verified for the first time in the electron diffraction experiments of Davisson and Germer.

The wave nature of particles, first envisaged by de Broglie became the foundation for the development of the explicit wave equation which describes the evolution of these matter waves in space and time. You will study about it in the next unit.

Thought experiments are not new in physics. Different kinds of thought experiments had been used by Galileo, Newton and Maxwell, among others, as part of their contributions to physics. In the words of philosopher Martin Cohen, a thought experiment “*is the discovery of a way of seeing the world*” rather than making an observation or measurement.

In this unit, we describe another fundamental principle of quantum mechanics, **the uncertainty principle**. In some ways it is also one of the most **fundamental differences** between classical and quantum physics. In classical physics, it is possible to measure the exact values of physical quantities simultaneously. For example, you can measure both the position and the velocity of a moving car at any instant of time as precisely as you wish (or as precisely as your measuring device lets you).

Yet, even in principle, it is not possible to do that in quantum physics. In fact, you will study that the more precisely you measure the position of an object, the less precisely you can measure its linear momentum.

In Sec. 6.2, we discuss **Heisenberg’s uncertainty principle**. In physics, thought experiments have traditionally played an important role in clarifying concepts and debating the foundations of a theory (read the margin remark). This is true especially in situations when actual experiments may be too difficult or even impossible to perform.

In Sec. 6.3, we describe some important “**thought**” experiments that illustrate the concept of the uncertainty principle. We focus on three thought experiments: the **gamma ray microscope** experiment devised by Heisenberg himself, the **single slit diffraction** experiment and the **double slit** experiment. In Sec. 6.4, we discuss the principle of **complementarity** and finally in Sec. 6.5 we discuss some **consequences of the uncertainty principle**.

In the next unit we will start with the mathematical formulation of quantum physics which led to the term “quantum mechanics”.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ apply Heisenberg’s uncertainty principle to microscopic systems;
- ❖ explain how the gamma-ray microscope, single slit and double slit experiments adhere to the uncertainty principle; and
- ❖ explain the consequences of the uncertainty principle.

6.2 THE UNCERTAINTY PRINCIPLE

Heisenberg's uncertainty principle, which he presented in 1927, is a statement of the **limit of the accuracy with which the momentum and the position** of a particle can be **simultaneously determined**. In his own words (read the margin remark):

"The product of the probable errors in the measurement of the location and momentum (of a particle) is invariably as large as Planck's constant divided by 4π ." (from his Nobel Lecture, The development of quantum mechanics, December 11, 1933)

In the most general form, the uncertainty principle is written as:

$$\Delta p \Delta q \geq \frac{h}{4\pi} \quad (6.1)$$

where Δp is the probable error in the measurement of the momentum p , also called the "uncertainty" and Δq is the probable error in measurement of the location (read the margin remark).

For a system described by the Cartesian coordinates, the location coordinates are (x, y, z) and the corresponding momenta along the x, y, z -directions are (p_x, p_y, p_z) . Following Eq. (6.1), we can write the uncertainty relation for x and p_x as:

$$\Delta x \Delta p_x \geq \frac{\hbar}{2} \quad (6.2a)$$

where we have used $\hbar = h/(2\pi)$. **What does the uncertainty principle [Eq. (6.2a)] tell us?** Suppose that in an experiment we simultaneously measure the position and momentum of a moving particle. And suppose we measure the position of the particle with an accuracy of Δx . Then the uncertainty principle tells us that the **minimum accuracy with which we can measure the momentum** p_x of the particle is $\Delta p_x = \frac{\hbar}{2\Delta x}$. Note that the

restriction is **on the accuracy of the simultaneous measurement of these variables**. If you were to measure just the position x , or just the momentum p_x , you could be as accurate as you liked for each measurement!

We can also write similar relations for y and p_y and also z and p_z :

$$\Delta y \Delta p_y \geq \frac{\hbar}{2} \quad (6.2b)$$

$$\Delta z \Delta p_z \geq \frac{\hbar}{2} \quad (6.2c)$$

There is also **no limit** on the accuracy of the measurement of any pair or more of **non-conjugate** variables, say y and p_z .

According to Eq. (6.2a), there cannot be a state in which p and x have definite values simultaneously. We can never simultaneously ascertain the values of both position and momentum with arbitrary accuracy. If the position of the microscopic particle is exactly defined (measured precisely) then the

In this unit, we use the term momentum for linear momentum everywhere.

You may wonder why we chose to use the notation " q " to denote the location or position instead of the more familiar " x ". That is because the uncertainty principle holds only for **canonically conjugate** pairs of variables p and q . You will study the mathematical definition of canonical conjugate variables in higher level courses in classical mechanics. For now, it is enough for you to understand that x and p_x (the linear momentum along the x -direction), y and p_y (the linear momentum along the y -direction) and z and p_z (the momentum along the z -direction) form canonically conjugate pairs of variables.



Werner Heisenberg (1901-1976), German theoretical physicist was one of the principal pioneers of quantum mechanics. After earning his Ph.D. from Munich, he worked with Max Born and then with Neils Bohr. He is also known for developing the matrix formulation of quantum mechanics along with Max Born and Pascual Jordan. He received the **Nobel Prize in Physics in 1932** for "the creation of quantum mechanics, the application of which has, inter alia, led to the discovery of the allotropic forms of hydrogen."

The value of the reduced Planck's constant
 $\hbar = 1.054 \times 10^{-34} \text{ Js}$

uncertainty in its momentum will be infinite, i.e., we will not have any idea of what its momentum (i.e., velocity) is. Similarly, if we are able to precisely measure the particle's momentum, we will have no knowledge of its position. So in quantum mechanics, a microscopic particle's motion cannot be described by equations like $x = a \sin \omega t$ because it implies a definite velocity at a definite position. In other words, the uncertainty principle does not allow the concept of a trajectory.

You may also think that perhaps this restriction on the accuracy of the measurement could be due to the limitations of the experimental facilities of that time. But that is not true. This limitation is built into very fabric of quantum theory and holds good even today. Like everything else in quantum theory that you have studied so far, this is measureable and **relevant** only in the world of microscopic particles, like electrons and atoms. The uncertainty principle, while true for the entire physical world is not **seen** in the world of cricket balls, cars, elephants and aeroplanes. In the context of what we have discussed before **unlike classical physics, a definite path of a microscopic particle with definite velocity at every point on the path is not possible in quantum mechanics.**

You will understand this point better when you work out Examples 6.1 and 6.2, and SAQ 1.

EXAMPLE 6.1 : THE UNCERTAINTY PRINCIPLE

- Calculate the minimum uncertainty in the position of (i) a ball of mass 150 g, and (ii) an electron, if their velocity can be measured to a precision of $0.50 \times 10^{-3} \text{ ms}^{-1}$.
- Calculate the minimum uncertainty in the momentum of a ^4He atom confined to a 0.40 nm region.

SOLUTION ■ We use Eq. (6.2a).

- The precision in the measurement of the velocity is $0.50 \times 10^{-3} \text{ ms}^{-1}$. So, the uncertainty in the measurement of the velocity is at least $\Delta v_x = 0.50 \times 10^{-3} \text{ ms}^{-1}$. We calculate the minimum uncertainty in the momentum using the relation between the momentum and the velocity:

$$\Delta p_x = m \Delta v_x = m (0.50 \times 10^{-3} \text{ ms}^{-1})$$

- For $m = 150 \text{ g} = 0.15 \text{ kg}$, we get:

$$\Delta x \geq \frac{\hbar}{2m\Delta v_x} = \frac{1.054 \times 10^{-34} \text{ Js}}{2(0.15 \text{ kg}) \times (0.50 \times 10^{-3} \text{ ms}^{-1})} = 7.027 \times 10^{-31} \text{ m}$$

The minimum uncertainty in the measurement of the position of the ball is $7.027 \times 10^{-31} \text{ m} \approx 7.0 \times 10^{-31} \text{ m}$ up to 2 significant digits.

- with $m = m_e = 9.109 \times 10^{-31} \text{ kg}$, we get

$$\Delta x \geq \frac{\hbar}{2m\Delta v_x} = \frac{1.054 \times 10^{-34} \text{ Js}}{2(9.109 \times 10^{-31} \text{ kg}) \times (0.50 \times 10^{-3} \text{ ms}^{-1})} = 0.115 \text{ m}$$

The minimum uncertainty in the measurement of the position of the electron is $0.115 \text{ m} \approx 0.12 \text{ m}$.

b) Using Eq. (6.2a) with $\Delta x = 0.40 \text{ nm} = 0.40 \times 10^{-9} \text{ m}$, we get:

$$\Delta p_x \geq \frac{\hbar}{2\Delta x} = \frac{1.054 \times 10^{-34} \text{ Js}}{2 \times (0.40 \times 10^{-9} \text{ m})} = 1.32 \times 10^{-25} \text{ kgms}^{-1}$$

So, the minimum uncertainty in the momentum is $1.3 \times 10^{-25} \text{ kgms}^{-1}$.

After working out Example 1a, you can understand that the limits imposed by the uncertainty principle are not at all relevant when we are carrying out measurements on macroscopic objects. An accuracy of $\approx 10^{-31} \text{ m}$ is not possible in any measuring device. On the other hand, for a microscopic object, because of its tiny mass, we would certainly approach these limits.

Example 1b is another example of the importance of the uncertainty principle for microscopic objects. We get an idea of what happens to ^4He atoms at low temperatures if we try to make them stay in one region by solidifying a group of atoms.

Since ^4He has a mass of $6.7 \times 10^{-27} \text{ kg}$, a momentum uncertainty of $1.3 \times 10^{-25} \text{ kgms}^{-1}$ means that at some time the ^4He atom has a momentum of at least that much, or a speed of at least $\Delta p / m = 20 \text{ ms}^{-1}$.

This limit is irrespective of the temperature. So, even as $T \rightarrow 0 \text{ K}$, this motion persists because of the Heisenberg uncertainty principle.

The associated kinetic energy is so large that ^4He will not solidify even for $T \rightarrow 0 \text{ K}$, unless more than 20 atm of external pressure is applied. This pressure pushes the atoms close enough together so that their attractive binding forces become large enough to hold the solid crystal together.

Let us now work out another example.

EXAMPLE 6.2 : THE UNCERTAINTY PRINCIPLE

Calculate the minimum energy of a particle of mass m confined in a one-dimensional box of length a . Using these results estimate the minimum kinetic energy and the corresponding speed for a particle of mass $1.0 \times 10^{-8} \text{ kg}$ confined to a region of $1.0 \times 10^{-6} \text{ m}$.

SOLUTION ■ We use Eq. (6.2a). The minimum uncertainty in the position of the particle is the size of the box. So we take $\Delta x = a$.

From Eq. (6.2a) we get: $\Delta p_x \geq \frac{\hbar}{2\Delta x} = \frac{\hbar}{2a}$

Since the minimum uncertainty in the momentum is $\Delta p_x = \frac{\hbar}{2a}$, the minimum value of the momentum of the particle is at least equal to $\frac{\hbar}{2a}$.

The minimum value of the kinetic energy of the particle is then:

$$K_{\min} = \frac{p_x^2}{2m} = \frac{(\hbar/2a)^2}{2m} = \frac{\hbar^2}{8ma^2} \quad (i)$$

For $m = 1.0 \times 10^{-8} \text{ kg}$ and $a = 1.0 \times 10^{-6} \text{ m}$, the minimum kinetic energy is

$$K_{\min} = \frac{(1.054 \times 10^{-34} \text{ Js})^2}{8 \times (10^{-8} \text{ kg}) \times (10^{-6} \text{ m})^2} = 0.13 \times 10^{-48} \text{ J}$$

You may now like to solve an SAQ.

SAQ 1 - The uncertainty principle

Suppose the position of an electron can be measured in an atom to within an accuracy of $0.2 \text{ \AA}$. What would be the uncertainty in its velocity? What would be its minimum kinetic energy?

After working out Example 6.2, you can see that the minimum kinetic energy predicted by the uncertainty principle for macroscopic objects is really tiny and this value would be too small to be observed.

From SAQ 1, however, note that for an electron the energies are of the order of actual atomic energies. So the uncertainty principle is definitely important for microscopic systems.

Recap

THE UNCERTAINTY PRINCIPLE

The uncertainty principle is a statement of the limit of the accuracy with which a component of the momentum of a particle and the corresponding position coordinate of the particle can be **simultaneously** measured. It is written as:

$$\Delta x \Delta p_x \geq \frac{\hbar}{2} \quad (6.2a)$$

$$\Delta y \Delta p_y \geq \frac{\hbar}{2} \quad (6.2b)$$

$$\Delta z \Delta p_z \geq \frac{\hbar}{2} \quad (6.2c)$$

This limitation is not due to the shortcoming of the measurement but is an outcome of quantum theory.

6.2.1 The Uncertainty Principle and Wave-Particle Duality

The uncertainty principle (or relation, as Heisenberg preferred to call it) can be deduced from the de Broglie hypothesis and the general properties of a group of waves or wave packet. You have already learnt that a particle with a definite momentum can only be represented by a single wave which has a definite wavelength. However, in that case there is no way of specifying the location of the particle! So, when $\Delta p = 0$, the uncertainty principle tells us that Δx is infinite. To get a finite value of Δx , it was necessary to represent the moving particle by a wave packet. This is possible by the superposition of waves of different wavelengths, which could happen only if $\Delta p > 0$ (Eq. 5.22).

Now let us further analyse the wave group that was formed by the superposition of two waves of slightly different wavelengths (Fig. 5.7). The resultant wave is given by

$$\psi(x, t) = 2A \cos \left[\left(\frac{\Delta k}{2} \right) x - \left(\frac{\Delta \omega}{2} \right) t \right] \sin(kx - \omega t) \quad (6.3)$$

Here we plot $\psi(x, t)$ as a function of x (for a particular instant of time):

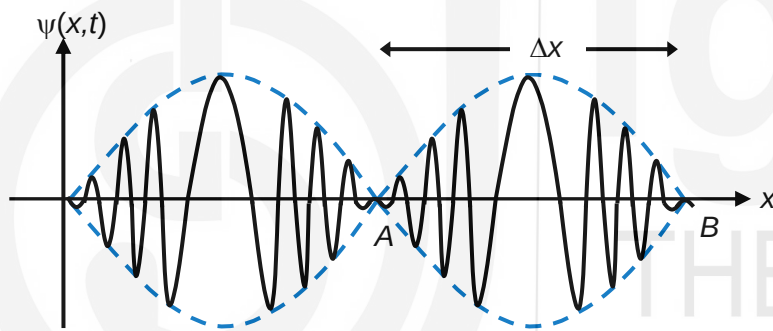


Fig. 6.1: The wave function $\psi(x, t) = A \sin(kx - \omega t) + A \sin[(k + \Delta k)x - (\omega + \Delta \omega)t]$

The dashed line is the envelope of the resultant wave which is given by the function $2A \cos \left[\left(\frac{\Delta k}{2} \right) x - \left(\frac{\Delta \omega}{2} \right) t \right]$. The size of the wave group (Δx) is the distance

between the two successive minima (A and B) shown in Fig. 6.1. We can write (see margin remark):

$$\Delta x \Delta k = 2\pi \quad (6.4)$$

This tells us that the product of Δx and Δk is a constant. You can see from Eq. (6.4) that if Δx were to increase, Δk would decrease. Now, as we have explained in the previous unit, this is not really a wave packet but a wave, made out of the superposition of two waves. For an actual wave packet made by the superposition of waves of any kind, which has a finite width Δx , it can be shown that, in general:

$$\Delta x \Delta k \approx 1 \quad (6.5)$$

The exact value of the right hand side of Eq. (6.1) depends on the type of function which represents the wave packet. So, if the spatial width Δx of the wave packet has to be large, the spread in the wave number, Δk , must be

Between any two zeros of the function $\cos \theta$, θ changes by π . So

$$\left(\frac{\Delta k}{2} \right) \Delta x = \pi \Rightarrow \Delta k \Delta x = 2\pi$$

small. For a matter wave in which the wave number is related to the momentum as $p_x = \hbar k$ (for one-dimensional motion), it would mean that the spread in the momentum (Δp_x) would have to be small. Similarly, if Δx is small, Δk and Δp_x must be large. Substituting $p_x = \hbar k$ in Eq. (6.5), we get

$$\Delta x \Delta p_x \approx \hbar \quad (6.6)$$

So, the fact that a moving particle must be represented by a wave packet itself tells us that there is a fundamental limit to the accuracy with which we can measure the particle's position and momentum. This, in fact, is the form in which the uncertainty relation was first stated. Note that this result [Eq. (6.6)] is a purely mathematical property of a wave packet! Hence, this relation is as fundamental as wave-particle duality.

You may note that Eqs. (6.2a and 6.6) differ by a factor of half. Remember that Eq. (6.6) ($\Delta x \Delta p_x \approx \hbar$) tells us that the product of the uncertainties in p_x and x is **of the order of the magnitude of** (as shown by the symbol $\approx$) $\hbar$. Eq. (6.2a) ($\Delta x \Delta p_x \geq \hbar/2$) tells us that the minimum value of $\Delta x \Delta p_x$ is $\hbar/2$. So, Eq. (6.6) adheres to the limits set by Eq. (6.2a).

Thus, we can say that a direct consequence of the wave-particle duality is the appearance of uncertainties (spreads) in the momentum and the position of a particle. If one of them becomes definite, the other becomes completely indefinite. This situation is in sharp contrast to that of classical mechanics according to which it is possible to determine precisely the position and the momentum of a particle, and therefore, its path (trajectory) at any time.

6.2.2 Energy-Time Uncertainty Principle

There is another form of the uncertainty principle which relates to the measurement of energy and the time required for the measurements, which is written as:

$$\Delta E \Delta t \geq \frac{\hbar}{2} \quad (6.7)$$

In essence the energy-time uncertainty principle tells us that the accuracy with which we can measure energy is limited by the time that we have at our disposal to make the measurement. For example, if you want to measure the energy of a quantum particle like an electron with an accuracy of ΔE , the time you must have to make this measurement is given by:

$$\Delta t \geq \frac{\hbar}{2 \Delta E} \quad (6.8)$$

For a microscopic particle to have a well-defined energy state ($\Delta E = 0$), the state must last for a very long time (we say that the energy state is “stationary”). Conversely, if a microscopic particle has a very short-lived quantum state, it cannot have a precise energy.

This is revealed in the width of spectral lines in the atomic spectra. Suppose the atom is an excited state which has a life time Δt and it makes a transition to a lower state. Then according to Eq. (6.7), the energy (or the frequency, since $E = h\nu$) of the radiation emitted in the transition has an uncertainty

$\Delta E \approx \frac{\hbar}{2\Delta t}$. Thus the radiation will not be monochromatic because $\Delta \nu \approx \frac{\Delta E}{h}$.

This is why spectral lines have a finite width, with frequencies between $\nu + d\nu$ and $\nu - d\nu$. The line width $\Delta \nu$ of the spectral line, also known as natural width, is given by:

$$\Delta \nu \approx \frac{1}{4\pi\Delta t} \quad (6.9)$$

Because time is a parameter and not something to be measured in an experiment, the energy-time uncertainty principle is somewhat different from the other uncertainty principles. As you have seen, it can tell us about the life time of an unstable particle. It also allows for the existence of “virtual” particles like the pion as explained in Sec. 6.5.

Let us now work out an example on the energy-time uncertainty principle.

EXAMPLE 6.3: ENERGY-TIME UNCERTAINTY PRINCIPLE

An atom in an excited state decays by the emission of a photon (read the margin remark). If the average life time of an excited atom is $\sim 2.0 \times 10^{-8}$ s, what is the minimum uncertainty in the energy of the emitted photon? What will be the order of the natural width ($\Delta \nu$) of the spectral line of the atomic emission?

SOLUTION ■ We use Eq. (6.7) with $\Delta t = 2.0 \times 10^{-8}$ s:

$$\Delta E \geq \frac{\hbar}{2\Delta t} = \frac{1.054 \times 10^{-34} \text{ Js}}{2 \times (2.0 \times 10^{-8} \text{ s})} = 0.26 \times 10^{-26} \text{ J}$$

So, the minimum uncertainty in the energy is 0.26×10^{-26} J.

We calculate the line width using Eq. (6.9) with $\Delta t = 2.0 \times 10^{-8}$ s:

$$\Delta \nu \approx \frac{1}{4\pi\Delta t} = \frac{10^8}{4\pi} \text{ Hz} \approx 0.8 \times 10^7 \text{ Hz}.$$

When we say that atom in an excited state *decays*, it means that the atom makes a transition from an excited state to a lower state (emitting a photon in the process).

You may now like to solve a few problems.

SAQ 2 - Energy-time uncertainty principle

- The average decay life time of an elementary particle is $2.0 \mu\text{s}$. Calculate the minimum uncertainty in the measurement of its energy. Also, calculate the minimum uncertainty in the measurement of its mass using the mass-energy equivalence.
- The uncertainty in the energy of a short-lived particle is measured to be 0.40 MeV . What is the smallest lifetime the particle can have?

"Heisenberg has laid a large quantum egg. In Göttingen they believe it (I don't)." – Albert Einstein

Heisenberg belonged to a school of thought that believed a proper theory is one that can be expressed in formal mathematics. In this pursuit he developed the matrix formulation of quantum mechanics in 1925. His version of quantum theory was to be based exclusively on relationships between quantities that are, in principle, "**observable**" or "determined experimentally". This is what led him to realize that there is a limit to the accuracy with which position and momentum could be determined simultaneously.

The act of measuring disturbs the energy and position of subatomic particles. This is called the **measurement problem in quantum mechanics**.

The uncertainty principle destroyed the centuries old classical idea of the universe in which there was (theoretically) no limit on the precision with which any physical quantity could be measured. Many leading scientists of the time found it difficult to accept the idea that even the most sophisticated of machines could not breach the limit set by this principle (see the margin remark for a quote of Einstein, one of the founders of the quantum theory!).

A number of thought experiments were proposed and debated in the Solvay Congress held at Brussels in 1930 to disprove the principle but without any success. In the words of another famous scientist, Richard Feynman:

"quantum mechanics maintains its perilous but still correct existence" to this date. The analysis of some of the thought experiments illustrates very well the physical implications of the principle. In the next section we describe some of these thought experiments.

6.3 SOME THOUGHT EXPERIMENTS

We begin by describing a thought experiment devised by Heisenberg to clarify the concept of his uncertainty principle. The idea was to understand whether *it is possible to make a measurement in ideal settings so as to violate the uncertainty principle*.

6.3.1 Heisenberg's Gamma Ray Microscope

This thought experiment starts with the premise (initial assumption) that it is possible to measure the position of an electron with an arbitrary accuracy. For this the electron is to be observed by a microscope and the image of the electron is to be created on a screen. To be observed in the microscope, it has to be illuminated. The light which is incident on the electron is collected by the lens of the microscope and the image is formed. Let us say that the electron is initially at rest. The possible experimental set-up is shown in Fig. 6.2.

As you have studied in Sec. 4.6, when a light photon is incident on an electron, it undergoes scattering (Compton Effect), say, at an arbitrary angle θ . This photon has to be collected by the aperture of the microscope. The scattering process changes the momentum of the electron (the electron recoils). So you can see that the very act of observation disturbs the electron. To minimize the disturbance, we take a very weak source of light and assume that just one photon strikes the electron, and it is collected by the lens to observe the electron.

Let the wavelength of the incident light be λ . So, the initial momentum of the incident photon is $\frac{h}{\lambda}$. Since the total momentum is conserved, the momentum of the electron and the photon after the scattering should be equal to the momentum of the incident photon.

Further, in order that this photon be collected by the microscope, the photon must be scattered into the aperture of the microscope. So, the scattering angle must lie between $-\alpha$ to α (see Fig. 6.2). When the scattering angle is

– α , the momentum of the scattered photon is $-\frac{h}{\lambda} \sin \alpha$, and the momentum of the electron in the x -direction after scattering is $p_{x1} = \frac{h}{\lambda} \sin \alpha$ (read the margin remark). When the scattering angle is α , the momentum of the scattered photon is $\frac{h}{\lambda} \sin \alpha$, and the momentum of the electron in the x -direction is $p_{x2} = -\frac{h}{\lambda} \sin \alpha$. Therefore, the minimum uncertainty in the momentum of the electron along the x -direction is:

$$\Delta p_x = p_{x1} - p_{x2} = \frac{2h \sin \alpha}{\lambda} \quad (6.10)$$

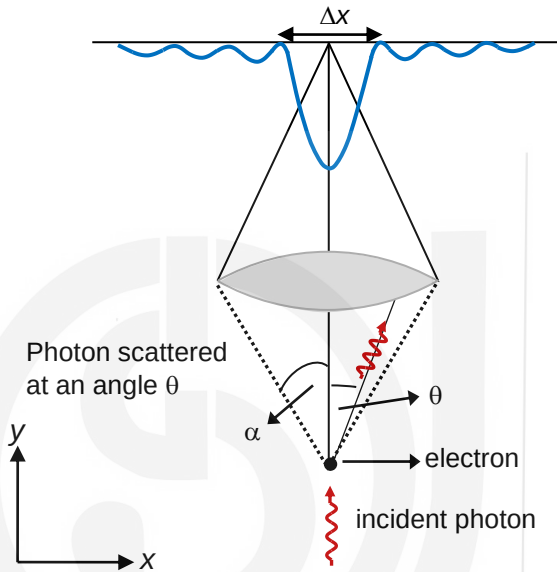


Fig. 6.2: Gamma ray microscope experiment.

We also know that because of the diffraction of light, there is a limit to the resolution of a microscope. This depends on the wavelength of the light and the numerical aperture of the lens. So, the maximum precision (minimum uncertainty) with which the position of the electron can be determined by the microscope is (see Fig. 6.2):

$$\Delta x \approx \frac{\lambda}{2 \sin \alpha} \quad (6.11)$$

To improve the precision of measurement, you could use electromagnetic radiation with the least possible wavelength, which are the gamma rays. Still, even in the most perfect experiment you could design, the product of the minimum uncertainties in the position and momentum of the electron is:

$$\Delta x \Delta p_x \approx \left(\frac{\lambda}{2 \sin \alpha} \right) \left(\frac{2h \sin \alpha}{\lambda} \right) \approx h \quad (6.12)$$

So you see that the product of the uncertainties in Δx and Δp_x is of the order of magnitude of h . Once again this product adheres to the limits set by the uncertainty principle. You could say that Δx may be made quite small even by

For the incident photon:

$$p_{0x}^{ph} = 0; p_{0y}^{ph} = \frac{h}{\lambda}$$

For the photon scattered at an angle θ

$$p_x^{ph} = \frac{h}{\lambda} \sin \theta;$$

$$p_y^{ph} = \frac{h}{\lambda} \cos \theta$$

From the law of conservation of momentum, we should have

$$p_{0x}^{ph} = 0 = p_x^{ph} + p_x$$

where p_x is the momentum of the electron in the x -direction after scattering. Therefore,

$$p_x = -p_x^{ph} = -\frac{h}{\lambda} \sin \theta$$

taking λ to be very small (i.e., by using γ -rays). This, however, would increase Δp , such that the product of Δx and Δp is always finite and given by the uncertainty relation:

$$\Delta x \Delta p_x \geq h \quad (6.13)$$

At this point, it is important to understand that this thought experiment is not a “**proof**” of the uncertainty principle. Rather, it is a validation of the limits contained in the principle in an idealized experimental situation. The principle itself is a consequence of the wave-particle duality of matter. Let us revise what you have learnt in this section before proceeding further.

Recap

GAMMA RAY MICROSCOPE EXPERIMENT

In this thought experiment, the position of the electron is assumed to be measured by using a microscope. The precision of measurement is maximized by using gamma rays. It is found that the product of minimum uncertainty in the simultaneous measurement of the position and momentum of the electron is in agreement with the uncertainty principle (Eq. 6.2a) and is given by:

$$\Delta x \Delta p_x \approx h$$

This thought experiment shows that the uncertainty principle is not a shortcoming of the method of measurement but is an outcome of quantum theory.

Let us look at one another famous thought experiment: the single-slit diffraction experiment.

6.3.2 The Single-Slit Diffraction Experiment

Let us consider a highly collimated beam of photons (or electrons or any other microscopic particles) moving along the x -direction. Suppose it is incident on a screen with a single slit of width d (see Fig. 6.3). You have earlier studied the single-slit diffraction pattern in Sec. 10.3 of Unit 10, BPHCT 137. The photons are diffracted by the slit and the diffraction pattern is shown in Fig. 6.3. The incident photons are travelling in the x -direction, so we can say that

$p_{0x} = p_0 = \frac{h}{\lambda}$ and $p_{0y} = 0$. Since the width of the slit (d) is finite, the position of the photons along the y -direction is uncertain by an amount d , i.e.,

$$\Delta y = d \quad (6.14)$$

After passing through the slit the photons will have a momentum along the y -direction as well. We cannot predict exactly where the photon will strike the screen. All we know is that the photon will arrive at the screen somewhere within the diffraction pattern. Thus, the uncertainty in momentum is given by the angular spread of the diffraction pattern. Since most of the photons will strike the screen in the large central maxima, we can use the angular spread of the central maxima to obtain an estimate for Δp_y .

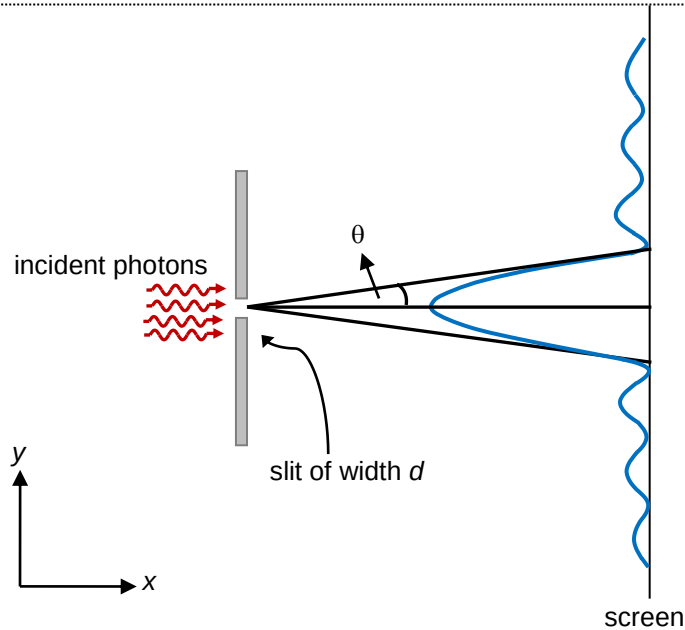


Fig. 6.3: The single-slit experiment with photons.

If the angle between the bright central maxima and the first dark minima is θ , we can say that over the central maximum, p_y changes from $-p_0 \sin \theta$ to $p_0 \sin \theta$. So, we can write:

$$\Delta p_y = 2p_0 \sin \theta \quad (6.15)$$

We also know from diffraction theory that the angle between the bright central maxima and the first dark minima is related to the slit-width by the relation:

$$\sin \theta = \frac{\lambda}{d} \quad (6.16)$$

Using the results of Eqs. (6.14 and 6.15) and $p_0 = \frac{h}{\lambda}$, we can write:

$$\Delta y \Delta p_y = (d) 2p_0 \sin \theta = (d) 2 \left(\frac{h}{\lambda} \right) \left(\frac{\lambda}{d} \right) = 2h \quad (6.17)$$

As you can see, this is also consistent with the uncertainty principle:

$\Delta y \Delta p_y \geq \frac{\hbar}{2}$. Trying to reduce the width of the slit (i.e., reduce d) leads to a greater spread of diffraction pattern, increasing the momentum uncertainty.

SINGLE-SLIT DIFFRACTION EXPERIMENT

A collimated beam of photons (or electrons or any other microscopic particles) moving along the x-direction, is incident on a screen with a single slit of width d and produces a diffraction pattern on a screen. The product of the minimum uncertainty in the simultaneous measurement of the position and momentum of the photon is in agreement with the uncertainty principle (Eq. 6.2b) and is given by: $\Delta y \Delta p_y \approx 2h$

This thought experiment shows that irrespective of the experimental arrangement, there is a limit to the accuracy with which the momentum and position of a particle can be simultaneously measured. It also confirms that it

is impossible to measure the position and momentum of a microscopic particle precisely at the same time.

Finally, we describe the double-slit experiment, which adds a new dimension to our understanding of the uncertainty principle. In the words of the eminent physicist Richard Feynman, the quantum double-slit experiment puts us “up against the paradoxes and mysteries and peculiarities of nature”. It also throws light on an interesting question: Is it ever possible to observe both the wave and particle properties in an experiment? The “orthodox” answer to this question is “no, it is not”. This is the so-called “Copenhagen Interpretation” of quantum mechanics which we discuss in the last section of this unit.

6.3.3 The Double-Slit Experiment

Imagine a double slit arrangement of the kind shown in Figure 6.4. A beam of mono-energetic microscopic particles (such as photons, electrons, protons etc.) are allowed to pass through two slits before falling on a fluorescent screen placed in front of it. After some time, if we plot the total number of particles arriving at the screen as a function of position, we observe an **interference pattern** (Fig. 6.4).

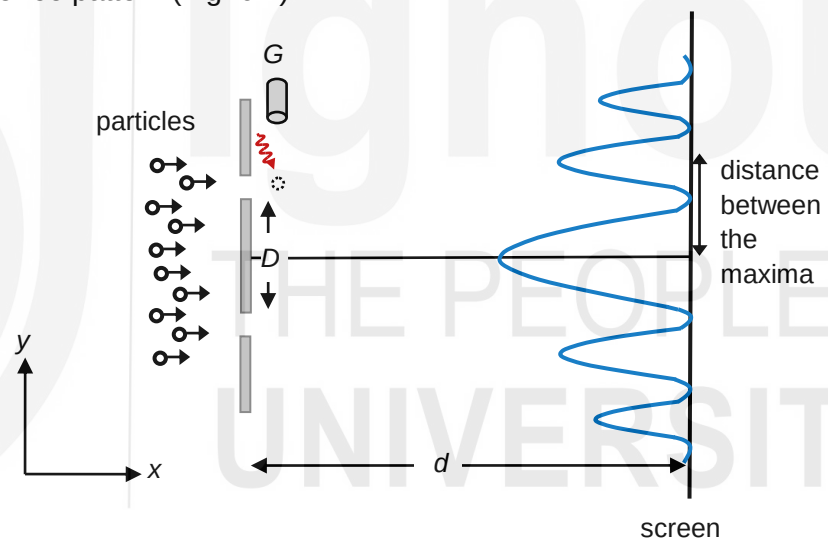


Fig. 6.4: A double-slit experiment with a beam of microscopic particles. The slit through which the electron passes is detected using a gamma ray microscope G.

You have studied this phenomenon in BPHCT 137. You know that interference is a typical wave characteristic. In the interference of light waves, a single wave front splits into two, each of these goes through a different slit and then they recombine to create the interference pattern. For the microscopic particles incident on the double slit, we explain this phenomenon as follows: The matter waves corresponding to the particle are split at the two slits and they interfere with one another.

But beware of thinking of these matter waves as classical waves, because the particles do arrive at the fluorescent screen in a particle like way: we get one localised flash every time a particle strikes the screen. However, the pattern of spots, made by a large number of particles hitting the screen looks like the wave interference pattern. But then we ask: Is this wave-like behaviour seen only when we observe a group of particles? What happens when only one

particle arrives at the slit? Quantum mechanics says that we will still get an interference pattern.

It is not easy to accept this picture. It appears that the particle goes through both slits at the same time. You may ask: can a single particle split, pass through both slits and the two halves interfere with one another? As Paul Dirac, one of the pioneers of quantum mechanics, put it, “*Each photon [or a microscopic particle] interferes only with itself.*”

Why don't we find out whether this is correct by making a measurement?

To check that out, the beam of particles is modulated so that only one particle reaches the double slit arrangement at a time. We now try to detect which slit the particle is going through, maybe by placing a detector in front of each slit of the arrangement. What we find is that the **interference pattern disappears!**

So, if we try to detect the single particle, it seemingly passes through one slit or the other, and no interference pattern is seen. However, if we do not try to detect the particle at either slit, the particle seems to pass through both slits simultaneously before interfering with itself. So, it acts like a wave.

So, the very act of observation/detection of the particle destroys its wave-like behaviour and it behaves like particle.

This is a consequence of the uncertainty principle. As soon as we try to precisely locate the particle and determine the slit (*A* or *B*) through which it passed, we lose information about its momentum (which decides the wavelength). Let us see how.

Suppose the distance between the slits is D and the distance between the slits and the screen is d . From Sec.10.4 of the course BPHCT137, you know that the distance between any two adjacent maxima in the interference pattern is $d\lambda/D$. In this case, λ is the de Broglie wavelength of the incident particle, which has a momentum p along the x -direction. Next, we introduce a detector to observe which slit the particle passes through (let us imagine that the detector is a gamma ray microscope). If the detector has to be able to tell us through which slit the particle passes, the wavelength of the photon used should be less than $D/2$ and its momentum then should be greater than $2h/D$. In the process of detection, that is, after collision with a photon, the particle would acquire a momentum p_y in the y -direction and the uncertainty in this momentum, Δp_y would be:

$$\Delta p_y > 2h/D \quad (6.18)$$

Dividing both sides of this equation by the initial momentum of the particle p we get:

$$\frac{\Delta p_y}{p} > \frac{2h}{Dp} = \frac{2\lambda}{D}$$

The corresponding uncertainty in the position of the particle on the screen is found by using the corresponding triangles (see Fig. 6.5):

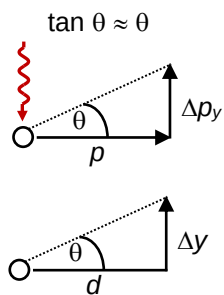


Fig. 6.5

In 1961, C. Jönsson of Tübingen, Germany, succeeded in showing double-slit interference effects for electrons by constructing very narrow slits and using relatively large distances between the slits and the observation screen.

Akira Tonomura and co-workers at Hitachi performed the double-slit experiment in 1989 in which there was just one electron in the apparatus at any one time. They observed the build-up of the fringe pattern with a very weak electron source and an electron biprism.

In recent times, the uncertainty principle, which is held to be one of the cornerstones of quantum mechanics, has been challenged by experiments using entangled pair of particles as we have described in Unit 5. In these experiments both wave and particle aspects may be observed simultaneously.

$$\frac{\Delta y}{d} = \frac{\Delta p_y}{p} > \frac{2\lambda}{D} \Rightarrow \Delta y > \frac{2\lambda d}{D} \quad (6.19)$$

In other words, the uncertainty in the position of the particle results from the measurement; it is a result of attempting to detect its position near the slit. You can see that this uncertainty is greater than the distance between the two adjacent maxima of the diffraction pattern on the screen. The uncertainty is enough to shift the interference pattern observed on the screen up and down in the y -direction, by a distance roughly equal to the distance between the two maxima. Such a random shift is just enough to smear out the interference pattern so that no interference is observed.

As long as we do not attempt to measure the particle's position at the slit, the interference pattern stays intact. So, the microscopic particle behaves as a localized particle when it is detected at the screen. But when not detected, an interference fringe pattern is observed even with a single particle! Such experiments were carried out with electrons (read the margin remark) and the results of this thought experiment were reproduced. Let us now revise the main features of the double-slit experiment.

DOUBLE-SLIT DIFFRACTION EXPERIMENT

- In the double-slit experiment, a beam of mono-energetic microscopic particles (such as photons, electrons, protons, etc.) passes through two slits and falls on a fluorescent screen placed in front of it.
- The particles exhibit wave-particle duality. When the total number of particles arriving at the screen is plotted as a function of position, an **interference** pattern is observed.
- If an attempt is made to determine the location of the particle precisely by detecting it at the slit through which it passes, the interference pattern disappears, as a consequence of uncertainty. So, information about its momentum (which decides the wavelength) is completely lost. As long as no attempt is made to measure the particle's position at the slit, the interference pattern stays intact.

So far, you have learnt that the particle behaves like both a particle and a wave, but the two aspects cannot be observed in an experiment simultaneously. Niels Bohr gave an explanation for this phenomenon, through his **principle of complementarity**, which we now explain.

6.4 COMPLEMENTARITY

It was pointed by Bohr that the **position and momentum measurements are really complementary and they are mutually exclusive processes**.

This means that we can concentrate on the momentum and measure the wavelength of the particle from the interference pattern and hence its momentum. But then we cannot tell which slit the particle went through. Or we can concentrate on the position and lose information about the wavelength and momentum. You have seen that when we try to find out which slit the

particle passes through, we lose the interference pattern and hence, the information about its wavelength and momentum.

In his complementarity principle, introduced in 1928, Bohr described this situation by stating that the wave and particle aspects of a physical system are complementary – when we localize (find out which slit the particle goes through), we reveal the particle aspect; and when we don't localize (don't worry about which slit the particle goes through), we reveal the wave aspect. However, we cannot reveal both the aspects at the same time – they are complementary.

You may well ask: Is it that the microscopic particles are both wave and particle and we can see only one attribute with a particular experimental arrangement? That is, they possess well defined position and linear momentum at each instant but we are unable to measure them simultaneously?

Or, is it that the particles just do not possess well defined position and momentum simultaneously?

While Einstein was of the former view which he never gave up, Bohr and Heisenberg took the latter viewpoint. Thus, the uncertainty relation propagates the view that these uncertainties arise as a result of an inherent limitation of nature; these are intrinsic to the nature of the quantum world. However precise may be the measuring devices or the method of measurement, there is no escape from these uncertainties.

REMEMBER: The Heisenberg uncertainty principle is clearly a consequence of wave-particle duality. It reflects the fact that quantum mechanics, although a complete theory, provides a less detailed description of a physical system than does classical physics. This description is governed by the complementarity principle.

The uncertainty principle is a fundamental principle of quantum mechanics. You have noticed the role of Planck's constant – it is so small that the limitations imposed by the uncertainty principle are significant only in the domain of microscopic particles, namely atoms, molecules, subatomic, nuclear and sub-nuclear particles. The uncertainty principle has some major consequences for our understanding of various phenomena in the microscopic world. Let us now study them.

6.5 CONSEQUENCES OF THE UNCERTAINTY PRINCIPLE

In this section we study some of the consequences of the Uncertainty principle. You will also see that for atoms and subatomic particles the uncertainty principle is of great help in making **order of magnitude estimates** of relevant quantities. When you study the applications of quantum mechanics in Unit 8 and in the next block, you will calculate exact values of some of these quantities, but you will see in this section that just by applying the uncertainty principle you can make a reasonable estimate.

Heisenberg and Bohr's interpretation of quantum mechanics is also referred to as the Copenhagen interpretation. Copenhagen is the birthplace of Niels Bohr.

6.5.1 The Path of an Object

From Newtonian mechanics, you know that you can define the path of a particle if you know its exact position and velocity simultaneously. Now you know that this knowledge is not permitted by the uncertainty principle for microscopic particles. Therefore, in the quantum world, we cannot define the path (or the orbit) of an object. In this light, Bohr's theory of the hydrogen atom is no longer valid because it assigns position and velocity simultaneously to the electron orbiting the nucleus.

Due to wave-particle duality, which ascribes wave nature to a particle, we can only determine the probability of finding the particle at a point at an instant of time. You will read about this in the next unit.

6.5.2 Zero-Point Energy

You have learnt in kinetic theory (Block 1, BPHCT 135) that the kinetic energies of atoms oscillating about their positions in crystals are proportional to the absolute temperature. Hence, according to kinetic theory, at absolute zero, the atoms would stop oscillating and would remain fixed in their lattice position. But, according to the uncertainty relation, both position and momentum cannot be specified at the same time with complete accuracy. This means that the atomic oscillators, even at absolute zero, would retain a certain amount of oscillatory motion, enough to obey the uncertainty relation. The energy possessed by the atomic oscillator at absolute zero is termed as **zero-point energy**. Experimental studies of the motion of the atom at a temperature (0.001 K), quite close to absolute zero, have shown the reality of the zero-point energy.

Let us see how the uncertainty principle explains the concept of the zero-point energy.

Consider a particle of mass m , confined to a small one-dimensional region, of size " a ". According to the uncertainty relation, the minimum uncertainty in its momentum is given by Eq. (6.2a) with $\Delta x \approx a$:

$$\Delta p_x \geq \frac{\hbar}{2a} \quad (6.20)$$

Since the momentum has a spread of at least $\frac{\hbar}{2a}$, the average momentum of the particle would be at least of this order. So, a particle confined to the small region of size a cannot be at rest, it must have a finite energy which corresponds to a momentum of $\frac{\hbar}{2a}$. The magnitude of the kinetic energy K of the particle is given by:

$$\langle K \rangle = \frac{(\Delta p_x)^2}{2m} \geq \frac{\hbar^2}{8ma^2} \quad (6.21)$$

Eq. (6.21) tells us that a quantum particle confined to a region must have an energy at least equal to $\frac{\hbar^2}{8ma^2}$. This energy is called the **zero-point energy**.

The uncertainty principle can be used to make order of magnitude estimates of zero-point energy for microscopic systems. We look at one such example now.

EXAMPLE 6.4: ZERO-POINT ENERGY

Calculate the minimum energy for an electron in an atom given that the typical size of an atom is $\sim 1\text{\AA}$.

SOLUTION ■ We use the relation $\Delta r \Delta p \geq \frac{\hbar}{2}$ (read the margin remark).

Since the electron is confined within the atom, we can say that the maximum uncertainty in its position is $\Delta r = 0.5 \times 10^{-10} \text{ m}$. The uncertainty in its momentum Δp_r is:

$$\Delta p \geq \frac{\hbar}{2\Delta r} = \frac{1.054 \times 10^{-34} \text{ Js}}{2 \times (0.5 \times 10^{-10} \text{ m})} = 1.054 \times 10^{-24} \text{ kgms}^{-1}$$

So the momentum of electron in the atom is at least

$$p \sim 1.054 \times 10^{-24} \text{ kgms}^{-1}$$

So, the minimum energy of the electron in the atom is:

$$E_{\min} = \frac{p^2}{2m_e} = \frac{(1.054 \times 10^{-24} \text{ kgms}^{-1})^2}{2 \times (9.109 \times 10^{-31} \text{ kg})} = 0.061 \times 10^{-17} \text{ J} = 3.8 \text{ eV}$$

You have studied in Unit 4 that the minimum energy (ground state) of an electron in the hydrogen atom is 13.6 eV.

6.5.3 The Size of an Atom

You can use uncertainty principle to determine the approximate size of an atom as well. Let us take the example of the hydrogen atom, which consists of a proton and an electron. Let us assume that the electron is at a distance r from the nucleus. Let us first estimate the kinetic energy of the electron. For the electron, we can write the spread in its spatial location as $\Delta r \approx r$.

The uncertainty in its momentum is $\Delta p \geq \frac{\hbar}{2r}$ (using $\Delta r \Delta p \geq \frac{\hbar}{2}$). The momentum of the electron is at least of the order of the uncertainty, so $p \approx \Delta p = \frac{\hbar}{2r}$ and the kinetic energy of the electron in the atom

$$K = \frac{(p)^2}{2m_e} \approx \frac{\hbar^2}{8m_e r^2} \quad (6.22)$$

The total energy of the electron in the atom is the sum of its kinetic and potential energies:

$$E = \frac{p^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 r} = \frac{\hbar^2}{8m_e r^2} - \frac{e^2}{4\pi\epsilon_0 r} \quad (6.23)$$

The electron in an atom is actually a three-dimensional system and the Hamiltonian is:

$$H = \frac{p^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 r},$$

where :

$$p^2 = p_x^2 + p_y^2 + p_z^2;$$

and

$$r^2 = x^2 + y^2 + z^2$$

r is the distance of the electron from the nucleus. In this example as also in Sec. 6.5.3, we estimate the energy by assuming it to be effectively a one-dimensional system in which the following uncertainty relation holds:

$$\Delta r \Delta p \geq \frac{\hbar}{2}$$

This gives us an idea **only of the order of magnitude** of the energy.

A more accurate estimate may be obtained by using:

$$E = \frac{p^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 r};$$

where :

$$p^2 \approx (\Delta p_x)^2 + (\Delta p_y)^2 + (\Delta p_z)^2$$

and

$$r^2 \approx (\Delta x)^2 + (\Delta y)^2 + (\Delta z)^2$$

Using

$$\Delta x = \Delta y = \Delta z = r$$

and

$$\Delta p_x = \Delta p_y = \Delta p_z = \frac{\hbar}{2r}$$

and following the steps leading to Eq. (6.24)

we get:

$$r = r_0 = 3\sqrt{3} \left(\frac{\hbar^2 \epsilon_0}{\pi m_e e^2} \right)$$

This gives an estimate of the first Bohr orbit to be $\sim 0.68 \text{ \AA}$ and the size of the atom to be $\sim 1.36 \text{ \AA}$.

Remember: This gives us an idea **only of the order of magnitude** of the radius. You will learn how to obtain the value $\sim 0.53 \text{ \AA}$ of the first Bohr orbit for a hydrogen atom in higher level courses. You need to solve the Schrödinger equation (Unit 7) for the hydrogen atom and calculate the expectation value of r (Unit 8). This is beyond the scope of this course.

To estimate the size of the atom we minimize the energy as a function of r . For that:

$$\begin{aligned} \frac{\hbar^2}{8m_e} \frac{d}{dr} \left(\frac{1}{r^2} \right) - \frac{e^2}{4\pi\epsilon_0} \frac{d}{dr} \left(\frac{1}{r} \right) &= 0 \\ \Rightarrow \frac{\hbar^2}{8m_e} \left(\frac{-2}{r^3} \right) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{-1}{r^2} \right) &= 0 \end{aligned}$$

After simplification, we get the minimum value of r as:

$$r = r_0 = \frac{\hbar^2 (4\pi\epsilon_0)}{4m_e e^2} = \frac{\hbar^2 \epsilon_0}{\pi m_e e^2} \quad (6.24)$$

Substituting the values of the constants, we get

$$r_0 = 0.13 \text{ \AA} \quad (6.25)$$

The typical size of the atom as estimated from the uncertainty principle would be $\approx 2r_0 = 0.26 \text{ \AA}$. The size calculated for the first Bohr orbit for a hydrogen atom is $\sim 0.53 \text{ \AA}$ (read the margin remark). Also notice that the nucleus attracts the electron, yet the uncertainty principle ensures that the electron is at a finite distance from the nucleus and does not come too close to it.

6.5.4 Existence of the Electron inside the Nucleus

The atomic nucleus typically has a size $\sim$ few fermi (1 fermi, or femtometer is $1 \times 10^{-15} \text{ m}$). The size of the nucleus is much less than the size of an atom, which as you have seen is $\sim 10^{-10} \text{ m}$. We can use the uncertainty principle to ascertain whether it would be possible to confine an electron within the nucleus.

Let us take the size of the nucleus to be 5 fermi. Then the uncertainty in the position of the electron would be $\Delta x \approx 5$ fermi. Using the uncertainty principle we can write the uncertainty in the momentum of the electron in the nucleus as:

$$\Delta p_x \geq \frac{\hbar}{2\Delta x} \Rightarrow \Delta p_x \geq \frac{1.05 \times 10^{-34} \text{ Js}}{2 \times (5 \times 10^{-15}) \text{ m}} = 1.054 \times 10^{-20} \text{ kgms}^{-1} \quad (6.26)$$

Typically the momentum of the electron would also be at least of this order. So, assuming that the kinetic energy of the electron is much larger than the rest mass energy, we can see that the value of the kinetic energy of the electron in the nucleus is at least (read the margin remark on the facing page):

$$E = pc = (1.054 \times 10^{-20} \text{ kgms}^{-1}) \times (3.0 \times 10^8 \text{ ms}^{-1}) = 3.16 \times 10^{-12} \text{ J} \approx 20 \text{ MeV}$$

Electrons emitted in the process of beta decay (during the radioactive decay of a nucleus) have energies much less than this ($\sim 1 \text{ MeV}$). So, electrons are not present inside the atomic nucleus.

In general, the uncertainty principle can give us an estimate of the energy required to confine a particle within a given region, like an atom or a nucleus. This energy is called the **confinement energy**. The smaller the region, smaller is the uncertainty in its position and, according to the uncertainty principle, larger would be the uncertainty in the momentum. The corresponding energy of the particle would also be higher. So, in general, the smaller the region in which the particle is confined, the greater is the energy required to confine the particle.

SAQ 3 - Confinement energy of a proton in the nucleus

The uncertainty in the position of a proton confined to the nucleus of an atom is roughly of the order of the diameter of the nucleus which is 5.0×10^{-15} m. What is the uncertainty in the proton's momentum?

6.5.5 The Angular Momentum of an Object

You know that the angular momentum $\vec{L}$ of an object is defined as a cross product of its position $\vec{r}$ and momentum $\vec{p}$. Since r and p are not known simultaneously, it follows that L is also uncertain. However, L^2 ($\vec{L} \cdot \vec{L}$) can have well defined values, as you will study in advanced quantum mechanics courses.

You may now like to work out an SAQ on the consequence of the uncertainty principle.

SAQ 4 - Zero-point energy

For a quantum mechanical point particle of mass m in a one-dimensional harmonic potential $V(x) = \frac{1}{2}m\omega^2x^2$, determine the minimum (or "zero-point") energy.

In this unit, you have learnt about the uncertainty principle. The discussion in this unit may require more than one reading. We end this unit with a quote from the Nobel lecture of Prof. Max Born in 1954 in the context of Heisenberg's famous paper on the uncertainty principle. It sums up the essence of how the uncertainty principle changed the way we look at the microscopic world:

"It showed that not only the determinism of classical physics must be abandoned, but also the naive concept of reality which looked upon the particles of atomic physics as if they were very small grains of sand. At every instant a grain of sand has a definite position and velocity. This is not the case with an electron. If its position is determined with increasing accuracy, the possibility of ascertaining the velocity becomes less and vice versa".

We now summarise the concepts you have studied in this unit.

Given that the mass of an electron is

$m_e = 9.1 \times 10^{-31}$ kg, we can calculate the kinetic energy as:

$$K = \frac{(p_x)^2}{2m_e} \approx 360 \text{ MeV}$$

This is much larger than the rest mass energy of the electron, which is 0.51 MeV. So, clearly we are dealing with relativistic energies. Hence, we use the relativistic formula for calculating the energy of the electron in the atomic nucleus.

Inside the nucleus, the protons and neutrons are bound by the strong nuclear force. In 1935, Japanese physicist Yukawa proposed (in the exchange force model) that a pair of nucleons would experience nuclear force when one of the pair spontaneously emits a particle and the other absorbs it. The creation and exchange of this particle violates both energy and momentum conservation. However, **the uncertainty principle allows such a particle to exist**. For this the particle must be very short lived and be confined to an extremely small region. Then energy conservation can be violated to an extent ΔE corresponding to the lifetime of the particle Δt and momentum conservation can be violated to an extent Δp_x up to a small nuclear region Δx .

6.6 SUMMARY

Concept	Description
The uncertainty principle	■ The uncertainty principle is a statement of the limit of the accuracy with which a component of the momentum of a particle and the corresponding position coordinate of a particle can be simultaneously measured. It is written as: $\Delta x \Delta p_x \geq \frac{\hbar}{2}$ $\Delta y \Delta p_y \geq \frac{\hbar}{2}$ $\Delta z \Delta p_z \geq \frac{\hbar}{2}$ This limitation is not due to the shortcoming of the measurement but is an outcome of quantum theory.
The energy-time uncertainty relation	■ The product of the uncertainty in the measurement of the energy and the uncertainty in the time interval during which the measurement is at least equal to $\hbar/2$: $\Delta E \Delta t \geq \frac{\hbar}{2}$
Thought Experiments	■ Several thought experiments illustrate that uncertainty is not a limitation of the experimental apparatus, but rather it is a fundamental tenet of quantum mechanics • In the Gamma Ray Microscope experiment, the position of the electron is assumed to be measured by using a microscope. The precision of measurement is maximized by using gamma rays. It is found that the product of minimum uncertainty in the simultaneous measurement of the position and momentum of the electron is in agreement with the uncertainty principle and is given by: $\Delta x \Delta p_x \approx h$ • In the single-slit diffraction experiment, a collimated beam of photons (or electrons or any other microscopic particles) moving along the x-direction, is incident on a screen with a single slit of width d and produces a diffraction pattern on a screen. The product of the minimum uncertainty in the simultaneous measurement of the position and momentum of the photon is in agreement with the uncertainty principle and is given by: $\Delta y \Delta p_y \approx 2h$ • In the double-slit diffraction experiment, a beam of mono-energetic microscopic particles (such as photons, electrons, protons, etc.) passes through two slits and falls on a fluorescent screen placed in front of it. The particles exhibit wave-particle duality. When the total number of particles arriving at the screen is plotted as a function of position, an interference pattern is observed.

If an attempt is made to determine the location of the particle precisely by detecting it at the slit through which it passes, the interference pattern disappears, as a consequence of uncertainty. So, information about its momentum (which decides the wavelength) is completely lost. As long as no attempt is made to measure the particle's position at the slit, the interference pattern stays intact.

Consequences of the uncertainty principle

■ Some important **consequences of the uncertainty principle** are that:

- The path (or orbit) of an object cannot be precisely defined.
- Atomic oscillators possess a finite amount of energy, called the **zero-point energy**, even at absolute zero temperatures.
- Electrons do not exist inside the nucleus.

Principle of Complementarity

■ The wave and particle aspects of a physical system are **complementary**. It is not possible to reveal both the particle and wave aspects of the system at the same time.

6.7 TERMINAL QUESTIONS

1. Show that the uncertainty principle can be expressed in the form $\Delta L \Delta \theta \geq \frac{\hbar}{2}$, where ΔL is the uncertainty in the angular momentum of the particle and $\Delta \theta$ is the uncertainty in its angular position.
2. The radius of a hydrogen atom is $5.3 \times 10^{-11} \text{ m}$. Estimate the minimum kinetic energy of the electron in this atom using the uncertainty principle.
3. Consider that a microscopic object is moving along the x-axis and the uncertainties in its position are Δx_0 and Δx , respectively, at $t = 0$ and $t = t$. Show that Δx is directly proportional to t and inversely proportional to Δx_0 . From this problem what do you learn about the spreading of the waves associated with the motion of an object?
4. Suppose we can measure the velocity of an electron in an atom with an accuracy of $1.0 \times 10^2 \text{ m s}^{-1}$ (orbital velocities are typically $\sim 10^6 \text{ m s}^{-1}$). What is the minimum uncertainty in position? Determine the ratio of the uncertainty in the position of the electron to the size of the atom, taking the typical size of the atom to be $\sim 1 \text{ \AA}$.
5. Estimate the minimum velocity of a proton inside the ^{235}U nucleus, which has a diameter of 12 fm.
6. The energy of a quantum particle of mass m bound by a special kind of spring is

$$E = \frac{p^2}{2m} + kx^4$$

where k is a positive constant. Use Heisenberg's uncertainty principle to calculate the minimum possible energy of the particle.

7. A subatomic particle created in an experiment has an average life time of 4.0×10^{-20} s, after which it decays into other particles. Using the uncertainty principle, calculate the minimum uncertainty in its energy. Using the relativistic energy-mass equivalence, calculate the minimum uncertainty in the measurement of the mass of the particle.
8. A nucleus in its excited state returns to its ground state by emitting a gamma ray. If the lifetime of the excited state is 5.0×10^{-12} s, calculate the uncertainty in the energy of the gamma ray.
9. Nitrogen molecules at room temperature are confined in a box of side 10.0 cm. Calculate the minimum uncertainty in each component of its momentum and its velocity. Compare this to the rms speed of a nitrogen molecule at room temperature, which is 511 m s^{-1} . The mass of a nitrogen molecule is 2.32×10^{-26} kg.

6.8 SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. The uncertainty the position is of the electron is $0.2 \text{ \AA}$ and therefore,

$$\Delta x = 2.0 \times 10^{-11} \text{ m}$$

Using Eq. (6.2a), the uncertainty in its velocity ($\Delta p_x = m_e \Delta v$) is:

$$\Delta v \geq \frac{\hbar}{2m_e \Delta x} = \frac{1.054 \times 10^{-34} \text{ Js}}{2 \times (9.109 \times 10^{-31} \text{ kg}) \times (2.0 \times 10^{-11} \text{ m})} = 2.9 \times 10^6 \text{ ms}^{-1}$$

So the velocity of the electron in the atom is at least

$$v \sim 2.9 \times 10^6 \text{ ms}^{-1}$$

And the kinetic energy of an electron with this speed is:

$$K = \frac{1}{2} m_e v^2 = \frac{1}{2} (9.109 \times 10^{-31} \text{ kg}) \times (2.9 \times 10^6 \text{ ms}^{-1})^2 = 3.8 \times 10^{-18} \text{ J}$$

2. a) We use Eq. (6.7) with $\Delta t = 2 \mu\text{s} = 2.0 \times 10^{-6} \text{ s}$. The uncertainty in the measurement of its energy is

$$\Delta E \geq \frac{\hbar}{2\Delta t} = \frac{1.054 \times 10^{-34} \text{ Js}}{2 \times (2 \times 10^{-6} \text{ s})} = 2.63 \times 10^{-29} \text{ J} = 1.6 \times 10^{-10} \text{ eV} \quad (\text{i})$$

So the minimum uncertainty in the energy measurement is $2.6 \times 10^{-29} \text{ J}$. Using Eq. (3.26) of Unit 3, Block 1 for the mass-energy equivalence, we can write

$$\Delta E = \Delta m c^2 \quad (\text{ii})$$

where Δm is the minimum uncertainty in the measurement of the mass of the elementary particle. So, we can write:

$$\Delta m = \frac{\Delta E}{c^2} = \frac{(2.6 \times 10^{-29} \text{ J})}{(3 \times 10^8 \text{ ms}^{-1})^2} = 2.9 \times 10^{-46} \text{ kg}$$

b) We use Eq. (6.7) with $\Delta E = 0.4 \text{ MeV}$ (see the margin remark). Hence,

$$\Delta t \geq \frac{1.054 \times 10^{-34} \text{ Js}}{2 \times (0.4 \times 1.6 \times 10^{-13} \text{ J})} = 8.23 \times 10^{-22} \text{ s}$$

The lifetime of the particle will be at least of the order of the minimum uncertainty in $\approx 8.2 \times 10^{-22} \text{ s}$.

$$\begin{aligned} 1 \text{ MeV} &= 10^6 \text{ eV} \\ &= 1.6 \times 10^{-13} \text{ J} \end{aligned}$$

3. We use Eq. (6.2a) with $\Delta x \sim 5.0 \times 10^{-15} \text{ m}$. Therefore, the uncertainty in the momentum is:

$$\Delta p_x \geq \frac{\hbar}{2\Delta x} = \frac{(1.054 \times 10^{-34} \text{ Js})}{2 \times (5 \times 10^{-15} \text{ m})} = 1.054 \times 10^{-20} \text{ kgms}^{-1}$$

4. Let the uncertainty in the position of the particle be Δx . Then the minimum uncertainty in the momentum of the particle is:

$$\Delta p_x = \frac{\hbar}{2\Delta x} \quad (\text{i})$$

The momentum of the oscillator is then at least equal to Δp_x and the minimum kinetic energy is:

$$K = \frac{(\Delta p_x)^2}{2m} = \frac{\hbar^2}{8m(\Delta x)^2} \quad (\text{ii})$$

So, the minimum total energy of the particle, which is the sum of its kinetic energy and its potential energy, is:

$$E = K + V = \frac{\hbar^2}{8m(\Delta x)^2} + \frac{1}{2} m \omega^2 (\Delta x)^2 \quad (\text{iii})$$

To calculate the minimum energy we impose the condition that

$$\begin{aligned} \frac{dE}{d(\Delta x)} &= 0 \Rightarrow \frac{-2\hbar^2}{8m\Delta x^3} + m\omega^2 \Delta x = 0 \\ \Rightarrow \Delta x &= \left(\frac{\hbar}{2m\omega} \right)^{1/2} \quad (\text{iv}) \end{aligned}$$

The minimum energy is obtained by replacing Δx from Eq. (iv) into Eq. (iii):

$$E = \frac{\hbar^2}{8m \left(\frac{\hbar}{2m\omega} \right)} + \frac{1}{2} m \omega^2 \left(\frac{\hbar}{2m\omega} \right) = \frac{1}{4} \hbar \omega + \frac{1}{4} \hbar \omega = \frac{1}{2} \hbar \omega$$

Terminal Questions

1. Consider a particle moving in a circle of radius r . If Δx is the arc length corresponding to angular position $\Delta \theta$, then we can rewrite Eq. (6.2a) as:

$$r\Delta\theta m\Delta v \geq \frac{\hbar}{2} \quad \text{or} \quad \Delta\theta mr\Delta v \geq \frac{\hbar}{2}$$

But $L = mrv$ for the particle and $\Delta L = mr\Delta v$ since m and r are constant. Hence, we obtain:

$$\Delta L \Delta\theta \geq \frac{\hbar}{2}$$

2. The uncertainty in the electron's position is $\Delta x = 5.3 \times 10^{-11} \text{ m}$ and

$$\Delta p_x \geq \frac{\hbar}{2\Delta x} = \frac{1.054 \times 10^{-34} \text{ Js}}{2 \times (5.3 \times 10^{-11} \text{ m})} = 1.0 \times 10^{-24} \text{ kg m s}^{-1}$$

The momentum of the electron is at least equal to $1.0 \times 10^{-24} \text{ kg m s}^{-1}$ and so its kinetic energy is

$$K = \frac{p_x^2}{2m_e} = \frac{(1.0 \times 10^{-24} \text{ kg m s}^{-1})^2}{2 \times (9.109 \times 10^{-31} \text{ kg})} = 5.5 \times 10^{-19} \text{ J} = 3.4 \text{ eV}$$

3. If v_g is the group velocity of the wave packet associated with the microscopic particle, then at time t :

$$\Delta x = v_g t = \frac{p_0}{m} t = \frac{h}{\lambda_0 m} t$$

where λ_0 is the initial wavelength of the wave packet at time $t = 0$. This is equal to Δx_0 , the uncertainty in the particle's position at time $t = 0$. Thus, we have

$$\Delta x = \frac{h}{m} \frac{t}{\Delta x_0}$$

This result tells us that Δx , i.e., the spread of the wave-packet increases with time. The narrower the packet is initially, the quicker it spreads. This is the hidden influence of the uncertainty principle. If the confinement length Δx_0 is small, the uncertainty in its momentum and, hence, its velocity is large:

$$\left(\Delta x \approx \frac{\hbar}{m\Delta x_0} \right)$$

This means that the wave-packet will contain many waves of high velocity much greater than the average group velocity p_0/m . Due to the fluctuation in velocity, the distance covered by the particle will also be uncertain by an amount $\Delta x(t)$, i.e., its spread will be large.

4. The uncertainty in the velocity $\Delta v = 1.0 \times 10^2 \text{ ms}^{-1}$. So the uncertainty in the momentum is:

$$\Delta p_x = m_e \Delta v = (9.109 \times 10^{-31} \text{ kg}) \times (1.0 \times 10^2 \text{ ms}^{-1}) = 9.109 \times 10^{-29} \text{ kg m s}^{-1}$$

The minimum uncertainty in the position is

$$\Delta x = \frac{\hbar}{2\Delta p_x} = \frac{1.054 \times 10^{-34} \text{ Js}^{-1}}{2 \times (9.109 \times 10^{-31} \text{ kg}) \times (1.0 \times 10^2 \text{ ms}^{-1})} = 578 \text{ nm}$$

The size of the atom is about $\sim 1\text{\AA} = 0.1\text{nm}$, so the ratio of the uncertainty in the position to the size of the atom is:

$$= \frac{578\text{ nm}}{0.1\text{ nm}} = 5780$$

5. The uncertainty in the position of the proton inside the nucleus is $\Delta x = 12\text{ fm} = 12 \times 10^{-15}\text{ m}$. The minimum uncertainty in momentum is

$$\Delta p_x = \frac{\hbar}{2\Delta x} = \frac{1.054 \times 10^{-34}\text{ Js}^{-1}}{2 \times (12 \times 10^{-15}\text{ m})} = 4.39 \times 10^{-21}\text{ kgms}^{-1}$$

So, the momentum of proton is at least $p_x \approx 4.39 \times 10^{-21}\text{ kgm s}^{-1}$.

The minimum velocity is:

$$v = \frac{p_x}{m_p} = \frac{(4.39 \times 10^{-21}\text{ kgms}^{-1})}{(1.67 \times 10^{-27}\text{ kg})} = 2.6 \times 10^6\text{ ms}^{-1}$$

6. We can write the minimum uncertainty in position as $\Delta x = \frac{\hbar}{2\Delta p_x}$

The total energy is:

$$E = \frac{(\Delta p_x)^2}{2m} + k \left(\frac{\hbar}{2\Delta p_x} \right)^4 = \frac{(\Delta p_x)^2}{2m} + \frac{k\hbar^4}{16(\Delta p_x)^4} \quad (\text{i})$$

To get the minimum energy we set $\frac{dE}{d\Delta p_x} = 0$. So,

$$\frac{\Delta p_x}{m} - \frac{4k\hbar^4}{16(\Delta p_x)^5} = 0 \Rightarrow 16\Delta p_x^6 - 4km\hbar^2 = 0$$

$$\text{So, } (\Delta p_x)^2 = \left(\frac{km\hbar^4}{4} \right)^{1/3} \quad (\text{ii})$$

Substituting for $(\Delta p_x)^2$ from Eq.(ii) into Eq.(i) we get the minimum energy as:

$$\begin{aligned} E_{\min} &= \frac{1}{2m} \left(\frac{km\hbar^4}{4} \right)^{1/3} + \frac{k\hbar^4}{16 \left(\frac{km\hbar^2}{4} \right)^{2/3}} = \frac{1}{2m} \left(\frac{km\hbar^4}{4} \right)^{1/3} + \frac{1}{4m} \left(\frac{km\hbar^4}{4} \right)^{1/3} \\ &= \frac{3}{4} \sqrt[3]{\frac{k\hbar^4}{4m^2}} \end{aligned}$$

7. We use Eq. (6.7) with $\Delta t = 4.0 \times 10^{-20}\text{ s}$:

$$\Delta E = \frac{1.054 \times 10^{-34}\text{ Js}}{2 \times (4.0 \times 10^{-20}\text{ s})} = 0.13 \times 10^{-14}\text{ J}$$

Using $\Delta E = \Delta mc^2$ we calculate the minimum uncertainty in the measurement of its mass as (Δm):

$$\Delta m = \frac{\Delta E}{c^2} = \frac{0.13 \times 10^{-14} \text{ J}}{(3.0 \times 10^8 \text{ ms}^{-1})^2} = 1.4 \times 10^{-32} \text{ kg}$$

8. Given that $\Delta t = 5.0 \times 10^{-12} \text{ s}$, the uncertainty in the energy of the gamma ray is:

$$\Delta E \geq \frac{\hbar}{2\Delta t} = \frac{1.054 \times 10^{-34} \text{ Js}}{2 \times 5.0 \times 10^{-12} \text{ s}} = 1.05 \times 10^{-23} \text{ J}.$$

So, the uncertainty in the energy of the gamma ray is $\approx 1.1 \times 10^{-23} \text{ J}$.

9. The uncertainty in the position for each molecule in the x-direction is $\Delta x = 10.0 \text{ cm} = 0.10 \text{ m}$. So,

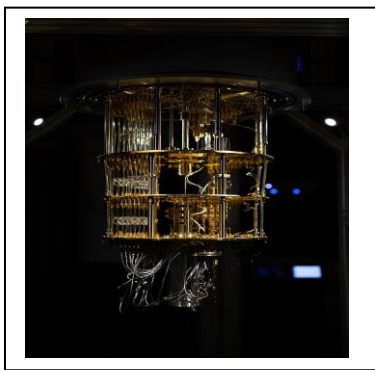
$$\Delta p_x \geq \frac{\hbar}{2\Delta x} = \frac{1.054 \times 10^{-34} \text{ Js}}{2 \times (0.1 \text{ m})} = 5.27 \times 10^{-34} \text{ kgms}^{-1}$$

The minimum uncertainty in the velocity of the molecule in the x- direction is

$$v_x = \frac{p_x}{m} = \frac{5.27 \times 10^{-34} \text{ kgms}^{-1}}{2.32 \times 10^{-26} \text{ kg}} = 2.3 \times 10^{-8} \text{ ms}^{-1}$$

The ratio of the uncertainty in v_x to the rms speed v_{rms} is:

$$\frac{v_x}{v_{rms}} = \frac{2.3 \times 10^{-8} \text{ ms}^{-1}}{511 \text{ ms}^{-1}} = 4.5 \times 10^{-11}$$



UNIT 7

SCHRODINGER EQUATION

This is a picture of the IQM Quantum Computer in Finland. In principle, a quantum computer would perform much better than a classical computer on certain tasks.
[https://upload.wikimedia.org/wikipedia/commons/a/ad/IQM_Quantum_Computer_Espoo_Finland.jpg]

Structure

7.1	Introduction	7.4	Time Independent Schrödinger Equation
	Expected Learning Outcomes	7.5	Acceptable Solutions of the Schrödinger Equation
7.2	One-dimensional Schrödinger Equation	7.5	Summary
7.3	Probabilistic Interpretation of the Wave Function	7.6	Terminal Questions
	Phase of the Wave Function	7.7	Solutions and Answers
	Probability Current Density and the Continuity Equation		
	Normalization of the Wave Function		

STUDY GUIDE

In this unit, you will study the Schrödinger equation, which describes the behaviour of matter waves. In order to follow the mathematical steps of this unit, you should be familiar with ordinary differential equations. Recall that you have studied about ordinary differential equations in BPHCT 131 (Units 3 and 4 of Block 1), and methods of solving them. You are also familiar with partial differential equations. Recall that you have learnt Maxwell's equations, which are partial differential equations in Block 4 of the course BPHCT 133. You should revise how to calculate partial derivatives from BPHCT133. Schrödinger equation is a partial differential equation. Also, the solutions of the Schrödinger equation are typically complex functions. So, you must revise the school level concepts of complex numbers. A brief introduction to complex numbers is given in the appendix to this unit, for quick revision. You may like to go through the appendix before you start studying the unit.

"If we look at the way the universe behaves, quantum mechanics gives us fundamental, unavoidable indeterminacy, so that alternative histories of the universe can be assigned probability."

Murray Gellman

7.1 INTRODUCTION

In other words, classical mechanics should appear as the short-wavelength limit of this theory. Recall that this condition is similar to the special theory of relativity, which reduces to Newtonian mechanics at velocities much smaller than the velocity of light.

The formal mathematical framework of quantum physics developed along two different tracks. In 1925, Werner Heisenberg and Max Born with Pascual Jordan, working separately, published the matrix version of quantum mechanics. In this approach, matrices are used to describe the observables of a quantum system. In the other approach developed by Erwin Schrödinger, the focus is on the description of the wave function corresponding to the quantum system. Much later, in 1940, Richard Feynman developed the “path-integral” formalism of quantum mechanics, which is beyond the scope of this course.

In Unit 5, you have studied that wave-particle duality is an inherent characteristic of all the radiation and matter that make up the physical universe. You have learnt about matter waves and the de Broglie wavelength, which is given in terms of momentum. You have also learnt the uncertainty principle, which sets a limit to the accuracy with which certain pairs of variables can be simultaneously measured. You know that the wave-particle nature of matter is significant only for microscopic particles like electrons, protons, atoms, etc.

The next step is the development of a mathematical framework for the study of quantum systems. How do we describe the motion of a quantum particle or a system of such quantum particles? How do these systems evolve in space and time? Clearly, we cannot make use of Newton's laws of motion for this purpose. So, a new theory is needed for describing the motion of quantum mechanical particles. It should be consistent with the wave-nature of particles. It should also reduce to Newtonian mechanics for macroscopic particles (read the margin remark).

In 1926, Erwin Schrödinger developed a version of quantum mechanics known as wave mechanics, which describes the evolution of the **wave function** associated with a quantum system. He deduced a differential equation satisfied by the wave function. In principle, it is the equation that can be applied to all quantum systems and used to calculate all their properties.

In Sec. 7.2, you will study the one-dimensional time dependent Schrödinger equation. What does the wave function physically mean? We discuss this in Sec. 7.3. In Sec. 7.4, we discuss the time independent one-dimensional Schrödinger equation and determine the stationary state solutions of this equation. These solutions are acceptable only under certain conditions about which you will study in Sec. 7.5. An appendix has been given at the end of the unit to explain the basic complex algebra used in the text.

In the next unit, you will learn how to calculate the dynamical variables of a quantum system from its wave function.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ write the one-dimensional time dependent Schrödinger equation and derive the time independent Schrödinger equation from it;
- ❖ give a probabilistic interpretation of the wave function;
- ❖ derive the continuity equation for the probability current density;
- ❖ normalise a given wave function; and
- ❖ state the properties of an acceptable wave function and identify it.

7.2 ONE-DIMENSIONAL SCHRÖDINGER EQUATION

In Unit 5, you have learnt that every material particle has an inherent wave nature that is described by a matter wave. You know from Newtonian mechanics that the physical state of a classical particle is described by a set of coordinates and velocities, which evolve in time according to Newton's laws. In Unit 6, you have learnt that for a quantum particle you **cannot measure** the position and the velocity of a particle simultaneously with arbitrary accuracy. So, you cannot describe the physical state of a quantum system using its position and momentum. You also cannot use the laws of classical mechanics to determine its evolution.

The state of a quantum system is described by a function of space coordinates (x, y, z) and time, which is called the **wave function**. The **concept of wave function** was introduced by Erwin Schrödinger. In general, the wave function of a system is a complex function. It describes the wave properties of a particle (read the margin remark also).

The fundamental postulate of quantum mechanics stated below tells us about the importance of the wave function of a quantum system:

Description of the System

Every particle (or a system of particles) is represented by a “wave function” $\psi(x, y, z, t)$, which is a function of space coordinates and time. The wave function determines all that can be known about the system it represents.

The next question to be asked is then – “What is the form of $\psi(x, y, z, t)$? In Unit 5, you saw that a free particle is described by a wave packet which is a superposition of the familiar sinusoidal travelling waves. Each component wave in the wave packet is a sinusoidal wave of constant wavelength and it seemed to work to describe the particle. But that was for the special case of a particle moving with a constant velocity and hence a precise momentum and a corresponding constant wavelength.

What if you have a particle moving in a force field? In that case, the magnitude of its linear momentum is changing with time. So, the wavelength of the particle would also be changing and in general, it would not be possible to represent it by a simple sinusoidal waveform.

So, in general, for a correct description of the evolution of the state of a quantum system described by a wave function, we need an **appropriate wave equation**. This equation should suitably describe the evolution of the quantum mechanical wave function in space and time.

Like the other differential equations you have studied in your earlier courses (read the margin remark), the quantum mechanical wave function is also to be a solution of a differential equation. The differential equation should involve derivatives with respect to the spatial coordinates and time.

The wave function, in fact, tells us everything that **can be known** about a quantum particle. This information is less than what we are used to in the macroscopic world. But remember that this is an inherent law of nature. It is not an inadequacy of the mathematical formalism being used to describe it. Suppose you start with a quantum system for which you know all physical parameters. Even then the state of the system at a later time will still be governed by indeterminacy, as defined by the uncertainty principle.

The dynamical behaviour of a classical particle moving under the influence of a force is described by Newton's second law, which is a differential equation. Similarly, Maxwell's equations of classical electromagnetism are partial differential equations.

The credit for discovering such a differential equation goes to Erwin Schrödinger, for which he received the Nobel Prize in 1936. How did he arrive at his equation? The answer is, he deduced it intuitively, breaking all traditions of such wave equations.

With reference to the origin of this equation, physicist Richard Feynman has said:

Where did we get that [Schrödinger's equation] from? Nowhere. It is not possible to derive from anything you know. It came out of the mind of Schrödinger, invented in his struggle to find an understanding of the experimental observation of the real world.



Austrian physicist Erwin Schrödinger (1887-1961) received his doctorate from the University of Vienna in 1910. While at the University of Zurich in 1926, he published his first paper introducing the differential equation for the wave function and showed that it gave the correct energy eigenvalues for a hydrogen-like atom. He also solved his equation for the quantum harmonic oscillator, rigid rotor, and the diatomic molecule problems. He received the **Nobel Prize in Physics in 1933 along with Paul Adrien Dirac**, for "their discovery of new productive forms of atomic theory".

The Schrödinger equation is one of the most successful equations of quantum mechanics because it predicts results, which can be verified experimentally. It is not possible to derive the Schrödinger equation, but it is possible to arrive at an explanation for the form of the equation, based on certain mathematical and physical arguments.

Let us first write down the conditions that the wave equation for a wave function should fulfil. For a particle of mass m having energy E and momentum p , the equation should be consistent with

i) the de Broglie relation $\lambda = \frac{h}{p}$ (7.1)

ii) Planck's formula $E = \frac{h}{\nu} = \hbar\omega$ (7.2)
where $\nu = \frac{2\pi}{\omega}$.

It should also be consistent with the relation for the total energy of the (classical) particle, which is the sum of its kinetic and potential energies:

iii) $E = \frac{p^2}{2m} + V(x, y, z, t)$ (7.3)

where $V(x, y, z, t)$ is the potential energy of the particle for the coordinates x, y, z and time t .

iv) Finally, the Schrödinger equation must be linear in x, y, z and t . What does this mean? Suppose $\psi_1(x, y, z, t)$ and $\psi_2(x, y, z, t)$ are two solutions of the Schrödinger equation for a given potential energy $V(x, y, z, t)$. Then any linear combination of ψ_1 and ψ_2 , say, $\psi = C_1\psi_1 + C_2\psi_2$, with C_1 and C_2 as arbitrary constants, must also be the solution of the same Schrödinger equation.

This linearity is essential so that two waves may be added to produce interference (as you have read in the double slit experiment in Unit 6).

If the linearity property is to be satisfied, the Schrödinger (differential) equation must be of degree 1, i.e., the wave function itself and its derivatives should appear in the differential equation only in the first power.

Using Eq. (7.1) and Eq. (5.12) in Eq. (7.3) we can write:

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} + V(x, y, z, t) \quad (7.4)$$

With these conditions let us try to arrive at an appropriate wave equation for the free particle in one-dimension. For a free particle, $V(x, y, z, t) = 0$. So, Eq. (7.4)

is:

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} \quad (7.5)$$

Let us start by assuming that an appropriate wave function for a free particle moving along the x-direction having a definite momentum $p = \hbar k$ and energy $E = \hbar\omega$ is given by:

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

Let us first calculate the first order partial derivatives of $\psi(x, t)$ with respect to the variables x and t . So,

$$\frac{\partial \psi(x, t)}{\partial t} = \frac{\partial}{\partial t} (Ae^{i(kx - \omega t)}) = -i\omega Ae^{i(kx - \omega t)} = -i\omega \psi(x, t) \quad (7.6)$$

$$\frac{\partial \psi(x, t)}{\partial x} = \frac{\partial}{\partial x} (Ae^{i(kx - \omega t)}) = ikAe^{i(kx - \omega t)} = ik\psi(x, t) \quad (7.7)$$

Multiplying both sides of Eq. (7.6) by $i\hbar$, we get:

$$i\hbar \frac{\partial \psi(x, t)}{\partial t} = (i\hbar) \times (-i\omega) \psi(x, t) \quad \text{or} \quad i\hbar \frac{\partial \psi(x, t)}{\partial t} = \hbar\omega \psi(x, t) \quad (7.8)$$

Differentiating Eq. (7.7) once again with respect to x , we get:

$$\frac{\partial}{\partial x} \left(\frac{\partial \psi(x, t)}{\partial x} \right) = \frac{\partial}{\partial x} [ik\psi(x, t)] = [ik]^2 \psi(x, t) = -k^2 \psi(x, t) \quad (7.9)$$

From Eqs. (7.8 and 7.9), we get

$$\hbar\omega = i\hbar \frac{1}{\psi(x, t)} \frac{\partial \psi(x, t)}{\partial t} \quad (7.10)$$

$$\text{and} \quad \hbar^2 k^2 = -\hbar^2 \frac{1}{\psi(x, t)} \frac{\partial^2 \psi(x, t)}{\partial x^2} \quad (7.11)$$

Substituting for $\hbar\omega$ and $\hbar^2 k^2$ from Eqs. (7.10 and 7.11) into Eq. (7.5), we get the following equation for the free particle:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} = i\hbar \frac{\partial \psi(x, t)}{\partial t} \quad (7.12)$$

This wave equation is for the special case of a free particle moving along the x-direction. However, Schrödinger made a bold extrapolation and postulated that the form of the differential equation does not change even for a particle of

Famous physicist Arnold Sommerfeld once referred to the Schrödinger equation as "the most remarkable of all remarkable discoveries of the 20th century". Over the years, and especially now, when this equation can be solved with great accuracy by advanced computers, we know that if we solve the Schrödinger equation accurately, we get the **correct answers even for the most complex systems.**

mass m moving in a potential $V(x, t)$, which varies with x and t . **The time-dependent Schrödinger equation for the one-dimensional motion of a particle of mass m moving in a potential $V(x, t)$ is given by:**

$$i\hbar \frac{\partial \psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + V(x, t) \psi(x, t) \quad (7.13)$$

Are you wondering what would happen if we had a wave equation with a second order time derivative? We would then have ended up with the relativistic energy-momentum relationship. Actually, to begin with, this is what Schrödinger himself attempted. But very soon he realised that such an equation did not work for electrons – it did not give the correct spectrum for the hydrogen atom. Incidentally, the correct relativistic equation for electrons, discovered by Dirac, does retain the first-order time derivative.

You should note that Eq. (7.13) is consistent with (i) to (iv). The appearance of $\hbar$ in the Schrödinger equation is, of course, crucial. This is how Schrödinger imposed the "quantum condition" on the wave equation of matter.

The Schrödinger equation is unlike any of the wave equations you have studied so far. Recall that wave equations usually connect a second-order time derivative of the function with its second order spatial derivative. But Schrödinger's equation contains only the first-derivative with respect to time but the second derivative with respect to space. Hence, time and space coordinates are not treated on an equal footing in this equation. Thus, Eq. (7.13) cannot be correct in the relativistic domain (read the margin remark); it is **the non-relativistic time dependent Schrödinger equation**. Let us work out a simple example on Eq. (7.13).

EXAMPLE 7.1 : TIME DEPENDENT SCHRÖDINGER EQUATION

A particle of mass m can move freely along the x -axis between $-L \leq x \leq L$ but is prohibited from going outside this region. Determine the value of the constant E for which the following wave function is a solution of the time dependent Schrödinger equation for the particle:

$$\psi(x, t) = \begin{cases} N \sin\left(\frac{\pi x}{L}\right) \exp\left(-\frac{iEt}{\hbar}\right) & \text{for } -L < x < L \\ 0 & \text{elsewhere} \end{cases}$$

SOLUTION ■ We use Eq. (7.13) with $\psi(x, t)$ as given.

We first determine the partial derivatives of ψ with respect to x and t :

$$\begin{aligned} \frac{\partial \psi}{\partial t} &= \frac{\partial}{\partial t} \left[N \sin\left(\frac{\pi x}{L}\right) \exp\left(-\frac{iEt}{\hbar}\right) \right] \\ &= \frac{-iE}{\hbar} \left[N \sin\left(\frac{\pi x}{L}\right) \exp\left(-\frac{iEt}{\hbar}\right) \right] = \frac{-iE}{\hbar} \psi(x, t) \end{aligned} \quad (i)$$

$$\frac{\partial \psi}{\partial x} = \frac{\pi}{L} N \cos\left(\frac{\pi x}{L}\right) \exp\left(-\frac{iEt}{\hbar}\right) \quad (ii)$$

$$\frac{\partial \psi}{\partial x^2} = -\left(\frac{\pi}{L}\right)^2 N \sin\left(\frac{\pi x}{L}\right) \exp\left(-\frac{iEt}{\hbar}\right) = -\left(\frac{\pi}{L}\right)^2 \psi(x, t) \quad (iii)$$

Note that it is given that the particle is free and, therefore, $V = 0$.

Substituting Eq. (i) and (iii) in Eq. (7.13) with $V = 0$, we get:

$$i\hbar \left[\frac{-iE}{\hbar} \psi(x,t) \right] = \frac{-\hbar^2}{2m} \left[-\left(\frac{\pi}{L} \right)^2 \psi(x,t) \right] \quad (i^2 = -1) \quad (\text{iv})$$

or
$$E \psi(x,t) = \frac{\hbar^2}{2m} \left(\frac{\pi}{L} \right)^2 \psi(x,t)$$

$\therefore E = \frac{\hbar^2}{2m} \left(\frac{\pi}{L} \right)^2 = \frac{h^2}{8mL^2}$

You may notice that the wave function in Example 7.1 is a complex function. This is the price to pay for having only a first order time derivative in the wave equation as you will see in Sec. 7.4. The coefficient of the time derivative in Eq. (7.13) is imaginary. Therefore, the wave function $\psi(x, t)$, which is a solution of Eq. (7.13), will, in general, be complex.

Let us now summarize what you have studied so far.

TIME DEPENDENT SCHRÖDINGER EQUATION

- Every quantum particle (or a system of quantum particles) is represented by a **“wave function”** $[\psi(x,y,z,t)]$, which is a function of space coordinates and time. The wave function determines all that can be known about the system it represents.
- The evolution of the wave function in space and time is given by the time independent Schrödinger equation which is a differential equation, involving derivatives with respect to the spatial coordinates and time.
- **The time-dependent Schrödinger equation for the one-dimensional motion of a particle of mass m moving in a potential $V(x, t)$ is given by**

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,t)}{\partial x^2} + V(x,t)\psi(x,t) \quad (7.13)$$

Clearly, the solutions of the Schrödinger equation cannot be real physical waves because they are complex functions with both a real and an imaginary part. A complex number cannot be related to a **measurable or observable** quantity. So, this quantum wave function does not represent a measurable disturbance in a medium, like classical water waves or even sound waves. A medium is, in fact, not even required for its propagation.

What exactly does the wave function $\psi(x,t)$ mean physically? In truth, even Schrödinger was not sure about that. At a certain point he even tried to interpret $\psi^* \psi$ as an electric charge density. This was something that worried many leading physicists of the time (read the margin remark). Eventually, it

*Erwin with his psi can do
Calculations quite a few.*

*But one thing has not been seen:
Just what does psi really mean?*

By Erich Hückel,
And translated from German

by
Felix Bloch, quoted in
Physics Today,
December, 1976

was Max Born who postulated the now accepted probabilistic interpretation for the product $\psi^* \psi$ where ψ^* is the complex conjugate of the function ψ . We will discuss this interpretation in the next section. But before that you may like to try the following SAQ.

SAQ 1 - Time dependent Schrödinger equation

If $\psi_1(x,t)$ and $\psi_2(x,t)$ are two solutions of the Schrödinger equation (Eq. 7.13), show that a linear combination of ψ_1 and ψ_2 , $\psi = a_1\psi_1 + a_2\psi_2$, with a_1 and a_2 , as arbitrary constants, is also a solution of the same Schrödinger equation.

7.3 PROBABILISTIC INTERPRETATION OF THE WAVE FUNCTION

“God knows I am no friend of probability theory, I have hated it from the first moment when our dear friend Max Born gave it birth. For it could be seen how easy and simple it made everything, in principle, everything ironed and the true problems concealed. Everybody must jump on the bandwagon [Ausweg]. And actually not a year passed before it became an official credo, and it still is.”
– Erwin Schrödinger in a letter to Albert Einstein

It is now clear that the wave function of a particle or system of particles, by itself does not correspond to any measured quantity. However, if it is to contain all the information regarding a physical system as postulated in Sec. 7.2, it must be possible to use the wave function to predict physical quantities. In order to extract any physical information from ψ , we must establish a quantitative connection between ψ and the observables of the particle. In 1926, Max Born proposed the following connection:

Probabilistic Interpretation of the Wave Function

The probability density of finding a particle at any point, when a measurement of its position is carried out, is proportional to $|\psi|^2 = \psi^* \psi$, which is the modulus square of the wave function of the particle at that point. ψ^* is the complex conjugate of the wave function ψ .

This probabilistic interpretation of the wave function is also called the **Born interpretation** (read the margin remark). $\psi^* \psi$ or $|\psi|^2$ is both real and positive and hence, it can be related to the probability.

For a one-dimensional system, if, at any instant t , a measurement is made to locate a particle represented by the wave function $\psi(x,t)$, then the probability $P(x,t)dx$ that the object will be found between the coordinates x and $x + dx$ is given by:

$$P(x,t)dx = \psi^*(x,t) \psi(x,t)dx = |\psi(x,t)|^2 dx \quad (7.14)$$

Here $P(x,t) = |\psi(x,t)|^2$ is called the “**probability density**” or “**probability amplitude**”. To put it in words:

The probability of finding a quantum mechanical particle in a small interval dx is given by $\psi^* \psi dx$ or $|\psi|^2 dx$ – the product of the modulus square of the wave function representing the particle and the interval itself.

The probability of finding the particle in some finite region $L = [x_1, x_2]$ can be written as:

$$P_L(t) = \int_{x_1}^{x_2} P(x,t) dx = \int_{x_1}^{x_2} \psi^*(x,t) \psi(x,t) dx \quad (7.15)$$

Since the probability has to be a pure number, Eq. (7.15) also tells you the physical dimension of the wave function. Since dx has the unit of length, $|\psi(x,t)|^2$ must have the unit of reciprocal of length. And so $\psi(x,t)$ itself must have the unit of the reciprocal of the square root of inverse length.

Since the particle must always be somewhere in space, the total probability of finding it in the whole space is unity. By integrating the probability over all space, we are led to the following condition

$$\int_{-\infty}^{\infty} P(x,t) dx = \int_{-\infty}^{\infty} \psi^*(x,t) \psi(x,t) dx = 1, \text{ at each instant of time} \quad (7.16)$$

The probabilistic interpretation of the wave function also requires that the wave function have the following properties:

- i) $\psi(x,t)$ should be **finite** and **single-valued** everywhere; otherwise the probability of finding an object in a region of space will not be finite and unique.
- ii) we restrict the wave functions used in quantum mechanics to the class of **square-integrable functions** for which

$$|\psi(x,t)|^2 dx < \infty \quad (7.17)$$

Further, in order that $\psi(x,t)$ represent a physical system, certain continuity conditions must also be imposed on $\psi(x,t)$, which we will discuss in Sec. 7.5 along with the conditions stated above. Let us now consider an example on the probabilistic interpretation of the wave function.

EXAMPLE 7.2 : PROBABILISTIC INTERPRETATION OF ψ

At $t = 0$, the wave function of a particle is given by:

$$\psi(x,t) = \begin{cases} Ax(a-x) & \text{for } 0 \leq x \leq a \\ 0 & \text{elsewhere} \end{cases}$$

Calculate the probability of finding the particle between $x = 0$ and $x = a/2$.

SOLUTION ■ We use Eq. (7.15) to calculate the probability of finding the particle between $x_1 = 0$ and $x_2 = a/2$ as

$$P_L(0, a/2) = A^2 \int_0^{a/2} [x(a-x)][x(a-x)] dx$$

Here $\psi^*(x,0) = \psi(x,0) = Ax(a-x)$

$$\begin{aligned} \text{So, } P_L &= A^2 \int_0^{a/2} x^2 (a^2 - 2ax + x^2) dx \Rightarrow P_L = A^2 \int_0^{a/2} [x^2 a^2 - 2ax^3 + x^4] dx \\ &= A^2 \left[\frac{a^2 x^3}{3} - \frac{2ax^4}{4} + \frac{x^5}{5} \right]_0^{a/2} = A^2 a^5 \left[\frac{1}{24} - \frac{1}{32} + \frac{1}{160} \right] \\ &= \frac{A^2 a^5}{8} \left[\frac{1}{3} - \frac{1}{4} + \frac{1}{20} \right] = \frac{A^2 a^5}{60} \end{aligned}$$

PROBABILISTIC INTERPRETATION OF THE WAVE FUNCTION

- When a measurement of a particle's position is carried out, the probability density of finding it at any point is proportional to $|\psi|^2 = \psi^* \psi$, which is the modulus square of the wave function of the particle at that point. ψ^* is the complex conjugate of the wave function ψ .
- For a one-dimensional system, the probability $P(x,t)dx$ that a particle will be found between the coordinates x and $x + dx$ is:

$$P(x,t)dx = \psi^*(x,t)\psi(x,t)dx = |\psi(x,t)|^2 dx \quad (7.14)$$

where $\psi(x,t)$ is the wave function of the particle.

- The probability of finding the particle in some finite region $L = [x_1, x_2]$ is:

$$P_L(t) = \int_{x_1}^{x_2} P(x,t)dx = \int_{x_1}^{x_2} \psi^*(x,t)\psi(x,t)dx \quad (7.15)$$

- At each instant of time we must have:

$$\int_{-\infty}^{\infty} P(x,t)dx = \int_{-\infty}^{\infty} \psi^*(x,t)\psi(x,t)dx = 1 \quad (7.16)$$

You may now like to work out an SAQ on this concept.

SAQ 2 - Probabilistic interpretation of the wave function

At $t = 0$, the wave function of a particle is given by:

$$\psi(x,0) = \begin{cases} \left(\frac{1}{\sqrt{4\pi}} \right) [\exp(ix) + \exp(-ix)] & \text{for } -\pi \leq x \leq \pi \\ 0 & \text{elsewhere} \end{cases}$$

Calculate the probability of finding the particle between $x = \pi/3$ and $x = \pi/2$.

7.3.1 Phase of the Wave Function

From the probabilistic interpretation of the wave function as given by Eq. (7.14), you can see that the relevant quantity is $|\psi(x,t)|^2$ and not $\psi(x,t)$. This also suggests that the wave function $\psi(x,t)$ is only uniquely defined up to an arbitrary complex phase of the form $e^{i\theta}$. To understand this, let us say that the wave function $\psi(x,t)$ is multiplied by a constant phase $e^{i\theta}$ to get a new wave function $\psi'(x,t)$. Then:

$$\psi'(x,t) = \psi(x,t)e^{i\theta} \quad \Rightarrow \quad \psi'^*(x,t) = \psi^*(x,t)e^{-i\theta}$$

and
$$\psi'^*(x,t)\psi'(x,t) = (\psi^*(x,t)e^{-i\theta})(\psi(x,t)e^{i\theta}) = \psi^*(x,t)\psi(x,t)$$

So, the probability density or the physical interpretation of the wave function is not changed when the wave function is multiplied by a complex phase.

Does that mean that the phase of the wave function is irrelevant as far as the physical picture is concerned?

To answer this question, let us consider a linear combination of two wave functions $\psi_1(x,t)$ and $\psi_2(x,t)$, which are two solutions of the same Schrödinger equation:

$$\psi(x,t) = \psi_1(x,t) + \psi_2(x,t) \quad (7.18)$$

As you know from SAQ 1, this linear combination is also a solution of the same Schrödinger equation. Now let us determine the probability density for $\psi(x,t)$ given by Eq. (7.18). We can write:

$$\psi^*(x,t) = \psi_1^*(x,t) + \psi_2^*(x,t) \quad (7.19)$$

So the probability density is :

$$\begin{aligned} P(x,t) &= \psi^*(x,t)\psi(x,t) \\ &= [\psi_1^*(x,t) + \psi_2^*(x,t)] \times [\psi_1(x,t) + \psi_2(x,t)] \\ &= |\psi_1(x,t)|^2 + |\psi_2(x,t)|^2 + \psi_1^*(x,t)\psi_2(x,t) + \psi_1(x,t)\psi_2^*(x,t) \end{aligned} \quad (7.20)$$

Now suppose we write

$$\psi_1 = \psi_{10}e^{i\theta_1}; \quad \psi_2 = \psi_{20}e^{i\theta_2} \quad \text{and} \quad \theta_1 - \theta_2 = \phi \quad (7.21)$$

where ψ_{10} and ψ_{20} are real. The expression for the probability density reduces to:

$$\begin{aligned} P(x,t) &= |\psi_{10}|^2 + |\psi_{20}|^2 + \psi_{10}\psi_{20}[e^{-i(\theta_1-\theta_2)} + e^{i(\theta_1-\theta_2)}] \\ &= |\psi_{10}|^2 + |\psi_{20}|^2 + 2\psi_{10}\psi_{20}\cos\phi \end{aligned} \quad (7.22)$$

Now the first two terms in the final expression represent the usual addition of the individual probability densities of each wave function but the third term is

the quantum “interference” term which depends on the **relative phase** difference between the waves given by ϕ . This explains the interference pattern that is observed for matter waves (as you have seen in the double slit experiment). So, the phase of the wave function is important and cannot be ignored.

7.3.2 Probability Current Density and the Continuity Equation

Note that Eq. (7.16) is true at every instant of time t . This means that, as time goes on, if the probability of finding a particle in any region decreases, correspondingly the probability of finding the particle in the remaining region must increase. In other words, **probability has to be conserved for the probabilistic definition of the wave function to hold**. Let us examine this aspect in some detail.

Let us first consider the example of a fluid moving in the positive x -direction between two points $x = x_1$ and $x = x_2$ with a velocity $v(x)$ which changes with x . Let $\rho(x)$ denote the mass per unit length of the fluid around the point x . The quantity $S_x = v(x)\rho(x)$ is then the mass of the fluid crossing a given point x per unit time. What would be the net mass accumulated per unit time in between the two points $x = x_1$ and $x = x_2$?

Clearly, it is equal to $S_{x=x_1} - S_{x=x_2}$. And if the mass of fluid is to be conserved in this region, then the net mass of fluid accumulated in unit time should be equal to the rate of change of mass in this region. So,

$$\frac{\partial}{\partial t} \left(\int_{x_1}^{x_2} \rho(x) dx \right) = S_{x=x_1} - S_{x=x_2} \quad (7.23)$$

We now extend this analogy to the probabilistic interpretation of the wave function. We say that if the total probability is to be conserved, the conservation equation should look like Eq. (7.23) where $\rho(x)$ should be replaced by the probability density $P(x, t)$ and S , by a function which we will call the **probability current density** $J(x, t)$. So, we are looking for an equation of the form:

$$\frac{\partial}{\partial t} \left(\int_{x_1}^{x_2} P(x, t) dx \right) = J(x_1, t) - J(x_2, t) \quad (7.24)$$

Let us now derive the expression of the probability current **density** so that the probability conservation equation [Eq. (7.24)] is obeyed. We start by writing Schrödinger equation (Eq. 7.13):

$$i\hbar \frac{\partial \psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + V(x, t)\psi(x, t) \quad (7.25)$$

And its complex conjugate

$$-i\hbar \frac{\partial \psi^*(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi^*(x, t)}{\partial x^2} + V(x, t)\psi^*(x, t) \quad (7.26)$$

To simplify the notation, we will, in the remaining part of the derivation, omit the arguments of the function. For example, we will write $\psi(x,t)$ as just ψ and $\psi^*(x,t)$ as just ψ^* . We assume that the potential function $V(x,t)$ is real so that $V^* = V$. We now multiply Eq. (7.25) from the left by ψ^* and Eq. (7.26) by ψ to get

$$i\hbar\psi^* \frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\psi^* \frac{\partial^2\psi}{\partial x^2} + V\psi^*\psi \quad (7.27a)$$

$$\text{and} \quad -i\hbar\psi \frac{\partial\psi^*}{\partial t} = -\frac{\hbar^2}{2m}\psi \frac{\partial^2\psi^*}{\partial x^2} + V\psi\psi^* \quad (7.27b)$$

Subtracting Eq. (7.27b) from Eq. (7.27a) we get

$$i\hbar\left(\psi \frac{\partial\psi^*}{\partial t} + \psi^* \frac{\partial\psi}{\partial t}\right) = -\frac{\hbar^2}{2m}\left(\psi^* \frac{\partial^2\psi}{\partial x^2} - \psi \frac{\partial^2\psi^*}{\partial x^2}\right) \quad (7.28)$$

Eq. (7.28) can be rewritten as (read the margin remark):

$$\frac{\partial(\psi\psi^*)}{\partial t} = -\frac{\hbar}{2mi} \frac{\partial}{\partial x} \left(\psi^* \frac{\partial\psi}{\partial x} - \psi \frac{\partial\psi^*}{\partial x} \right) \quad (7.29)$$

We can integrate Eq. (7.29) with respect to x from $x = x_1$ and $x = x_2$ to get,

$$\frac{\partial}{\partial t} \int_{x_1}^{x_2} \psi\psi^* dx = -\frac{\hbar}{2mi} \left(\psi^* \frac{\partial\psi}{\partial x} - \psi \frac{\partial\psi^*}{\partial x} \right) \bigg|_{x_1}^{x_2} \quad (7.30)$$

Comparing Eqs. (7.30) and (7.24), we find that the probability density $P(x,t)$ and the probability current density $J(x,t)$ should be defined as:

$$P(x,t) = \psi^*(x,t)\psi(x,t)$$

and

$$J(x,t) = \frac{\hbar}{2mi} \left(\psi^* \frac{\partial\psi}{\partial x} - \psi \frac{\partial\psi^*}{\partial x} \right) \quad (7.31a)$$

With this definition, we get Eq. (7.24):

$$\frac{\partial}{\partial t} \int_{x_1}^{x_2} P(x,t) dx = J(x_1,t) - J(x_2,t)$$

The LHS of this equation is the rate of change of probability density with time.

Eq. (7.24) is, therefore, a conservation law. It expresses the fact that **a change in the particle density in a region of space is compensated for by a net change of flux from that region.**

Within this region (dx), particles are neither created nor destroyed (i.e., there are neither sources nor sinks).

$$\begin{aligned} & \frac{\partial}{\partial x} \left(\psi^* \frac{\partial\psi}{\partial x} \right) \\ &= \frac{\partial\psi^*}{\partial x} \frac{\partial\psi}{\partial x} + \psi^* \frac{\partial^2\psi}{\partial x^2} \\ & \frac{\partial}{\partial x} \left(\psi \frac{\partial\psi^*}{\partial x} \right) \\ &= \frac{\partial\psi}{\partial x} \frac{\partial\psi^*}{\partial x} + \psi \frac{\partial^2\psi^*}{\partial x^2} \\ & \frac{\partial}{\partial x} \left(\psi^* \frac{\partial\psi}{\partial x} - \psi \frac{\partial\psi^*}{\partial x} \right) \\ &= \psi^* \frac{\partial^2\psi}{\partial x^2} - \psi \frac{\partial^2\psi^*}{\partial x^2} \end{aligned}$$

We may rewrite Eq. (7.24) in terms of P and J as

$$\frac{\partial P(x,t)}{\partial t} + \frac{\partial J(x,t)}{\partial x} = 0 \quad (7.31b)$$

Doesn't this equation look familiar to you? It has the form of a continuity equation analogous to the continuity equation between the charge density and current density in electromagnetic theory (see the margin remark). This is one reason why $P(x,t)$ is referred to as the **probability density** and $J(x,t)$ is called the **probability current density**. So, Eq. (7.31b) is a conservation law, which tells us that the time rate of change of probability density has to be compensated by the net change in the probability flux.

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot \vec{J} = 0$$

where $\vec{J}$ is the current density and ρ is the charge density.

The derivation of this equation is based on the consideration that the potential function is real. You can now also see why we need to impose continuity conditions on ψ . Both ψ and its derivatives must be finite and continuous for all values of x , provided $V(x)$ is finite. That these restrictions on the solutions are necessary may be judged from the following considerations:

The probability density $P(x,t)$ and the probability flux $J(x,t)$ represent physical quantities and, therefore, have to be well defined. If ψ or its first derivative $\frac{\partial \psi}{\partial x}$ were not finite for some values of x then $P(x,t)$ and/or $J(x,t)$ would not be well defined for all values of x . Further, both ψ and $\frac{\partial \psi}{\partial x}$ must be continuous.

Otherwise $J(x,t)$ would be singular at some points and these points would act as sources or sinks of probability current. In other words, creation or destruction of matter would take place. This, as you know, is impossible in non-relativistic physics.

PROBABILITY CURRENT DENSITY

The Schrödinger equation can be used to derive a continuity equation, which connects the probability density $P(x,t)$ with an associated probability current density $J(x,t)$ as follows:

$$\frac{\partial P(x,t)}{\partial t} + \frac{\partial J(x,t)}{\partial x} = 0 \quad (7.31b)$$

$$\text{where} \quad J(x,t) = \frac{\hbar}{2mi} \left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right) \quad (7.31a)$$

The continuity equation tells us that a particle moving in a real potential is neither destroyed nor is another particle created. If the probability of finding a particle in any region decreases, correspondingly the probability of finding the particle in the remaining region must increase.

SAQ 3 - Probability density and probability current density

The wave function of an object of mass m is given by:

$$\psi(x, t) = e^{-(\alpha + i\beta)x} e^{-i\omega t}$$

Obtain the values of $P(x, t)$ and $J(x, t)$.

7.3.3 Normalization of the Wave Function

Recall Eq. (7.16), which tells us that since the quantum particle must be somewhere in space, the probability integrated over all space must equal one. For the one-dimensional case, we write this condition as:

$$\int_{-\infty}^{\infty} P(x, t) dx = \int_{-\infty}^{\infty} \psi^*(x, t) \psi(x, t) dx = 1 \quad (7.32)$$

A wave function $\psi(x, t)$ satisfying this condition is said to be **normalized**.

Normalisation of the wave function is a statement of the fact that the particle can be found somewhere with certainty. The condition

$$\int_{-\infty}^{\infty} \psi^*(x, t) \psi(x, t) dx = 1 \quad (7.33)$$

is known as the **normalization condition** for the wave function. In quantum mechanics, this condition plays an important role, as you will see when we apply the Schrödinger equation to specific physical systems.

The Schrödinger equation is a linear differential equation. So, if a function $\psi(x, t)$ is a solution of the Schrödinger equation,

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

a function $\psi'(x, t) = A\psi(x, t)$ will also be a solution of the same equation. Here A is a (complex) constant. In other words, the solution obtained from the Schrödinger equation is undetermined up to a constant A . The constant A is determined by imposing the normalization condition. So we can write:

$$\int_{-\infty}^{\infty} (A^* \psi^*(x, t)) (A \psi(x, t)) dx = 1 \Rightarrow |A|^2 = \frac{1}{\left[\int_{-\infty}^{\infty} \psi^*(x, t) \psi(x, t) dx \right]} \quad (7.34)$$

If we are able to determine the value of A from Eq. (7.34), then the wave function $\psi'(x, t) = A\psi(x, t)$ is the normalized wave function of the system and A is the normalization constant.

If the integral in the bracket is infinite, we would not be able to determine the value of A which would satisfy Eq. (7.16). Such wave functions that cannot be

normalized or are “non-normalizable” do not represent a physical system in the strictest sense. This is also true for the trivial solution of the Schrödinger equation, which is $\psi(x, t) = 0$.

So once again, note that wave functions for a physical system are the **square-integrable** solutions of Schrodinger equation, ($\int |\psi(x, t)|^2 dx < \infty$), for which we must also have $\psi(x, t) \rightarrow 0$ as $|x| \rightarrow \infty$.

So, we can conclude that the wave function for a system must be consistent with both Eqs. (7.16 and 7.34). Note that the normalization constant A is time independent. Hence, a wave function which is normalised at any instant of time stays normalised at all other times.

However, there exists a category of wave functions for which the value of the integral in Eq. (7.34) is infinite. It is a wave function whose norm is infinite or, in other words, the wave function cannot be normalized. Wave functions of this form do not go to zero as $|x| \rightarrow \infty$.

You should understand from our discussion that these do not correspond to a physical state. But, such functions are extensively used in quantum mechanics to describe free particles. Let us now work out an example on the normalization of the wave function.

EXAMPLE 7.3 : NORMALIZATION OF THE WAVE FUNCTION

Determine the normalization constant N for the following wave function:

$$\psi(x, t) = \begin{cases} Nx(a-x)e^{-\frac{iEt}{\hbar}} & \text{for } 0 \leq x \leq a \\ 0 & \text{elsewhere} \end{cases}$$

SOLUTION ■ We use the normalization condition given by Eq. (7.33).

The complex conjugate of the given wave function is

$$\psi^*(x, t) = N^* x(a-x)e^{iEt/\hbar}$$

Since the wave function is zero at all positions other than $0 \leq x \leq a$, the normalisation condition gives:

$$\int_0^a \psi^* \psi dx = 1 \quad \Rightarrow \quad N^* N \int_0^a x^2 (a-x)^2 dx = 1$$

$$\text{or } |N|^2 \int_0^a x^2 (a^2 - 2ax + x^2) dx = 1 \quad \Rightarrow \quad \int_0^a (a^2 x^2 - 2ax^3 + x^4) dx = 1$$

$$\text{or } |N|^2 \left[a^2 \frac{x^3}{3} - \frac{2ax^4}{4} + \frac{x^5}{5} \right]_0^a = 1 \quad \Rightarrow \quad |N|^2 a^5 \left[\frac{1}{30} \right] = 1$$

$$\therefore |N| = \sqrt{\frac{30}{a^5}}$$

Let us revise the condition for normalization of the wave function.

NORMALIZATION OF THE WAVE FUNCTION

A wave function $\psi(x,t)$ satisfying the following condition is said to be normalized:

$$\int_{-\infty}^{\infty} \psi^*(x,t) \psi(x,t) dx = 1 \quad (7.33)$$

For a wave function, $\psi'(x,t) = A\psi(x,t)$, the normalization constant A is determined as follows:

$$|A|^2 = \frac{1}{\int_{-\infty}^{\infty} \psi^*(x,t) \psi(x,t) dx} \quad (7.34)$$

Let us now further analyse the Schrödinger equation.

7.4 TIME INDEPENDENT SCHRÖDINGER EQUATION

The Schrödinger equation represents the time development of the wave function $\psi(x,t)$. So, if you were given the wave function at any initial instant of time, let us say at $t = 0$, [i.e., $\psi(x,0)$], you could use the Schrödinger equation to arrive at the wave function corresponding to a later time t : $\psi(x,t)$. You have seen that the probability density for the position of particle at any instant of time is related to the wave function $\psi(x,t)$. So, from the knowledge of the initial position distribution, you can find the position distribution at any later time. What about the momentum of the particle?

At the end of this unit, you will study that it is possible to transform the wave function $\psi(x,t)$, which is a function of x and t in such a way that we obtain a wave function in terms of the momentum (p) and t [$\phi(p,t)$]. From this we can get the probability distribution of the momentum of the particle. Thus, if we have the position and momentum probability distributions of the particle at one time, the probability distribution at any later time can be determined with the help of the Schrödinger equation.

Isn't this situation analogous to the one in classical mechanics? In classical mechanics, if the position and momentum (velocity) of a particle are known at some initial time then we can use Newton's equation of motion to find the position and momentum of the particle at any later time. So, Newtonian mechanics (for the classical particle) and Schrödinger equation (for the quantum particle) both tell us how the initial state evolves with time. However, there is a difference between classical and quantum mechanics. What is it?

Recollect that in Newtonian mechanics, the initial position and velocity are just two numbers $x(t=0)$ and $v(t=0)$. On the other hand, for a quantum

mechanical system you need the entire function at $t = 0$, which is $\psi(x, 0)$, the value of the wave function for all x . Also in quantum mechanics, the uncertainty principle tells us that both the position and the momentum of the particle cannot be known precisely at the same instant of time. We can know only their distributions.

In many problems of classical mechanics such as Kepler's planetary orbits, Rutherford scattering, we assume that the particle has a definite energy and/or angular momentum.

However, in quantum mechanics, if we assume the energy of the particle to be known precisely, i.e., if $\Delta E = 0$ then, according to the uncertainty

relation $\Delta E \Delta t \geq \frac{\hbar}{2}$, Δt would be infinite.

This means that an infinite amount of time should be available to make energy measurements. In other words, **for a particle in a state with a precise energy, the probability density $\psi^*(x, t)\psi(x, t)$ would not change with time.**

We use this fact to arrive at the **time independent Schrödinger equation.**

Consider a wave function of the following form:

$$\psi(x, t) = \psi(x)e^{ig(t)} \quad (7.35)$$

where $g(t)$ is some arbitrary function of time. The probability density $P(x, t)$ corresponding to this wave function is:

$$P(x, t) = \psi(x, t)\psi^*(x, t) = |\psi(x)|^2 e^{ig(t)} e^{-ig(t)} = |\psi(x)|^2 \quad (7.36)$$

which **is independent of time**. So, if the state of the system is represented by a wave function of the form given in Eq. (7.35), the energy of the system does not change with time, i.e., its energy is conserved. Hence, if the particle is initially in a specified “energy” state represented by Eq. (7.35), then it stays in it indefinitely unless it is disturbed by some external agency. Such states are called **stationary states**. And $\psi(x)$ is called the **stationary state wave function**.

Classically, the energy (which is also termed the Hamiltonian) is a constant of motion if it does not contain time explicitly. Now, the Hamiltonian is the sum of the kinetic energy and the potential energy. Thus, for the total energy to be conserved, the potential in which the particle is moving should be independent of time. For such potentials, the space and time dependence of the wave function $\psi(x, t)$ can be separated and we can write the wave function as the product of two functions, one of which is a function of x alone and the other which is a function of time alone, as shown below:

$$\psi(x, t) = \psi(x)f(t) \quad (7.37)$$

With this, the one-dimensional Schrödinger equation of Eq. (7.13) may be separated into two ordinary differential equations in x and t by the method of separation of variables as we now show.

To start with, we write the partial derivatives of $\psi(x, t)$ with respect to x and t :

$$\frac{\partial}{\partial t} [\psi(x, t)] = \frac{\partial}{\partial t} [\psi(x) f(t)] = \psi(x) \frac{df(t)}{dt} \quad (7.38)$$

$$\frac{\partial}{\partial x} [\psi(x, t)] = \frac{\partial}{\partial x} [\psi(x) f(t)] = \frac{d\psi(x)}{dx} f(t); \quad \frac{\partial^2}{\partial x^2} [\psi(x, t)] = \frac{d^2\psi(x)}{dx^2} f(t) \quad (7.39)$$

We substitute $\frac{\partial}{\partial t} [\psi(x, t)]$ and $\frac{\partial^2}{\partial x^2} [\psi(x, t)]$ from Eqs. (7.38 and 7.39) in

Eq. (7.13) with $V(x, t) = V(x)$ and use $\psi(x, t) = \psi(x) f(t)$ to get:

$$i\hbar\psi(x) \frac{df(t)}{dt} = -\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} f(t) + V(x)\psi(x)f(t) \quad (7.40)$$

Dividing both sides of Eq. (7.40) by $\psi(x)f(t)$ we can write:

$$\frac{i\hbar}{f(t)} \frac{df(t)}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{d^2\psi(x)}{dx^2} + V(x) \quad (7.41)$$

The left side of Eq. (7.41) is constant for fixed x at all t . Similarly, its right side is constant for fixed t at all values of x . Hence, Eq. (7.41) will hold only when both its left hand and right hand sides are equal to a constant C , which is independent of x and t . Therefore,

$$\frac{i\hbar}{f(t)} \frac{df(t)}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{d^2\psi(x)}{dx^2} + V(x) = C \quad (7.42)$$

We get the following two ordinary differential equations:

$$i\hbar \frac{df(t)}{dt} = Cf(t) \quad (7.43)$$

$$\text{and} \quad -\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = C\psi(x) \quad (7.44)$$

We can solve Eq. (7.43) by the standard methods which you have studied in Unit 4 of BPHCT-131 for first order ordinary differential equations. The solution is:

$$f(t) = Ae^{-iCt/\hbar} \quad (7.45)$$

where A is a constant. You should verify this solution before studying further.

What are the dimensions of C ? You know that the argument of the exponential function is just a number. Since $\hbar$ has the dimensions (energy $\times$ time), from Eq. (7.45), you can see that C should have the dimensions of energy. So, we can denote it by E . From the de Broglie relation for the frequency of the wave function $\psi(x, t)$, $E = \hbar\omega$ where E is the total energy of the particle. So, we can

write $\omega = \frac{E}{\hbar}$ and $f(t)$ is just:

$$f(t) = Ae^{-iEt/\hbar} = Ae^{-i\omega t} \quad (7.46)$$

So we are now left with only the following equation for $\psi(x)$:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad (7.47)$$

This is known as the **time independent Schrödinger equation**.

We can now write the general solution or the stationary state solution of the time dependent Schrödinger equation for a particle of definite energy E as

$$\psi(x, t) = \psi(x) \exp\left(-\frac{iEt}{\hbar}\right) \quad (7.48)$$

where $\psi(x)$ is the solution of Eq. (7.47). The probability density is just

$$P(x, t) = \psi^*(x)\psi(x) \quad (7.49)$$

which is independent of time. You should note that

Eq. (7.47) contains no imaginary quantities and hence $\psi(x)$ is not necessarily complex although $\psi(x, t)$ is. The normalisation condition (Eq. 7.33) for the stationary wave function reduces to the form:

$$\int_{-\infty}^{\infty} \psi^*(x)\psi(x)dx = 1 \quad (7.50)$$

Let us now work out an example on these ideas.

EXAMPLE 7.4 : TIME INDEPENDENT SCHRÖDINGER EQUATION

In a region of space a particle of mass m and zero energy has a wave function $\psi(x) = N x e^{-x^2/16}$, where N is a constant. Using the time independent Schrödinger equation, determine the potential energy $V(x)$ for the particle.

SOLUTION ■ We use Eq. (7.47).

For zero energy ($E = 0$), Eq. (7.47) reduces to:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = 0$$

$$\therefore V(x)\psi(x) = \frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} \quad (i)$$

$$\text{We have to calculate } \frac{d^2\psi}{dx^2} = \frac{d}{dx} \left[\frac{d}{dx} (N x e^{-x^2/16}) \right]$$

The first order derivative of the wave function is

$$\frac{d\psi}{dx} = N e^{-x^2/16} - N \frac{x^2}{8} e^{-x^2/16}$$

The second order derivative is

$$\begin{aligned}\frac{d^2\psi}{dx^2} &= -\frac{x}{8} \cdot N e^{-x^2/16} - \frac{Nx}{4} e^{-x^2/16} + \frac{Nx^3}{64} e^{-x^2/16} \\ &= N x e^{-x^2/16} \left[-\frac{1}{8} - \frac{2}{8} + \frac{2x^2}{8 \times 16} \right] = \left[\frac{x^2}{64} - \frac{3}{8} \right] \psi(x) \quad (\text{ii})\end{aligned}$$

Substituting $\frac{d^2\psi}{dx^2}$ from Eq. (ii) into Eq. (i) we get:

$$V(x)\psi(x) = \frac{\hbar^2}{2m} \left[\frac{x^2}{64} - \frac{3}{8} \right] \psi(x) \Rightarrow \left[V(x) - \frac{\hbar^2}{2m} \left(\frac{x^2}{64} - \frac{3}{8} \right) \right] \psi(x) = 0$$

Since $\psi(x)$ is arbitrary, $\psi(x) \neq 0$, and

$$V(x) = \frac{\hbar^2}{2m} \left(\frac{x^2}{64} - \frac{3}{8} \right) = \frac{\hbar^2}{16m} \left(\frac{x^2}{8} - 3 \right)$$

Let us revise time independent Schrödinger equation.

TIME INDEPENDENT SCHRÖDINGER EQUATION

The **time independent Schrödinger equation** is:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad (7.47)$$

When the energy E of a quantum mechanical system does not change with time, the state of the system is represented by a wave function of the form:

$$\psi(x, t) = \psi(x) \exp\left(-\frac{iEt}{\hbar}\right) \quad (7.48)$$

Such states are called **stationary states** and $\psi(x)$ is called the stationary state wave function. The stationary state wave function is the solution of the **time independent Schrödinger equation**.

You may now like to work out the following SAQ.

SAQ 4 - Normalisation of the wave function

Calculate the normalisation constant N for the stationary state wave function for a system given by:

$$\psi(x) = N \exp\left(-\frac{x^2}{2}\right) \quad \text{for } -\infty \leq x \leq \infty$$

So far we have been studying the one-dimensional Schrödinger equation, both in its time dependent and time independent form. In general, the three-dimensional time dependent Schrödinger equation for the wave function $\psi = \psi(x, y, z, t)$ is given by:

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + V(x, y, z, t) \psi = i\hbar \frac{\partial \psi}{\partial t} \quad (7.51)$$

And the time independent Schrödinger equation in three-dimensions is:

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi(x, y, z)}{\partial x^2} + \frac{\partial^2 \psi(x, y, z)}{\partial y^2} + \frac{\partial^2 \psi(x, y, z)}{\partial z^2} \right) + V(x, y, z) \psi(x, y, z) = E \psi(x, y, z) \quad (7.52)$$

We write it in a more compact form as:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(x, y, z) + V(x, y, z) \psi(x, y, z) = E \psi(x, y, z) \quad (7.53)$$

In this course you will be solving only the one-dimensional Schrödinger equation for a few simple physical systems. Further, we confine our study to those problems which require solving one-dimensional time-independent Schrödinger equation, i.e., we shall study stationary state problems. The three-dimensional Schrödinger equation is used to study, for example, the electron in the hydrogen atom. You will study it in the Master's level Physics courses.

Before we end this section we would like to write down the wave function in terms of the momentum p , i. e., $\phi(p, t)$, for the one-dimensional wave function $\psi(x, t)$. It can be derived from the real-space wave function $\psi(x, t)$ by a mathematical tool called the Fourier transform. The Fourier transform is an important tool and you will study about it in senior level courses in mathematics or physics. We define:

$$\phi(p, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \psi(x, t) e^{-ipx/\hbar} dx \quad (7.54)$$

It turns out that quantum mechanics can be formulated just as well in terms of the momentum wave function. In analogy with the probabilistic interpretation of $\psi(x, t)$, $|\phi(p, t)|^2$ is the probability density of a measurement of the momentum yielding a value between p and $p + dp$. The normalization condition for $\phi(p, t)$ is

$$\int_{-\infty}^{\infty} \phi(p, t)^* \phi(p, t) dp = 1 \quad (7.55)$$

This is the momentum representation of quantum mechanics. It demonstrates also that we can formulate quantum mechanics in different ways, one of which is also the matrix formulation.

Let us now examine the conditions that the wave function $\psi(x)$ has to satisfy in order to be a physically acceptable solution of the Schrödinger equation.

7.5 ACCEPTABLE SOLUTIONS OF THE SCHRÖDINGER EQUATION

We have already seen that the probabilistic interpretation of the wave function imposes certain conditions on it. Let us see what these conditions mean:

- i) $\psi(x)$ **should be finite and single-valued everywhere.**

As you know, the wave function is related to the probability density. To ensure that the probability associated the wave function has a unique value, the wave function must also have unique value for any given value of x and t . So, the wave function must be **single-valued**.

The wave function for a system has to satisfy the condition:

$$\int_{-\infty}^{\infty} P(x,t) dx = \int_{-\infty}^{\infty} \psi^*(x,t) \psi(x,t) dx = 1 \quad (7.15)$$

If the wave function for a particle is infinite in any finite region, the value of this integral would be infinite. If that is so, the probability of finding it anywhere would be infinite and the probability of finding the particle in a region where the wave function is finite would be zero. This should not be the case. **So, the wave function should also be finite.**

- ii) $\psi(x)$ **should be square-integrable.**

Once again, if $\psi(x)$ is not square-integrable, then the condition

$$\int_{-\infty}^{\infty} \psi^*(x,t) \psi(x,t) dx = 1$$

cannot be satisfied and $\psi(x)$ cannot be interpreted in terms of a probability density, which must integrate over all space to give a value of 1. This condition also implies that the wave function must tend to zero for infinite distances.

- iii) **Both $\psi(x)$ and $\frac{d\psi}{dx}$ should be continuous everywhere.**

These conditions arise because the wave function must satisfy the Schrödinger equation, which is a second order differential equation.

We can rewrite the time independent Schrödinger equation [Eq. (7.47)] as:

$$\frac{d^2\psi(x)}{dx^2} = \frac{2m}{\hbar^2} (V(x) - E) \psi(x) \quad (7.56)$$

For a solution to exist, the second derivative of the wave function should exist, which means that the first derivative of the function should also exist.

From Eq. (7.56), you can see that if $V(x)$, E and $\psi(x)$ are finite then

$\psi''(x)$ $\left(\text{or } \frac{d^2\psi}{dx^2} \right)$ is also finite. This implies that $\psi'(x)$ $\left(\text{or } \frac{d\psi}{dx} \right)$ is continuous.

In other words, the plot of $\psi(x)$ versus x must be smooth. However, if in any region the potential energy becomes infinite, $\psi(x)$ must be zero in those regions since no particle can have infinite potential energy. And at

the boundary of such regions, $\psi'(x)$ may be discontinuous. A rapid change in $\psi(x)$ would mean that the derivative of the function was very large. If $\psi(x)$ were to be a step function, the first derivative would be infinite at the point. As you will see in the next unit, the momentum of a physical system is related to the first derivative of the wave function. Hence, if the value of the first derivative of the wave function is infinite, it is not physically realistic.

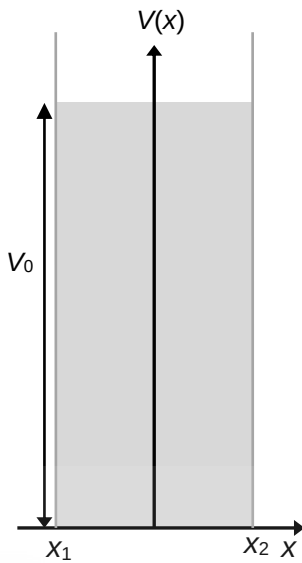


Fig. 7.1: Finite potential well.

The form of the wave function that satisfies Eq. (7.56) depends on the potential function $V(x)$ as well as the boundary condition imposed while solving the differential equation. This depends on the nature of the problem.

To understand this point, let us take the example of a particle of energy E , bound inside a potential well as shown in Fig. 7.1. Here $V(x) > E$ in the regions $x_1 \leq x \leq x_2$. Classically, if the particle is initially between x_1 and x_2 , then for all times to come it will be confined to the same region, i.e., the particle will always be bounded between x_1 and x_2 . Then we say that the particle is in a bound state.

Quantum mechanically, we expect that there will be a large probability of finding the particle in the region $x_1 < x < x_2$. However, there also exists a decreasingly small probability of finding the particle outside this region, which is forbidden classically. For this the wave function corresponding to the bound state must satisfy the (boundary) condition that the wave function vanishes at infinity. A very interesting result follows from the consideration of such a boundary condition, which you will study in detail in the next block. Here we just mention it:

The (acceptable) solutions of the time independent Schrödinger equation exist only for certain discrete values of the total energy E . Thus, energy quantization is an inherent property of the Schrödinger equation for the bound states.

You will study in the next unit that the predictions of observable physical quantities involve the wave function of the system and its derivatives. Hence, if these were not finite and single valued, they would not be able to represent measurable quantities. We now summarise the properties and the boundary conditions that a wave function must satisfy to be acceptable:

PROPERTIES OF THE WAVE FUNCTION

1. $\psi(x)$ must be single valued, finite and continuous for all values of x .
2. $\psi'(x)$ must be finite and continuous for all values of x , except at those points where $V \rightarrow \infty$. At these points $\psi'(x)$ has a finite discontinuity but $\psi(x)$ remains continuous.
3. For bound states, the probability of finding the particle between x and $x + dx$, i.e., $|\psi|^2 dx$ must vanish as $|x| \rightarrow \infty$. Hence, $|\psi(x)| \rightarrow 0$ as $|x| \rightarrow \infty$. So, $\psi(x)$ should be a square-integrable wave function.

All of quantum mechanics follows from a small set of assumptions or postulates, which you will study as you go along and we will summarise them for you at the end of the next unit, when you are familiar with the required terminology. In this unit, you have studied the **first postulate of quantum mechanics**, which tells us that the state of any quantum mechanical system is completely specified by a **wave function** $\psi(\vec{r}, t)$. It is a function of the spatial coordinates and time. In the next unit, you will learn how to derive the physically observable properties of a quantum system.

Let us now sum up what you have learnt in this unit.

7.6 SUMMARY

Concept	Description
Description of a system	Every quantum particle (or a system of quantum particles) is represented by a wave function $[\psi(x, y, z, t)]$, which is a function of space coordinates and time. The wave function determines all that can be known about the system it represents.
Time dependent Schrödinger equation	The evolution of the wave function in space and time is given by the time independent Schrödinger equation which is a differential equation, involving derivatives with respect to the spatial coordinates and time. The time-dependent Schrödinger equation for the one-dimensional motion of a particle of mass m moving in a potential $V(x, t)$ is given by
Probabilistic interpretation of the wave function	$i\hbar \frac{\partial \psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + V(x, t) \psi(x, t)$ - The probability density of finding a particle at any point, when a measurement of its position is carried, is proportional to $\psi ^2 = \psi^* \psi$, which is the modulus square of the wave function of the particle at that point. ψ^* is the complex conjugate of the wave function ψ. - For a one-dimensional system, the probability $P(x, t)dx$ that a particle will be found between the coordinates x and $x + dx$ is: $P(x, t)dx = \psi^*(x, t)\psi(x, t)dx = \psi(x, t) ^2 dx$ where $\psi(x, t)$ is the wave function of the particle. - The probability of finding the particle in some finite region $L = [x_1, x_2]$ is:

$$P_L(t) = \int_{x_1}^{x_2} P(x, t)dx = \int_{x_1}^{x_2} \psi^*(x, t)\psi(x, t)dx$$

At each instant of time we must have:

$$\int_{-\infty}^{\infty} P(x,t) dx = \int_{-\infty}^{\infty} \psi^*(x,t) \psi(x,t) dx = 1$$

Probability current density

- A **continuity equation** can be derived from the Schrödinger equation which connects the probability density $P(x,t)$ with an associated **probability current density** $J(x,t)$:

$$\frac{\partial P(x,t)}{\partial t} + \frac{\partial J(x,t)}{\partial x} = 0$$

$$\text{where } J(x,t) = \frac{\hbar}{2mi} \left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right)$$

The continuity equation tells us that a particle moving in a real potential is neither destroyed, nor is another particle created.

Normalization of the wave function

- A wave function $\psi(x,t)$ satisfying the following condition is said to be **normalized**:

$$\int_{-\infty}^{\infty} P(x,t) dx = \int_{-\infty}^{\infty} \psi^*(x,t) \psi(x,t) dx = 1$$

For a wave function $\psi'(x,t) = A\psi(x,t)$, the normalization constant A is determined as follows:

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

Time independent Schrödinger equation

- If the state of a quantum mechanical system is represented by a wave function of the form :

$$\psi(x,t) = \psi(x) \exp\left(-\frac{iEt}{\hbar}\right)$$

the energy E of the system does not change with time. Such states are called **stationary states**. And $\psi(x)$ is called the stationary state wave function. The stationary state wave function is the solution of the time independent Schrödinger equation:

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

Properties of the wave function

- 1. $\psi(x)$ must be single valued, finite and continuous for all values of x , $\psi'(x)$ must be finite and continuous for all values of x , except at those points where $V \rightarrow \infty$. At these points $\psi'(x)$ has a finite discontinuity but $\psi(x)$ remains continuous.
- 2. For bound states, the probability of finding the particle between x

and $x + dx$, i.e., $|\psi|^2 dx$ must vanish as $|x| \rightarrow \infty$. Hence, $|\psi(x)| \rightarrow 0$ as $|x| \rightarrow \infty$. So, $\psi(x)$ should be a square-integrable wave function.

7.7 TERMINAL QUESTIONS

- For a free particle show that the wave function
 - $\psi(x,t) = A \sin(kx - \omega t)$ **is not** a solution of the time-dependent Schrödinger equation; and
 - $\psi(x,t) = A \exp[i(kx - \omega t)]$ **is** a solution of the time-dependent Schrödinger equation.
- The wave function of an object of energy E and momentum p is given by $\psi(x,t) = A e^{i(px - Et)/\hbar}$.
 - Does ψ represent a bound state?
 - Can the wave function be normalized?
 - Using the above, calculate the probability current density $J(x,t)$ in terms of the velocity v of an object and a constant A , which is complex.
- The wave function of a system is given by $\psi(x) = Nx \exp(-x^2/2)$ for $-\infty < x < \infty$. Obtain the value of the normalization constant N .
- A certain wave function is given by

$$\psi(x) = N(1 + ix) \exp(-x) \quad \text{for } x > 1$$

$$= 0 \quad \text{for } x < 1$$

Obtain the value of the normalization constant N . Why can it **not** represent a physical system?
- The wave function for a particle is given by :

$$\psi(x) = N \sin(5x) \quad \text{for } 0 < x < \pi$$

Determine the normalisation constant N and the probability of finding the particle between $x = \pi/4$ and $x = 3\pi/4$.

- The potential energy of a simple harmonic oscillator of mass m and frequency ν is equal to $2m(\pi\nu x)^2$. Write down its time independent Schrödinger equation and show that it can be rewritten as:

$$\frac{d^2\psi}{d\xi^2} + \left(\frac{\alpha}{\beta} - \xi^2 \right) \psi = 0$$

where $\alpha = \frac{2m}{\hbar^2} E$, $\beta = 2\pi m \nu / \hbar$ and $\xi = \sqrt{\beta} x$, and E is the total energy of the oscillator. For what value of α/β is the function

$$\psi(\xi) = \exp(-\xi^2/2) \quad \text{a solution of the differential equation?}$$

7. The quantum mechanical wave function for a particle is given by:

$$\psi(x) = \begin{cases} Ax^{3/2}e^{-\alpha x} & \text{for } x > 0 \\ 0 & \text{for } x < 0 \end{cases}$$

Determine (a) the normalization constant A and (b) the most probable position of the particle.

8. In a region of space, a particle of mass m has a wave function:

$$\psi(x) = \begin{cases} Nx e^{-\alpha x} & \text{for } x > 0 \\ 0 & \text{for } x < 0 \end{cases}$$

where α is a positive constant. Calculate:

- the normalization constant N , and
- the potential energy of the particle if the total energy of the particle is zero.

9. The wave function for a particle is defined by:

$$\psi(x) = \begin{cases} N \cos\left(\frac{2\pi x}{L}\right) & \text{for } -\frac{L}{4} \leq x \leq \frac{L}{4} \\ 0 & \text{otherwise} \end{cases}$$

Determine

- the normalization constant N , and
- the probability that the particle will be found between $x = 0$ and $x = L/6$.

10. An electron has the following wave function:

$$\psi(x) = Ae^{-x}(1 - e^{-x}), 0 < x < \infty$$

Determine the normalization constant A .

11. The wave function of a particle is given as

$$\psi(x) = \begin{cases} e^x & \text{for } x < 0 \\ e^{-x} & \text{for } x > 0 \end{cases}$$

Show that the wave function is normalized and calculate the probability of finding the particle between $-2 < x < 2$.

12. Explain which of the following wave functions are **NOT** acceptable for a physical system:

- a) $\psi(x) = Ne^{-x^2/2}$ for $-\infty < x < \infty$
- b) $\psi(x) = Ne^{-x}$ for $0 \leq x < \infty$
- c) $\psi(x) = N \sin x$ for $0 < x < \infty$
- d) $\psi(x) = N \tan x$ for $0 < x < \infty$

7.8 SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. Because $\psi_1(x, t)$ and $\psi_2(x, t)$ are solutions of Eq. (7.13) we can write:

$$i\hbar \frac{\partial \psi_1}{\partial t}(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi_1}{\partial x^2}(x, t) + V(x, t)\psi_1(x, t) \quad (i)$$

and $i\hbar \frac{\partial \psi_2}{\partial t}(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi_2}{\partial x^2}(x, t) + V(x, t)\psi_2(x, t) \quad (ii)$

Multiplying Eq. (i) by a_1 and Eq. (ii) by a_2 , we can write,

$$i\hbar \frac{\partial}{\partial t}(a_1\psi_1) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}(a_1\psi_1) + V(x, t)a_1\psi_1 \quad (iii)$$

and $i\hbar \frac{\partial}{\partial t}(a_2\psi_2) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}(a_2\psi_2) + V(x, t)a_2\psi_2 \quad (iv)$

Adding Eqs. (iii) and (iv) we get

$$i\hbar \frac{\partial}{\partial t}(a_1\psi_1 + a_2\psi_2) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}(a_1\psi_1 + a_2\psi_2) + V(x, t)(a_1\psi_1 + a_2\psi_2) \quad (v)$$

So the linear combination $\psi = a_1\psi_1 + a_2\psi_2$ is also a solution of Eq. (7.13).

2. We can write the wave function $\psi(x) = \frac{1}{\sqrt{4\pi}} [e^{ix} + e^{-ix}] = \frac{1}{\sqrt{\pi}} \cos x$

and the complex conjugate $\psi^*(x) = \frac{1}{\sqrt{4\pi}} [e^{-ix} + e^{ix}] = \frac{1}{\sqrt{\pi}} \cos x$

With $x_1 = \pi/3$ and $x_2 = \pi/2$ in Eq. (7.15) we get (see the margin remark):

$$P_L(\pi/3, \pi/2) = \frac{1}{\pi} \int_{\pi/3}^{\pi/2} \cos^2 x dx = \frac{1}{2\pi} \int_{\pi/3}^{\pi/2} (1 + \cos 2x) dx = 0.01$$

3. The complex conjugate of the wave function is: $\psi^*(x, t) = e^{-(\alpha - i\beta)x} e^{i\omega t}$

With $\psi(x, t) = e^{-(\alpha + i\beta)x} e^{-i\omega t}$ we get

$$\begin{aligned} & \int_{\pi/3}^{\pi/2} (1 + \cos 2x) dx \\ &= \left[x + \frac{\sin 2x}{2} \right]_{\pi/3}^{\pi/2} \\ &= \left[\left(\frac{\pi}{2} - \frac{\pi}{3} \right) + \frac{1}{2} \left(\sin \pi - \sin \frac{2\pi}{3} \right) \right] \\ &= \left[\frac{\pi}{6} - \frac{\sqrt{3}}{4} \right] \\ &= [0.52 - 0.43] = 0.09 \end{aligned}$$

$$P(x,t) = \psi^*(x,t)\psi(x,t) = e^{-2\alpha}$$

To calculate the probability current density $J(x,t)$ using Eq. (7.31a) we first calculate the required partial derivatives of the wave function and its conjugate as

$$\frac{\partial \psi}{\partial x} = -(\alpha + i\beta)e^{-(\alpha+i\beta)x}e^{-i\omega t} = -(\alpha + i\beta)\psi$$

$$\frac{\partial \psi^*}{\partial x} = -(\alpha - i\beta)e^{-(\alpha-i\beta)x}e^{i\omega t} = -(\alpha - i\beta)\psi^*$$

$$\text{So, } \psi^* \frac{\partial \psi}{\partial x} = -(\alpha + i\beta)\psi^*\psi = -(\alpha + i\beta)e^{-2\alpha}$$

$$\psi \frac{\partial \psi^*}{\partial x} = [-(\alpha - i\beta)]\psi\psi^* = -(\alpha - i\beta)e^{-2\alpha}$$

$$\text{So, } J(x,t) = \frac{\hbar}{2mi}e^{-2\alpha}[-(\alpha + i\beta) + (\alpha - i\beta)] = \frac{\hbar}{2mi}e^{-2\alpha}(-2i\beta) = \frac{\hbar\beta e^{-2\alpha}}{m}$$

4. Using the normalisation condition Eq. (7.50) we can write

$$\int_{-\infty}^{\infty} \left(N^* e^{-x^2/2} \right) \left(N e^{-x^2/2} \right) dx = 1$$

$$\Rightarrow |N|^2 \int_{-\infty}^{\infty} e^{-x^2} dx = 1$$

Using Table 7.1 (4), we get:

$$|N|^2(\sqrt{\pi}) = 1 \quad \Rightarrow \quad |N|^2 = \frac{1}{\sqrt{\pi}}$$

So, the normalization constant N is:

$$N = \left(\frac{1}{\pi} \right)^{1/4}$$

Terminal Questions

1. a) We first calculate the partial derivatives

$$\frac{\partial \psi}{\partial t} = \frac{\partial}{\partial t} [A \sin(kx - \omega t)] = -\omega A \cos(kx - \omega t)$$

$$\frac{\partial \psi}{\partial x} = Ak \cos(kx - \omega t); \quad \frac{\partial^2 \psi}{\partial x^2} = -Ak^2 \sin(kx - \omega t)$$

Substituting these in Eq. (7.13) with $V(x) = 0$, we get

$$\text{LHS of Eq. (7.13) is: } i\hbar[-\omega A \cos(kx - \omega t)]$$

At the end of this unit we have given a table of integrals which you can use to solve integrals of this type.

RHS of Eq. (7.13) is: $\frac{\hbar^2}{2m} Ak^2 \sin(kx - \omega t)$

As you can see, these are not equal. So, $\psi(x, t) = A \sin(kx - \omega t)$ is not a solution of the time dependent Schrödinger equation for a free particle.

$$\begin{aligned} \text{b) } \frac{\partial \psi}{\partial t} &= \frac{\partial}{\partial t} A e^{i(kx - \omega t)} = i \omega A e^{i(kx - \omega t)} \\ \frac{\partial \psi}{\partial x} &= ik A e^{i(kx - \omega t)}; \quad \frac{\partial^2 \psi}{\partial x^2} = -k^2 A e^{i(kx - \omega t)} \end{aligned}$$

Substituting the above results in Eq. (7.13) with $V(x) = 0$, we get:

$$\text{LHS : } i \hbar [-i \omega A e^{i(kx - \omega t)}] = \hbar \omega \psi$$

$$\text{RHS : } \frac{\hbar^2 k^2}{2m} [A e^{i(kx - \omega t)}] = \frac{\hbar^2 k^2}{2m} \psi$$

So, if Eq. (7.13) is to hold for this form of the wave function, then we must have:

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

Therefore, ψ is a solution of Eq. (7.13) for $\hbar \omega = \frac{\hbar^2 k^2}{2m}$

2. a) No, it does not as $\psi(x)$ does not go to zero as $|x| \rightarrow \infty$
- b) No, its norm is infinite.
- c) Using Eq. (7.31a) the probability current density is:

$$\begin{aligned} J(x, t) &= \frac{\hbar}{2mi} \left[A^* A e^{-i(px - Et)/\hbar} \left(\frac{ip}{\hbar} \right) e^{i(px - Et)/\hbar} \right] \\ &\quad - \frac{\hbar}{2mi} \left[A A^* e^{i(px - Et)/\hbar} \left(-\frac{ip}{\hbar} \right) e^{-i(px - Et)/\hbar} \right] \\ &= \frac{\hbar}{2mi} A A^* \left(\frac{2ip}{\hbar} \right) = v A A^* \quad (\because p = mv) \end{aligned}$$

3. Applying the normalisation condition, we get $|N|^2 \int_{-\infty}^{\infty} x^2 e^{-x^2} dx = 1$

Using Table 7.1(5), we get: $|N|^2 \left(\frac{\sqrt{\pi}}{2} \right) = 1$

$$\therefore |N|^2 = \frac{2}{\sqrt{\pi}} \quad \text{and} \quad N = \left(\frac{4}{\pi} \right)^{1/4}$$

4. Using the normalization condition (Eq. 7.33) with $\psi^* = N^* (1 - ix) e^{-x}$ we get

$$\begin{aligned}
 & \int x^2 e^{-2x} dx \\
 &= -\frac{x^2 e^{-2x}}{2} \\
 &+ \int x e^{-2x} dx \\
 &= -\frac{x^2 e^{-2x}}{2} \\
 &- \frac{x}{2} e^{-2x} - \frac{1}{4} e^{-2x}
 \end{aligned}$$

$$|N|^2 \int_1^{\infty} (1+ix)(1-ix)e^{-2x} dx = 1$$

$$\therefore |N|^2 \int_1^{\infty} (1+x^2)e^{-2x} dx = 1 \Rightarrow |N|^2 \int_1^{\infty} e^{-2x} dx + |N|^2 \int_1^{\infty} x^2 e^{-2x} dx = 1$$

$$\text{or } |N|^2 \left[-\frac{e^{-2x}}{2} \right]_1^{\infty} + |N|^2 \left[-\frac{x^2}{2} e^{-2x} - \frac{x}{2} e^{-2x} - \frac{1}{4} e^{-2x} \right]_1^{\infty} = 1$$

$$\text{or } |N|^2 \left(\frac{e^{-2}}{2} + \frac{5e^{-2}}{4} \right) = 1 \Rightarrow |N|^2 \left(\frac{7e^{-2}}{4} \right) = 1 \text{ (read the margin remark)}$$

$$\text{or } N = 2e/\sqrt{7}$$

This wave function cannot represent a physical system because it is discontinuous at $x = 1$. Check this out by taking the limit $x \rightarrow 1$ from right ($-\infty$) and left ($-\infty$). Both the limits are unequal.

$$\begin{aligned}
 & N^2 \int_0^{\pi} \sin^2 5x dx = 1 \\
 & \Rightarrow \frac{N^2}{2} \int_0^{\pi} [1 - \cos 10x] dx \\
 &= 1 \\
 & \Rightarrow \frac{N^2}{2} \left[x - \frac{1}{10} \sin 10x \right]_0^{\pi} \\
 &= 1 \\
 & \text{or } \frac{N^2}{2} [\pi] = 1 \\
 & \Rightarrow N^2 = \frac{2}{\pi}
 \end{aligned}$$

5. Using the normalization condition of Eq. (7.50) we can write

$$\int_0^{\pi} (N \sin 5x)^* (N \sin 5x) dx = 1 \Rightarrow |N|^2 \int_0^{\pi} \sin^2 5x dx = 1$$

$$\Rightarrow |N|^2 = \frac{2}{\pi} \quad \text{or} \quad N = \sqrt{\frac{2}{\pi}} \quad \text{(see the margin remark)}$$

So, the normalized wave function is $\psi(x) = \sqrt{\frac{2}{\pi}} \sin 5x$

The probability of finding the particle between $x = \pi/4$ and $x = 3\pi/4$ is

$$P_L = \int_{\pi/4}^{3\pi/4} \left(\sqrt{\frac{2}{\pi}} \sin 5x \right) \left(\sqrt{\frac{2}{\pi}} \sin 5x \right) dx = \left(\frac{2}{2\pi} \right) \int_{\pi/4}^{3\pi/4} [1 - \cos 10x] dx$$

$$= 0.56 \quad \text{(see the margin remark)}$$

6. The time dependent Schrodinger equation for a simple harmonic oscillator is

$$-\frac{\hbar^2}{2m} \left(\frac{d^2 \psi}{dx^2} \right) + 2m(\pi v x)^2 \psi = E \psi \quad (i)$$

where we have substituted $V(x) = 2m(\pi v x)^2$. Changing the variable to

$$\xi = \sqrt{\beta} x, \text{ where } \beta = \frac{2\pi m v}{\hbar}, \text{ we get}$$

$$\frac{d\psi}{dx} = \frac{d\psi}{d\xi} \frac{d\xi}{dx} = \sqrt{\beta} \frac{d\psi}{d\xi}; \quad \frac{d^2 \psi}{dx^2} = \beta \frac{d^2 \psi}{d\xi^2}$$

Thus, Eq. (i) becomes

$$\begin{aligned}
 & \left(\frac{2}{2\pi} \right) \int_{\pi/4}^{3\pi/4} [1 - \cos 10x] dx \\
 &= \frac{1}{\pi} \left[x - \frac{\sin 10x}{10} \right]_{\pi/4}^{3\pi/4} \\
 &= \frac{1}{\pi} \left(\frac{2\pi}{4} \right) \\
 &- \frac{1}{10\pi} \left(\sin \frac{15\pi}{2} - \sin \frac{5\pi}{2} \right) \\
 &= \frac{1}{\pi} \left[\frac{\pi}{2} - \frac{1}{10} (-1 - 1) \right] \\
 &= \frac{1}{\pi} \left[\frac{\pi}{2} + \frac{1}{5} \right] = 0.56
 \end{aligned}$$

$$-\frac{\hbar^2}{2m}\beta\frac{d^2\psi}{d\xi^2} + 2m\pi^2v^2\frac{\xi^2}{\beta}\psi = E\psi$$

$$\text{or } -\frac{\hbar^2}{2m}\left(\frac{2\pi mv}{\hbar}\right)\frac{d^2\psi}{d\xi^2} + \left(\frac{2m\pi^2v^2\hbar}{2\pi mv}\right)\xi^2\psi = E\psi$$

$$\text{or } \frac{d^2\psi}{d\xi^2} + \left(\frac{\pi v\hbar}{\pi v\hbar}\xi^2\right)\psi = -\frac{2m}{\hbar^2\beta}E\psi$$

$$\text{or } \frac{d^2\psi}{d\xi^2} + \left(\frac{2mE}{\hbar^2\beta} - \xi^2\right)\psi = 0$$

Defining $\alpha = \frac{2mE}{\hbar^2}$, we can write Eq. (i) as

$$\frac{d^2\psi}{d\xi^2} + \left(\frac{\alpha}{\beta} - \xi^2\right)\psi = 0$$

Substituting $\psi(\xi) = \exp\left(-\frac{\xi^2}{2}\right)$ in Eq. (ii), we get:

$$-\psi + \xi^2\psi + \frac{\alpha}{\beta}\psi - \xi^2\psi = 0$$

$$\text{or } \left(\frac{\alpha}{\beta} - 1\right)\psi = 0 \Rightarrow \frac{\alpha}{\beta} = 1 \text{ since } \psi \neq 0$$

7. We use Eq. (7.50) to determine A:

$$\int_0^\infty (Ax^{3/2}e^{-\alpha x})(Ax^{3/2}e^{-\alpha x})dx = 1 \Rightarrow A^2 \int_0^\infty x^3 e^{-2\alpha x} dx = 1$$

Using Table 7.1(2) with $m = 3$ and $a = 2\alpha$ we get:

$$A^2 \frac{3!}{(2\alpha)^4} = 1 \Rightarrow \frac{6A^2}{(2\alpha)^4} = 1 \Rightarrow A^2 = \frac{(2\alpha)^4}{6}$$

$$\therefore A = \frac{4\alpha^2}{\sqrt{6}}$$

The probability density of finding the particle is defined by Eq.(7.14) as

$$P(x) = \psi^*(x)\psi(x) = A^2 x^3 e^{-2\alpha x}$$

The most probable position of the particle is at the maximum of the function $P(x)$. To determine this position we determine the value of x at which the condition $\frac{dP(x)}{dx} = 0$ is valid.

$$\frac{dP(x)}{dx} = 0 \Rightarrow A^2(3 - 2\alpha x)x^2 e^{-2\alpha x} = 0 \text{ (see margin remark)}$$

$$\begin{aligned} \frac{d\psi}{d\xi} &= \frac{d}{d\xi} \left[\exp\left(-\frac{\xi^2}{2}\right) \right] \\ &= -\xi \exp\left(-\frac{\xi^2}{2}\right) \\ \text{(ii)} \quad \frac{d^2\psi}{d\xi^2} &= -\exp\left(-\frac{\xi^2}{2}\right) \\ &\quad + \xi^2 \exp\left(-\frac{\xi^2}{2}\right) \\ &= -\psi + \xi^2\psi \end{aligned}$$

So, the most probable position of the particle x_0 is given by

$$3 - 2\alpha x = 0 \Rightarrow x_0 = \frac{3}{2\alpha}$$

8. a) To calculate the normalization constant, we use Eq.(7.50),

$$\int_0^{\infty} (Nxe^{-\alpha x})^* (Nxe^{-\alpha x}) dx = 1 \Rightarrow |N|^2 \int_0^{\infty} x^2 e^{-2\alpha x} dx = 1$$

Using Table 7.1 (2) with $m = 2$ and $a = 2\alpha$ we get

$$|N|^2 \left[\frac{2!}{(2\alpha)^3} \right] = 1 \Rightarrow |N|^2 = 4\alpha^3$$

$$N = 2\alpha^{3/2}$$

So the wave function is $\psi(x) = 2\alpha^{3/2} x e^{-2\alpha x}$

b) To determine the potential energy we use Eq.(7.47) with $E = 0$, as in Example 7.4 we can write:

$$V(x)\psi(x) = \frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} \quad (i)$$

We calculate the derivatives to get:

$$\frac{d\psi}{dx} = \frac{d}{dx} (Nxe^{-\alpha x}) = Ne^{-\alpha x} - \alpha Nx e^{-\alpha x}$$

$$\frac{d^2\psi}{dx^2} = -\alpha Ne^{-\alpha x} - \alpha Ne^{-\alpha x} + \alpha^2 Nx e^{-\alpha x} = \left(\alpha^2 - \frac{2\alpha}{x} \right) Nx e^{-\alpha x}$$

$$= \left(\alpha^2 - \frac{2\alpha}{x} \right) \psi(x)$$

Substituting in Eq. (i) we get:

$$V(x)\psi(x) = \frac{\hbar^2}{2m} \left[\alpha^2 - \frac{2\alpha}{x} \right] \psi(x)$$

$$\Rightarrow \left[V(x) - \frac{\hbar^2}{2m} \left(\alpha^2 - \frac{2\alpha}{x} \right) \right] \psi(x) = 0 \quad \text{or} \quad V(x) = \frac{\hbar^2}{2m} \left(\alpha^2 - \frac{2\alpha}{x} \right)$$

9. a) Using Eq.(7.50) we write:

$$\begin{aligned} & \int_{-L/4}^{L/4} \left[1 + \cos\left(\frac{4\pi x}{L}\right) \right] dx \\ &= \left[x + \frac{L}{4\pi} \sin\left(\frac{4\pi x}{L}\right) \right]_{-L/4}^{L/4} \\ &= \left[\frac{2L}{4} \right] \end{aligned} \quad (i)$$

$$\int_{-L/4}^{L/4} \left[N \cos\left(\frac{2\pi x}{L}\right) \right]^* \left[N \cos\left(\frac{2\pi x}{L}\right) \right] dx = 1 \Rightarrow |N|^2 \int_{-L/4}^{L/4} \cos^2\left(\frac{2\pi x}{L}\right) dx = 1$$

$$\Rightarrow \frac{|N|^2}{2} \int_{-L/4}^{L/4} \left[1 + \cos\left(\frac{4\pi x}{L}\right) \right] dx = 1 \quad (i)$$

$$\Rightarrow \frac{|N|^2}{2} \left[\frac{2L}{4} \right] = 1 \quad (\text{see the margin remark})$$

$$\Rightarrow |N|^2 = \frac{4}{L} \quad \text{or} \quad N = \frac{2}{\sqrt{L}}$$

b) We use Eq. (7.15) to determine the probability,

$$\text{with } \psi(x) = \frac{2}{\sqrt{L}} \cos\left(\frac{2\pi x}{L}\right):$$

$$P = \left(\frac{4}{L}\right) \int_0^{L/6} \cos^2 \frac{2\pi x}{L} dx = \frac{2}{L} \int_0^{L/6} \left[1 + \cos\left(\frac{4\pi x}{L}\right)\right] dx = \frac{2}{L} \left[x + \frac{L}{4\pi} \sin\left(\frac{4\pi x}{L}\right) \right]_0^{L/6}$$

as calculated in Eq. (i). We get:

$$P = \frac{2}{L} \left[\frac{L}{6} + \frac{L}{4\pi} \sin \frac{4\pi}{6} - \frac{L}{4\pi} \sin 0 \right] = \frac{2}{L} \left[\frac{L}{6} + \frac{L}{4\pi} \frac{\sqrt{3}}{2} \right] = \frac{1}{3} + \frac{\sqrt{3}}{4\pi}$$

10. We write the normalisation condition for the wave function as:

$$\begin{aligned} \int_0^\infty [Ae^{-x}(1-e^{-x})]^* [Ae^{-x}(1-e^{-x})] dx &= 1 \\ \Rightarrow |A|^2 \int_0^\infty e^{-2x} (1-e^{-x})^2 dx &= 1 \Rightarrow |A|^2 \int_0^\infty [e^{-2x} (1+e^{-2x} - 2e^{-x})] dx = 1 \\ \Rightarrow |A|^2 \int_0^\infty (e^{-2x} + e^{-4x} - 2e^{-3x}) dx &= 1 \end{aligned} \quad (i)$$

From Table 7.1 (1) we can write:

$$\begin{aligned} \int_0^\infty e^{-2x} dx &= \frac{1}{2}; \int_0^\infty e^{-4x} dx = \frac{1}{4}; \int_0^\infty e^{-3x} dx = \frac{1}{3} \\ |A|^2 \left[\frac{1}{2} + \frac{1}{4} - \frac{2}{3} \right] &= 1 \Rightarrow |A|^2 \left[\frac{1}{12} \right] = 1 \text{ or } A = \sqrt{12} \end{aligned}$$

11. If the wave function is normalized Eq. (7.50) will be true. So we

evaluate (see the margin remark):

$$\int_{-\infty}^\infty \psi^* \psi dx = \int_0^\infty e^{-2x} dx + \int_{-\infty}^0 e^{2x} dx = \int_0^\infty e^{-2x} dx + \int_0^\infty e^{-2t} dt$$

Using Table 7.1(1), we get

$$\int_{-\infty}^\infty \psi^* \psi dx = \frac{1}{2} + \frac{1}{2} = 1$$

So, the wave function ψ is normalized. To determine the probability P we use Eq. (7.15):

$$P = \int_{-2}^2 \psi^* \psi dx = \left[\int_{-2}^0 e^{2x} dx + \int_0^2 e^{-2x} dx \right]$$

Using the substitution

$$t = -x \Rightarrow dt = -dx,$$

we get

$$\begin{aligned} \int_{-\infty}^0 e^{-2x} dx &= - \int_\infty^0 e^{-2t} dt \\ &= \int_0^\infty e^{-2t} dt \end{aligned}$$

$$\begin{aligned} &= \left[-\frac{e^{-2x}}{2} \right]_0^2 + \left[\frac{e^{2x}}{2} \right]_{-2}^0 = \left[\left(-\frac{e^{-4}}{2} + \frac{e^{-0}}{2} \right) + \left(\frac{e^0}{2} - \frac{e^{-4}}{2} \right) \right] \\ &= [1 - e^{-4}] \end{aligned}$$

12. The wave functions given in (c) and (d) are not acceptable.

c) $\psi(x) = N \sin(x)$ is not an acceptable wave function because it is not square-integrable.

d) $\psi(x) = N \tan(x)$ is not an acceptable wave function because it has singularities at $x = \pi/2, 3\pi/2, \dots$ etc.



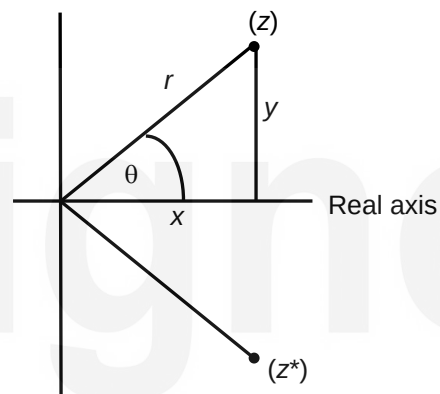
Table 7.1: Some Useful Integrals

S. No.	Integrals
1.	$\int_0^{\infty} e^{-ax} dx = \frac{1}{a} \text{ (Re}(a) > 0)$
2.	$\int_0^{\infty} x^m e^{-ax} dx = \frac{1}{a^{m+1}} m! \text{ (Re}(a) > 0) \quad \text{for } m = 1, 2, 3, \dots$
3.	$\int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a}} \quad (a > 0)$
4.	$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}} \quad (a > 0)$
5.	$\int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a^3}} \quad (a > 0)$
6.	$\int_0^{\infty} x^{n-1} e^{-x} dx = \Gamma(n) = (n-1)! \quad \text{for } n = 1, 2, 3, \dots$ (also called the Gamma Function)
7.	$\int_0^{\infty} x^m e^{-ax^2} dx = \frac{\Gamma\left[\left(\frac{m+1}{2}\right)\right]}{2a^{\left(\frac{m+1}{2}\right)}}$
8.	$\Gamma(n+1) = n\Gamma(n) = n! \text{ for integer values of } n$
9.	$\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$

Appendix

COMPLEX NUMBERS

Imaginary number	$i = \sqrt{-1}$
Complex number	$z = x + iy$ (Cartesian form)
Real part	$x = \text{Re } z$
Imaginary part	$y = \text{Im } z$
Complex conjugate	$z^* = x - iy$
Modulus	$ z $ where $ z ^2 = zz^* = x^2 + y^2 = r^2$
Phase	θ where $\tan \theta = \frac{y}{x}$
Complex plane	Imaginary axis



Power series

$$x = r \cos \theta = r \left(1 - \frac{\theta^2}{2!} + \dots \right)$$

$$y = r \sin \theta = r \left(\theta - \frac{\theta^3}{3!} + \dots \right)$$

$$z = r(\cos \theta + i \sin \theta)$$

$$= r \left[1 + i\theta + \frac{(i\theta)^2}{2!} + \frac{(i\theta)^3}{3!} + \dots \right]$$

Complex number

$$re^{i\theta} \text{ (polar form)}$$

Phase factors

$$e^{i\theta} = \cos \theta + i \sin \theta \text{ and } e^{-i\theta} = \cos \theta - i \sin \theta$$

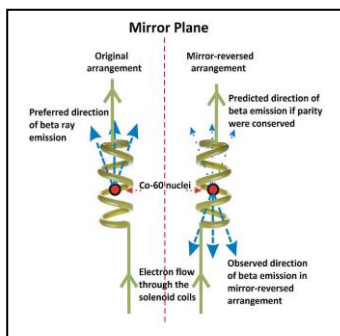
Real part

$$\text{Re } e^{i\theta} = \cos \theta = (e^{i\theta} + e^{-i\theta})/2$$

Imaginary part

$$\text{Im } e^{i\theta} = \sin \theta = (e^{i\theta} - e^{-i\theta})/2i$$

UNIT 8



For a long time it was believed that every natural process conserves parity. In 1956, however, an experiment by C. S. Wu showed that parity conservation is violated in beta decay.

OBSERVABLES AND OPERATORS

Structure

- | | |
|---|--|
| <p>8.1 Introduction</p> <p>Expected Learning Outcomes</p> <p>8.2 Quantum Mechanical Operators</p> <p>The Parity Operator</p> <p>Properties of Operators</p> <p>Commutators in Operator Algebra</p> <p>Basic Commutator Algebra</p> <p>Linear and Antilinear Operators</p> | <p>8.3 Expectation Values</p> <p>Hermitian Operators</p> <p>Eigenfunctions and Eigenvalues</p> <p>Commuting and Non-Commuting Operators</p> <p>Orthonormal Eigenfunctions</p> <p>8.4 Ehrenfest Theorem</p> <p>8.5 Some Postulates of Quantum Mechanics</p> <p>8.6 Summary</p> <p>8.7 Terminal Questions</p> <p>8.8 Solutions and Answers</p> |
|---|--|

STUDY GUIDE

In this unit you will study more of the mathematical framework that describes quantum physics. You will learn how to describe dynamical variables using operators. You will also learn how to calculate the expectation values of dynamical variables for a quantum system described by a wave function. In these calculations, differential and integral calculus are used extensively. So, you should be familiar with ordinary and partial derivatives and the calculation of integrals. There are several Examples, SAQs and TQs in this unit and you should work these out yourself to understand the concepts.

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“Mathematics is the tool specially suited for dealing with abstract concepts of any kind and there is no limit to its power in this field.”

Paul Dirac

8.1 INTRODUCTION

On a historical note, in the previous unit we mentioned how quantum mechanics developed along two parallel tracks, one of which was the “wave-mechanics” of Schrödinger, in which all the physical properties of the quantum system had to come from the (abstract) wave function. Heisenberg’s approach was, in his own words, “**founded exclusively on relationships between quantities which in principle are observable**”. An observable is a physical quantity which is measurable in an experiment. Along with Born and Jordan, he came to the conclusion that all physical observables must be represented by matrices. And the eigenvalues of the matrix are actually all possible values that one could get if an experiment is carried out to measure that observable.

In Unit 7, you have studied that the state of any quantum mechanical system is completely specified by a “**wave function**” $\psi(\vec{r}, t)$, which is a function of the spatial coordinates and time. The evolution of the wave function is given by the Schrödinger equation, which is a differential equation which relates the partial derivatives of $\psi(\vec{r}, t)$. You saw that the wave function does not correspond to any measurable disturbance but the modulus square of the wave function ($\psi^* \psi$ or $|\psi|^2$) corresponds to the probability density of locating a quantum particle at a particular position at any instant of time.

In this unit, we will derive the physically observable properties of a quantum system. You will learn that each physical quantity is associated with an ‘**operator**’. What is an operator? You will find an answer to this question in Sec. 8.2. You will learn the method of converting a dynamical variable (position, momentum, energy, etc.) into a quantum mechanical operator. This method is also one of the postulates of quantum mechanics: each observable is associated with an operator. The operator acts on the wave function, which varies with spatial coordinates and time. You will study the properties of operators. In particular, you will study about the **commutation** relations between pairs of operators. These relations tell us if the physical quantities associated with the operators may be simultaneously observed precisely for a quantum system or not.

In Sec. 8.3, we explain the concept of the **expectation value** of the quantum mechanical operator associated with an observable. It helps us to relate these operators to physically observable quantities. In certain circumstances, it is possible that when an operator operates on a wave function, the result may be a multiple of the same wave function. This gives rise to what we call the eigenvalue-eigenfunction equation, which you will also study in Sec. 8.3. In Sec. 8.4, you will learn about the Ehrenfest theorem which shows the similarity, as well as one of the basic differences between classical and quantum mechanics. Finally, in Sec. 8.5, we summarise for you some of the postulates of quantum mechanics that you will have studied till the end of this unit.

The concepts presented in this unit may appear too mathematical and abstract to you in the first reading. However, the formalism presented here is a very powerful and elegant way of working with quantum mechanical systems. In the next block, we will apply the concepts of this block to simple systems.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ express a classical dynamical variable as a quantum mechanical operator;
- ❖ define the hermitian operator and the parity operator and apply their properties to quantum mechanical systems;
- ❖ compute the expectation value of an operator;

- ❖ derive elementary results of commutator algebra;
- ❖ calculate the eigenvalues and eigenfunctions of a given operator; and
- ❖ derive and interpret Ehrenfest theorem.

8.2 QUANTUM MECHANICAL OPERATORS

To start with, let us understand **what an operator is**. You are familiar with the notion of a **function** in mathematics. A function is a **rule** for changing a number into another number. For example, suppose we have a function $f(x) = 2x^2 + 3$, then you can see that $f(1) = 2(1)^2 + 3 = 5$, and so on.

An **operator is a rule that turns one function into another function**. So, if an operator is applied to a function, you get a new function. The operator could be a constant, say α , in which case, when it operates on the function $f(x)$, the function gets multiplied by α . If the operator is x^2 , then function $f(x)$ gets multiplied by x^2 . If the operator is $\frac{d}{dx}$, the action of the operator would be to take the derivative of $f(x)$.

Let us see how each of these operators would operate on the function $f(x) = 2x^2 + 3$:

1. $\alpha f(x) = \alpha(2x^2 + 3) = 2\alpha x^2 + 3\alpha = g(x)$
2. $x^2 f(x) = x^2(2x^2 + 3) = 2x^4 + 3x^2 = h(x)$
3. $\frac{d}{dx} f(x) = \frac{d}{dx}(2x^2 + 3) = 4x = p(x)$

You can see that in each of the above cases you get a new function.

Let us now talk about **quantum mechanical operators**. Do you recall from classical mechanics how the dynamical state of a system is determined at each instant of time? It is determined by knowing certain physical quantities such as the position, velocity, linear momentum, angular momentum, energy, etc. of the particles constituting the system. These are the **dynamical variables** of the system. The dynamical variables associated with a system can be measured, and provide information about the system at a particular point in space-time. In general, such measurable quantities that describe a physical system are called **observables**.

Every observable in classical mechanics is associated with an “**operator**” in quantum mechanics, which operates upon the “wave function” of the system. So, in quantum mechanics, an **observable** that corresponds to a physical quantity, such as energy, spin, momentum or position is associated with the corresponding operator. You can think that the operator is like the measuring device, which acts on the wave function and gets you a real number, which is the outcome of the measurement.

This brings us to a **postulate of quantum mechanics**, which talks about the observables of a quantum mechanical system:

Every physical observable is associated with an operator, which acts on the wave function.

Suppose that a quantum mechanical operator $\hat{O}$ acts on a wave function ψ . Then we express this operation as:

$$\hat{O}\psi = \chi \quad (8.1)$$

where χ is some other function. Note that to distinguish an operator from the corresponding dynamical variable, we write the operator with the symbol “^” (or hat) on top of the variable.

Most of these dynamical variables or observables are functions of position (x, y, z) , linear momentum (p_x, p_y, p_z) and time (t) variables. Thus, if we can represent position and linear momentum by operators we shall be able to express most of the remaining dynamical variables as operators. A method to convert x and p_x into quantum mechanical operators is postulated in quantum mechanics as follows:

The operators for the other spatial coordinates (y and z) and their associated momentum coordinates (p_y and p_z) are postulated in the same way as shown in Eqs. (8.2 and 8.4).

$$\text{i) } \hat{x}\psi = x\psi \quad \Rightarrow \quad \hat{x} = x \quad (8.2)$$

i.e., when the operator $\hat{x}$ operates upon ψ , the result is simply the multiplication of ψ by the variable x . The operator corresponding to the dynamical variable x is x itself.

$$\text{ii) } \hat{p}_x\psi = -i\hbar \frac{\partial}{\partial x}\psi \quad (8.3)$$

Thus, the momentum operator $\hat{p}_x$ acting on the wave function results in its differentiation with respect to the conjugate position coordinate x and the result is multiplied by $-i\hbar$. So, the operator representing the dynamical variable p_x is $-i\hbar \frac{\partial}{\partial x}$:

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x} \quad (8.4)$$

Remember that Eqs. (8.2 and 8.3) are postulated, i.e., they cannot be proved. Notice that the time variable has been retained as itself in the operator formalism. In quantum mechanics, time is not treated as an operator. It is a dynamical variable.

The position and momentum operators are used in the construction of operators of other dynamical variables such as angular momentum, energy, etc. How do we do this? For this, we take the classical expression for any dynamical variable O in terms of x and p_x , and use Eqs. (8.2 and 8.4) to obtain its operator form as a function of x , $-i\hbar \frac{\partial}{\partial x}$, t as $\hat{O} = \hat{O}(x, -i\hbar \frac{\partial}{\partial x}, t)$.

To understand this method further, consider the example of the kinetic energy T of a free particle of mass m executing one-dimensional motion along the x -direction.

You know that T is given by $p_x^2 / 2m$.

The quantum mechanical operator of the kinetic energy is obtained by replacing p_x by $\hat{p}_x$. Then using Eq. (8.4) we get:

$$\hat{T} = \frac{\hat{p}_x^2}{2m} = \left(-i\hbar \frac{\partial}{\partial x} \right)^2 / 2m = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \quad (\because i^2 = -1) \quad (8.5)$$

If potential energy of the particle is given by the function $V(x)$, then its potential energy operator will also be $V(x)$ since $\hat{x}$ is x itself:

$$\hat{V}(x) = V(x) \quad (8.6)$$

The Hamiltonian (sum of the kinetic and potential energies) in the one-dimensional Schrödinger equation can be written in an operator form as:

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \hat{V}(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \quad (8.7)$$

So, in the operator notation, the one-dimensional time independent Schrödinger equation (Eq. 7.47) can be written as:

$$\hat{H}\psi(x) = E\psi(x) \quad (8.8)$$

The three-dimensional form of the Hamiltonian operator is (read the margin remark):

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(r) \quad (8.9)$$

Let us revise what you have studied so far.

OPERATORS IN QUANTUM MECHANICS

Recap

- Every physical observable in quantum mechanics is associated with an operator which acts on the wave function. When a quantum mechanical operator $\hat{O}$ acts on a wave function ψ , we get:

$$\hat{O}\psi = \chi \quad (8.1)$$

where χ is some other function.

- The quantum mechanical operators associated with the position and momentum variables, x and p_x , are defined as follows:

$$\hat{x} = x \quad (8.2)$$

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x} \quad (8.4)$$

- To construct the operator for any other dynamical variable we write the classical expression for it in terms of the position and momentum variables and replace these variables by their corresponding operators.

In this way you can convert most of the dynamical variables into quantum mechanical operators.

Let us now work out an example to explain how to convert a dynamical variable into the corresponding quantum mechanical operator:

EXAMPLE 8.1: QUANTUM MECHANICAL OPERATORS

- Express the variables p_y and p_z in operator form.
- Write the three components of the angular momentum $\vec{L}$ in terms of x , y , z and p_x , p_y and p_z . Hence, obtain the quantum mechanical operators for L_x , L_y and L_z .

SOLUTION ■ We use the basic method used in deducing Eq. (8.4):

- The form of these operators can be deduced from the form for the operator $\hat{p}_x$ given in Eq. (8.4). So,

$$\hat{p}_y = -i\hbar \frac{\partial}{\partial y} \quad (i)$$

$$\text{and} \quad \hat{p}_z = -i\hbar \frac{\partial}{\partial z} \quad (ii)$$

- The components of the angular momentum $\vec{L}$ are:

$$L_x = yp_z - zp_y; \quad L_y = zp_x - xp_z; \quad L_z = xp_y - yp_x$$

Using the results of Eqs. (8.2), (8.4) and (i) and (ii) of this example, we get:

$$\hat{L}_x = -i\hbar y \frac{\partial}{\partial z} + i\hbar z \frac{\partial}{\partial y} \quad (iii)$$

$$\hat{L}_y = -i\hbar z \frac{\partial}{\partial x} + i\hbar x \frac{\partial}{\partial z} \quad (iv)$$

$$\hat{L}_z = -i\hbar x \frac{\partial}{\partial y} + i\hbar y \frac{\partial}{\partial x} \quad (v)$$

An important quantum mechanical operator that we will use later in our discussion is the **parity operator**. We will introduce it here.

8.2.1 The Parity Operator

Parity is a simple but very useful concept in quantum mechanics. Consider a wave function $\psi(x)$. If on changing x to $-x$, the following relationship is obtained

$$\psi(-x) = \pm \psi(x) \quad (8.10)$$

then we say that the function $\psi(x)$ has a definite parity:

- If $\psi(-x) = \psi(x)$, then $\psi(x)$ is of **even** parity, and
- if $\psi(-x) = -\psi(x)$, then $\psi(x)$ is of **odd** parity.

All functions which do not obey Eq. (8.10) are said to have **mixed parity**. The parity operation is equivalent to **transforming a right-handed system of coordinates into a left-handed one**. The **parity operator** is defined by

$$\hat{P}\psi(x,t) = \psi(-x,t) \quad (8.11)$$

and
$$\hat{P}A\left(x, -i\hbar \frac{\partial}{\partial x}, t\right) = A\left(-x, i\hbar \frac{\partial}{\partial x}, t\right) \quad (8.12)$$

Note that the parity operator is a space inversion operator, i.e., under its operation x is replaced by $-x$: $x \rightarrow -x$. Thus if $\psi(x)$ describes the state of a system, $\hat{P}\psi(x,t)$ describes its mirror image.

So far, we have discussed a method to obtain quantum mechanical operators from the corresponding classical expression by changing x by $\hat{x}$, t by t and p_x by $-i\hbar \frac{\partial}{\partial x}$. However, there is no classical expression, in terms of x and p_x , which changes the sign of the argument of a function by its operation. Hence, we say that the **parity operator has no classical analogue**. Let us revise what you have studied so far.

THE PARITY OPERATOR

Recap

- The **parity operator** is a space inversion operator.
- The parity operation is equivalent to **transforming a right-handed system of coordinates into a left-handed one**.
- For a one-dimensional system the action of the parity operator is defined as follows:

$$\hat{P}\psi(x,t) = \psi(-x,t) \quad (8.11)$$

and
$$\hat{P}A\left(x, -i\hbar \frac{\partial}{\partial x}, t\right) = A\left(-x, i\hbar \frac{\partial}{\partial x}, t\right) \quad (8.12)$$

You can work out an SAQ on the action of the parity operator.

SAQ 1 - Parity operator

For the wave function $\psi_1(x) = A \exp(ikx)$, determine the wave function $\psi_2(x) = \hat{P}\psi_1(x)$. What will be the parity of the wave function $\psi(x) = [\psi_1(x) + \psi_2(x)]$?

You have just learnt that in quantum mechanics, the measurable classical dynamical variables like position, momentum, etc. are associated with operators. These operators act on a wave function and change it in some way. We have summarised the results obtained so far for ready reference.

Table 8.1 Dynamical Variables and Corresponding Operators

Dynamical Variable	Operator
Position coordinate x	x
x component of the momentum p_x	$-i\hbar \frac{\partial}{\partial x}$
y component of the momentum p_y	$-i\hbar \frac{\partial}{\partial y}$
z component of the momentum p_z	$-i\hbar \frac{\partial}{\partial z}$
Kinetic energy $T = p_x^2 / 2m$	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$
Potential energy $V(x,t)$	$V(x,t)$
Total energy $H = \frac{p_x^2}{2m} + V(x,t)$	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x,t)$
x component of the angular momentum : L_x	$-i\hbar y \frac{\partial}{\partial z} + i\hbar z \frac{\partial}{\partial y}$
y component of the angular momentum : L_y	$-i\hbar z \frac{\partial}{\partial x} + i\hbar x \frac{\partial}{\partial z}$
z component of the angular momentum : L_z	$-i\hbar x \frac{\partial}{\partial y} + i\hbar y \frac{\partial}{\partial x}$

Let us now discuss some important properties of these operators

8.2.2 Properties of Operators

We now state the properties of operators, in other words, the rules governing the actions of operators on functions.

For any two operators $\hat{A}$ and $\hat{B}$ operating on a wave function ψ , we can write for the sum and difference of the two operators:

$$(\hat{A} + \hat{B})\psi = \hat{A}\psi + \hat{B}\psi \quad (8.13a)$$

$$\text{and } (\hat{A} - \hat{B})\psi = \hat{A}\psi - \hat{B}\psi \quad (8.13b)$$

Two operators $\hat{A}$ and $\hat{B}$ are equal if, for all ψ ,

$$\hat{A}\psi = \hat{B}\psi \quad (8.13c)$$

The identity operator $\hat{I}$ leaves the wave function unchanged:

$$\hat{I}\psi = \psi \quad (8.13d)$$

The n^{th} power of an operator is equivalent to n successive operations of the operator. For example,

$$\hat{A}^2\psi = \hat{A}(\hat{A}\psi) \quad (8.13e)$$

Many dynamical variables involve the product of two operators, for example L_x , L_y and L_z .

For the product of any two operators $\hat{A}$ and $\hat{B}$ acting on ψ we can write:

$$\hat{A}\hat{B}\psi = \hat{A}(\hat{B}\psi) \quad (8.13f)$$

So, first $\hat{B}$ acts on the function ψ and then $\hat{A}$ acts on $\hat{B}\psi$. However, usually the result of carrying out the operation $\hat{A}\hat{B}\psi$ is not the same as carrying out the operation $\hat{B}\hat{A}\psi = \hat{B}(\hat{A}\psi)$, in which $\hat{B}$ acts on the function $\hat{A}\psi$. So, in general:

$$\hat{A}\hat{B}\psi \neq \hat{B}\hat{A}\psi \quad (8.13g)$$

Let us put the main properties of the operators at one place for easy recall.

PROPERTIES OF OPERATORS

Recap

For any two operators $\hat{A}$ and $\hat{B}$ operating on a wave function ψ :

$$(\hat{A} + \hat{B})\psi = \hat{A}\psi + \hat{B}\psi \quad (8.13a)$$

$$(\hat{A} - \hat{B})\psi = \hat{A}\psi - \hat{B}\psi \quad (8.13b)$$

$$\hat{A}\hat{B}\psi = \hat{A}(\hat{B}\psi) \quad (8.13f)$$

$$\text{In general, } \hat{A}\hat{B}\psi \neq \hat{B}\hat{A}\psi \quad (8.13g)$$

If for all ψ , $\hat{A}\psi = \hat{B}\psi$, the operators $\hat{A}$ and $\hat{B}$ are equal.

The identity operator $\hat{I}$ leaves the wave function unchanged: $\hat{I}\psi = \psi$

Eq. (8.13g) is of particular importance in quantum mechanics and defines what is called the **commutator** of two operators.

8.2.3 Commutators in Operator Algebra

In general, the product of two operators does not obey the commutative law, i.e. $\hat{A}\hat{B} \neq \hat{B}\hat{A}$. We can rewrite this as inequality as follows

$$\hat{A}\hat{B}\psi \neq \hat{B}\hat{A}\psi \rightarrow [\hat{A}\hat{B} - \hat{B}\hat{A}]\psi \neq 0$$

We define the **commutator** of the two operators $\hat{A}$ and $\hat{B}$ as the difference $\hat{A}\hat{B} - \hat{B}\hat{A}$ and denote it by the commutator bracket $[\hat{A}, \hat{B}]$:

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \quad (8.14a)$$

In general,

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \neq 0 \quad (8.14b)$$

So, in general, the operators $\hat{A}$ and $\hat{B}$ do not commute with one another and the value of the commutator bracket $[\hat{A}, \hat{B}]$ is non-zero. What does this result mean? It means that we have to be careful, about the order of operators in considering operator products in quantum mechanics. However, if the commutator of the operators $\hat{A}$ and $\hat{B}$ is zero, we say that $\hat{A}$ and $\hat{B}$ **commute**, i.e. $\hat{A}\hat{B} = \hat{B}\hat{A}$. Then we can interchange their order.

To understand these concepts better, let us take a concrete example of operators. Let us examine whether the operators $\hat{x}$ and $\hat{p}_x$ commute with one another. For this purpose we evaluate the action of the commutator $[\hat{x}, \hat{p}_x]$ on an arbitrary wave function ψ :

$$[\hat{x}, \hat{p}_x]\psi = [\hat{x}\hat{p}_x - \hat{p}_x\hat{x}]\psi = \hat{x}(\hat{p}_x\psi) - \hat{p}_x(\hat{x}\psi) \quad (8.15)$$

Using Eqs. (8.2 and 8.4) for the definition of $\hat{x}$ and $\hat{p}_x$ in Eq. (8.15) we get:

$$\begin{aligned} [\hat{x}, \hat{p}_x]\psi &= x \left(-i\hbar \frac{\partial \psi}{\partial x} \right) - \left(-i\hbar \frac{\partial}{\partial x} \right) (x\psi) \\ &= -i\hbar x \frac{\partial \psi}{\partial x} + i\hbar \frac{\partial x}{\partial x} \psi + i\hbar x \frac{\partial \psi}{\partial x} \\ &= i\hbar \psi \end{aligned} \quad (8.16)$$

Since the wave function ψ is arbitrary, we can write:

$$[\hat{x}, \hat{p}_x] = i\hbar \quad (8.17)$$

So you see that the operators $\hat{x}$ and $\hat{p}_x$ do not commute with one another (or we can say that $\hat{x}$ and $\hat{p}_x$ are **non-commutating operators**) and the value of the commutation bracket is $i\hbar$. This result also tells us that we have to take care of the order of these operators when we apply them on a wave function. For instance, if the momentum operator acts first on a wave function followed by the position operator, it yields a certain result.

The result is different if the position operator operates first and is followed by the momentum operator.

The commutator of two operators plays an important role in quantum mechanics. In particular this is important when the two operators correspond to what are known as “canonically conjugate” variables like x and p_x , y and p_y and z and p_z . To find out the commutation relation between a pair of operators, you determine the action on an arbitrary function as we have shown in the derivation of the result of Eq.(8.17)

You can now solve SAQ 2 to work this out for yourself.

SAQ 2 - Commutator Relations

Using the definitions given in Table 8.1, show that

a) $[\hat{y}, \hat{p}_y] = i\hbar$

b) $[\hat{z}, \hat{p}_z] = i\hbar$

c) $[\hat{x}, \hat{p}_y] = 0$

d) $[\hat{x}, \hat{p}_z] = 0$

This result has an interesting fallout. Sometimes, you may come across a situation where the product xp_x occurs in a classical dynamical variable. Now in quantum mechanics, the order of operators matters, so in which order do we put $\hat{x}$ and $\hat{p}_x$? In such a case, we simply symmetrise the product.

This means that you replace the product xp_x by the operator $\frac{1}{2}(\hat{x}\hat{p}_x + \hat{p}_x\hat{x})$:

$$\hat{x}\hat{p}_x \rightarrow \frac{1}{2}(\hat{x}\hat{p}_x + \hat{p}_x\hat{x}) \quad (8.18)$$

We do the same when we convert a dynamical variable containing the product of y and p_y or z and p_z .

8.2.4 Basic Commutator Algebra

We now write down the rules of commutator algebra, which are easy to prove using the definition of a commutator.

1. For operators $\hat{A}$, $\hat{B}$ and $\hat{C}$, we can write:

i) $[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}] \quad (8.19a)$

ii) $[\hat{A}, \hat{B} + \hat{C}] = [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}] \quad (8.19b)$

iii) $[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B} \quad (8.19c)$

iv) $[\hat{A}, \hat{B}\hat{C}] = \hat{B}[\hat{A}, \hat{C}] + [\hat{A}, \hat{B}]\hat{C} \quad (8.19d)$

2. Any operator always commutes with its own power:

$$[\hat{A}^n, \hat{A}] = 0; \quad n = 0, 1, 2, 3, \dots \quad (8.19e)$$

An operator always commutes with a constant,

$$[\hat{C}, \hat{A}] = 0 \quad (8.19f)$$

where $\hat{C} = C$ (a constant).

Let us now work out an example based on these rules.

EXAMPLE 8.2: COMMUTATOR ALGEBRA

If $f(x)$ is a dynamical variable, which can be expanded in powers of x , show that:

$$[\hat{f}(\hat{x}), \hat{p}_x] = i\hbar \frac{\partial}{\partial x} f(x)$$

SOLUTION ■ We can write a function $f(x)$ as:

$$f(x) = a_0 + a_1x + a_2x^2 + a_3x^3 + \dots + a_nx^n$$

So, $\hat{f}(\hat{x}) = a_0 + a_1\hat{x} + a_2\hat{x}^2 + \dots + a_n\hat{x}^n$ where $a_0, a_1, \dots, a_n$ are constants.

$$\text{and } [\hat{f}(\hat{x}), \hat{p}_x] = [a_0, \hat{p}_x] + a_1[\hat{x}, \hat{p}_x] + [a_2\hat{x}^2, \hat{p}_x] + \dots + a_n[\hat{x}^n, \hat{p}_x] \quad (i)$$

From Eqs. (8.4 and 8.19f), we know that

$$[a_0, \hat{p}_x] = 0 \quad (ii)$$

$$[\hat{x}, \hat{p}_x] = i\hbar \quad (iii)$$

Now, using Eq. (8.19c) we can write

$$[\hat{x}^2, \hat{p}_x] = [\hat{x}\hat{x}, \hat{p}_x] = \hat{x}[\hat{x}, \hat{p}_x] + [\hat{x}, \hat{p}_x]\hat{x} = 2i\hbar\hat{x} \quad (iv)$$

Similarly, using the results of Eq.(iv) we get:

$$[\hat{x}^3, \hat{p}_x] = [\hat{x}\hat{x}^2, \hat{p}_x] = \hat{x}[\hat{x}^2, \hat{p}_x] + [\hat{x}, \hat{p}_x]\hat{x}^2 = 3i\hbar\hat{x}^2 \quad (v)$$

In general, we get:

$$[\hat{x}^n, \hat{p}_x] = (n)i\hbar\hat{x}^{n-1} \quad (vi)$$

Substituting the results of Eqs. (ii) to (vi) in Eq. (i) and using $\hat{x} = x$, we get:

$$[f(\hat{x}), \hat{p}_x] = i\hbar[a_1 + 2a_2x + \dots + na_nx^{n-1}] = i\hbar \frac{\partial f(x)}{\partial x}$$

You may like to work out an SAQ based on what you have studied so far.

SAQ 3 - Commutator algebra

Prove Eqs. (8.19 a, d and e).

Let us put the results at one place for easy recall.

COMMUTATORS AND THEIR PROPERTIES

Recap

The **commutator** of the two operators $\hat{A}$ and $\hat{B}$ denoted by the commutator bracket $[\hat{A}, \hat{B}]$ is defined as:

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \quad (8.14a)$$

For operators $\hat{A}$, $\hat{B}$ and $\hat{C}$, we can write:

$$\text{i) } [\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}] \quad (8.19a)$$

$$\text{ii) } [\hat{A}, \hat{B} + \hat{C}] = [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}] \quad (8.19b)$$

$$\text{iii) } [\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B} \quad (8.19c)$$

$$\text{iv) } [\hat{A}, \hat{B}\hat{C}] = \hat{B}[\hat{A}, \hat{C}] + [\hat{A}, \hat{B}]\hat{C} \quad (8.19d)$$

An operator always commutes with its own power:

$$[\hat{A}^n, \hat{A}] = 0; \quad n = 0, 1, 2, 3, \dots \quad (8.19e)$$

An operator always commutes with a constant:

$$[\hat{C}, \hat{A}] = 0 \quad \text{where } \hat{C} = C \text{ (a constant)} \quad (8.19f)$$

For the position and momentum operators we have:

$$[\hat{x}, \hat{p}_x] = i\hbar; \quad [\hat{y}, \hat{p}_y] = i\hbar; \quad [\hat{z}, \hat{p}_z] = i\hbar$$

Most operators in quantum mechanics have another property that we shall talk about now.

8.2.5 Linear and Antilinear Operators

Most of the relevant operators in quantum mechanics have the property of “linearity”. For any two wave functions ϕ and ψ , a linear operator $\hat{A}$ satisfies the following condition:

$$\hat{A}(\phi + \psi) = \hat{A}\phi + \hat{A}\psi \quad (8.20a)$$

$$\text{and} \quad \hat{A}(c\psi) = c\hat{A}\psi \quad (8.20b)$$

where c is an arbitrary complex number. In general, we can combine Eqs. (8.20a and b) and write for a linear operator:

$$\hat{A}(\lambda\phi + \mu\psi) = \lambda(\hat{A}\phi) + \mu(\hat{A}\psi) \quad (8.20c)$$

where λ and μ are complex numbers.

Occasionally you come across another type of operator in quantum mechanics: the **antilinear** operators. These have the following property:

$$\hat{A}(\lambda\phi + \mu\psi) = \lambda^*(\hat{A}\phi) + \mu^*(\hat{A}\psi) \quad (8.21)$$

It is easy to see that both $\hat{x}$ and $\hat{p}_x$ satisfy Eq. (8.20c). Let us see how in the following example.

EXAMPLE 8.3 : LINEARITY OF THE POSITION AND MOMENTUM OPERATORS

Show that the operators $\hat{x}$ and $\hat{p}_x$ are linear operators.

SOLUTION ■ We show that $\hat{x}$ satisfies Eq. (8.20c) with constants a and b as:

$$\hat{x}[a\psi + b\phi] = x[a\psi + b\phi] = ax\psi + bx\phi = a(\hat{x}\psi) + b(\hat{x}\phi)$$

So, $\hat{x}$ is a linear operator. Similarly, for $\hat{p}_x$:

$$\hat{p}_x[a\psi + b\phi] = -i\hbar \frac{\partial}{\partial x}[a\psi + b\phi] = -i\hbar a \frac{\partial \psi}{\partial x} - i\hbar b \frac{\partial \phi}{\partial x} = a(\hat{p}_x\psi) + b(\hat{p}_x\phi)$$

So, $\hat{p}_x$ is a linear operator.

So far, we have introduced you to the concept that for a quantum system each dynamical variable or observable is associated with a linear operator. The next step is to obtain a measure or estimate of this observable using the wave function of the system.

8.3 EXPECTATION VALUES

To start with let us consider a quantum particle associated with the (one dimensional) normalized wave function $\psi(x, t)$.

Suppose you carry out a measurement of the position x of the particle. You know that there is a finite probability $P(x, t)dx = |\psi(x, t)|^2 dx$ of finding the particle between x and $x + dx$, for any value of x , as long as the wave function is not zero in that interval. So, we cannot state the definite position of the particle.

Now suppose we make repeated measurements of the position of particle at an instant of time t , on identical systems, each of which is described by the same (normalized) wave function $\psi(x, t)$ at that instant of time. Then we can say something about the **average position** of the particle.

This average value of x is called the **expectation value** of x at time t . It is denoted by $\langle x \rangle$ and defined as follows (read the margin remark):

$$\langle x \rangle = \int_{-\infty}^{\infty} xP(x,t)dx \quad (8.22)$$

where $P(x,t)$ is the probability density of observing a value of the position between x and $x + dx$. Note that the integration in Eq. (8.22) is over the entire range of x . Using Born's probabilistic interpretation of the wave function [Eq. (7.15)], we can write $P(x,t) = \psi^*(x,t)\psi(x,t)$. Therefore,

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

which can also be written as:

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^*(x,t)x\psi(x,t)dx \quad (8.23)$$

When the wave function is **not normalized** $\left(\int_{-\infty}^{\infty} \psi^*(x,t)\psi(x,t)dx \neq 1 \right)$, then

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} \psi^*(x,t)x\psi(x,t)dx}{\int_{-\infty}^{\infty} \psi^*(x,t)\psi(x,t)dx} \quad (8.24)$$

Note that since $\hat{x} = x$, we can also write Eq. (8.24) as:

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^*(x,t)\hat{x}\psi(x,t)dx \quad (8.25)$$

In general $\langle x \rangle$ can be a function of time, except when $\psi(x,t)$ is a stationary state. For a stationary state you know that $|\psi(x,t)|^2$ is time independent and so $\langle x \rangle$ is also time-independent. This is how the measurable average value of the observable x is determined for a quantum mechanical system.

Let us now consider the measurement of some other dynamical variable D of the system, which corresponds to the operator $\hat{D}$. Once again we measure D repeatedly with the system always in the same normalized state $\psi(x,t)$. In general, each individual measurement will yield a different result. **The average of the measured value of D is postulated to be:**

$$\langle D \rangle = \int \psi^*(x,t)\hat{D}\psi(x,t)dx \quad (8.26)$$

$\langle D \rangle$ is known as the **expectation value of the operator $\hat{D}$** .

Remember that the operator acts on the function following it, i. e., it operates on the wave function $\psi(x,t)$ in the Eq. (8.26). So, the term $\psi^*(x,t)\hat{D}\psi(x,t)$ implies $\psi^*(x,t)[\hat{D}\psi(x,t)]$, which is the product of $\psi^*(x,t)$ with $[\hat{D}\psi(x,t)]$.

In Unit 12 of the course BPHCT-135, you have studied that the average value of a variable x which is distributed according to the probability distribution $f(x)$ is given by:

$$\begin{aligned} \langle x \rangle &= \frac{\int_{-\infty}^{\infty} xf(x)dx}{\int_{-\infty}^{\infty} f(x)dx} \\ &= \int_{-\infty}^{\infty} xf(x)dx \quad \text{for } \int_{-\infty}^{\infty} f(x)dx = 1 \end{aligned}$$

For example, the expectation value of the momentum operator $\hat{p}_x$ is:

$$\langle p_x \rangle = \int_{-\infty}^{\infty} \psi^*(x,t) \left(-i\hbar \frac{\partial}{\partial x} \right) \psi(x,t) dx \quad (8.27)$$

Now, since observables are measurable attributes of any physical system, they are **real** quantities. So, the expectation value $\langle D \rangle$ can be an observable only if it is **real**.

Hence, we can say that:

An observable is a dynamical variable having a real expectation value.

In general, for a three-dimensional system, we can write the expression for the expectation value of an operator as:

$$\langle D \rangle = \iiint \psi^*(x,y,z,t) \hat{D} \psi(x,y,z,t) d\tau \quad (8.28)$$

where the integration element $d\tau$ is the volume element $dx dy dz$ and the integration is over the entire range of the wave function. Let us now work out an example for calculating the expectation value.

EXAMPLE 8.4 : EXPECTATION VALUE

The normalized wave function of a particle moving in the x-direction is given by:

$$\psi(x) = \begin{cases} \sqrt{\frac{30}{a^5}} x(a-x), & 0 < x < a \\ 0 & \text{elsewhere} \end{cases}$$

Calculate $\langle x \rangle$.

SOLUTION ■ Using Eq.(8.23), we get:

$$\begin{aligned} \langle x \rangle &= \int_0^a \left[\sqrt{\frac{30}{a^5}} x(a-x) \right] x \left[\sqrt{\frac{30}{a^5}} x(a-x) \right] dx = \frac{30}{a^5} \int_0^a x^3 (a-x)^2 dx \\ &= \frac{30}{a^5} \left[a^6 \left(\frac{1}{60} \right) \right] = \frac{a}{2} \quad (\text{read the margin remark}). \end{aligned}$$

$$\begin{aligned} &\int_0^a x^3 (a-x)^2 dx \\ &= \int_0^a [x^3(a^2 + x^2 - 2ax)] dx \\ &= \int_0^a (a^2 x^3 + x^5 - 2ax^4) dx \\ &= \left[a^2 \frac{x^4}{4} + \frac{x^6}{6} - 2a \frac{x^5}{5} \right]_0^a \\ &= \left[\frac{a^6}{4} + \frac{a^6}{6} - \frac{2a^6}{5} \right] \\ &= a^6 \left[\frac{1}{4} + \frac{1}{6} - \frac{2}{5} \right] \\ &= a^6 \left(\frac{1}{60} \right) \end{aligned}$$

You can solve an SAQ on calculating the expectation value.

SAQ 4 - Expectation value

Calculate $\langle x \rangle$ for the wave function:

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right), 0 < x < L$$

EXPECTATION VALUE

The expectation value of the operator $\hat{D}$ corresponding to the dynamical variable D is the average of the measured value of D in any quantum mechanical system in a state described by a wave function $\psi(x, y, z, t)$. It is defined as:

$$\langle D \rangle = \iiint \psi^*(x, y, z, t) \hat{D} \psi(x, y, z, t) d\tau \quad (\psi \text{ is normalized}) \quad (8.28)$$

For a one-dimensional system

$$\langle D \rangle = \int \psi^*(x, t) \hat{D} \psi(x, t) dx \quad (8.26)$$

An observable is a dynamical variable having a real expectation value.

In quantum mechanics such observables with real expectation values are represented by operators which are called **Hermitian operators**. Let us now study briefly about them.

8.3.1 Hermitian Operators

Let us start with the formal definition of the Hermitian operator. **An operator $\hat{D}$ is said to be a Hermitian operator, if for any two states of the system, ϕ and ψ we can write:**

$$\iiint \phi^* (\hat{D} \psi) d\tau = \iiint (\hat{D} \phi)^* \psi d\tau \quad (8.29)$$

For a one-dimensional system, the volume element $d\tau$ is simply dx and the limit of integration is from $-\infty$ to $+\infty$. However, for a three-dimensional system, $d\tau$ is the volume element $dx dy dz$. Then, this is a volume integral as you have studied in Unit 3 of BPHCT 133 and the integration is over the entire space, i.e., the limits of integration for all variables vary from $-\infty$ to $+\infty$.

You will come across integrals like the ones shown in Eq. (8.29) quite often in this course. So, we adopt a short-hand notation for this integral, which you will also find in several text books of quantum mechanics. Since in this course we will be studying only one-dimensional systems, we are writing the notation with the integration over dx only. Just remember that this notation is used for integrals over three dimensions as well. For any two wave functions ϕ and ψ :

$$(\phi, \psi) = \int \phi^* \psi dx \quad (8.30a)$$

$$\text{and} \quad (\phi, D\psi) = \int \phi^* (\hat{D} \psi) dx \quad (8.30b)$$

Note that in the shorthand notation on the LHS of Eq. (8.30b), we have used the same symbol D for the dynamical variable D and the corresponding operator $\hat{D}$. The integral $(\phi, D\psi)$ is also known as the inner product or the scalar product of ϕ with $\hat{D}\psi$.

Putting $\phi = \psi$ in Eq. (8.30a), we have

$$(\psi, \psi) = \int \psi^* \psi dx \quad (8.31)$$

(ψ, ψ) is known as the **norm** of the wave function. If ψ is a normalized wave function, the norm is equal to unity or $(\psi, \psi) = 1$. The norm of a wave function representing a state of a system is always positive. It can be zero only when $\psi = 0$, i.e., that state of the system does not exist.

In the following example, we check whether the linear momentum operator $\hat{p}_x$ is a Hermitian operator.

EXAMPLE 8.5: IS THE LINEAR MOMENTUM OPERATOR HERMITIAN?

Is the linear momentum operator $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$ a Hermitian operator?

SOLUTION ■ We use Eq. (8.30b) as a Hermitian operator satisfies it. So, to check whether $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$ is a Hermitian operator, we must see whether $\hat{p}_x$ satisfies Eq. (8.30b) for any two states ϕ and ψ , that is:

$$\int_{-\infty}^{\infty} \phi^* \left(-i\hbar \frac{\partial}{\partial x} \psi \right) dx = \int_{-\infty}^{\infty} \left(-i\hbar \frac{\partial}{\partial x} \phi \right)^* \psi dx \quad (i)$$

For a one-dimensional system, ϕ and ψ are functions of one variable:

$\phi = \phi(x)$, $\psi = \psi(x)$ and $\hat{p}_x = -i\hbar \frac{d}{dx}$. So, we can write the partial derivatives as ordinary derivatives in Eq. (i):

$$\int_{-\infty}^{\infty} \phi^* \left(-i\hbar \frac{d}{dx} \psi \right) dx = \int_{-\infty}^{\infty} \left(-i\hbar \frac{d}{dx} \phi \right)^* \psi dx \quad (ii)$$

We simplify the LHS of Eq. (i) using a standard mathematical identity from integral calculus, [Eq. (1) of the margin remark, replacing $u(x) = \phi^*(x)$ and $v(x) = \psi(x)$]:

$$\int \phi^* \left(-i\hbar \frac{d}{dx} \psi \right) dx = -i\hbar \int \phi^* \left(\frac{d\psi}{dx} \right) dx = -i\hbar \left[\phi^* \psi - \int \psi \left(\frac{d\phi^*}{dx} \right) dx \right] \quad (ii)$$

$$= -i\hbar \left[\phi^* \psi \right] + \left[\int \psi \left(-i\hbar \frac{d\phi}{dx} \right)^* dx \right], \quad \because \left(-i\hbar \frac{d\phi}{dx} \right)^* = i\hbar \left(\frac{d\phi}{dx} \right)^* \quad (iii)$$

Applying the limits on the integrals we get the result of Eq. (i).

$$\int_{-\infty}^{\infty} \phi^* \left(-i\hbar \frac{d}{dx} \psi \right) dx = -i\hbar \left[\phi^* \psi \right]_{-\infty}^{\infty} + \int_{-\infty}^{\infty} \psi \left(-i\hbar \frac{d\phi}{dx} \right)^* dx = \int_{-\infty}^{\infty} \psi \left(-i\hbar \frac{d\phi}{dx} \right)^* dx \quad (iv)$$

The first term on the RHS vanishes because normalizable wave functions go to zero at $x \rightarrow \infty$ and $x \rightarrow -\infty$.

For two continuously differentiable functions $u(x)$ and $v(x)$, the rule for the differentiation of the product of the functions, we have:

$$\frac{d}{dx}(uv) = u \left(\frac{dv}{dx} \right) + v \left(\frac{du}{dx} \right)$$

So, we can write

$$\int \frac{d}{dx}(uv) dx$$

$$= \int u \left(\frac{dv}{dx} \right) dx + \int v \left(\frac{du}{dx} \right) dx$$

$$\Rightarrow uv$$

$$= \int uv' dx + \int vu' dx$$

$$\int u \left(\frac{dv}{dx} \right) dx = uv - \int v \left(\frac{du}{dx} \right) dx$$

(1)

So, we find that $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$ is a Hermitian operator. This is also true of

$$\hat{p}_y = -i\hbar \frac{\partial}{\partial y} \text{ and } \hat{p}_z = -i\hbar \frac{\partial}{\partial z}.$$

You can work out the following SAQ to check that most commonly used operators in quantum mechanics are Hermitian.

SAQ 5 - Hermitian operators in quantum mechanics

a) Show that position operator $\hat{x}$ and the potential energy operator $\hat{V}(x)$ are Hermitian.

b) Show that the kinetic energy operator $\hat{T} = \frac{\hat{p}_x^2}{2m} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$ and the

Hamiltonian operator $\hat{H} = \frac{\hat{p}_x^2}{2m} + \hat{V}(x)$ are Hermitian.

The operators, which satisfy Eq. (8.29) are also known as **self-adjoint** operators. The adjoint or Hermitian conjugate $\hat{D}^\dagger$ of an operator $\hat{D}$, is defined by the relation:

$$\int \phi^* (\hat{D}\psi) d\tau = \int (\hat{D}^\dagger \phi)^* \psi d\tau \quad (8.32)$$

Comparing Eq. (8.29) for a Hermitian operator and Eq. (8.32), we can see that for a Hermitian operator $\hat{D}$:

$$\hat{D} = \hat{D}^\dagger \quad (8.33)$$

We now write down a few useful properties for the adjoint of operators $\hat{A}, \hat{B}$ and a complex number λ :

$$\text{i) Adjoint of the adjoint of an operator: } (\hat{D}^\dagger)^\dagger = \hat{D} \quad (8.34a)$$

$$\text{ii) } (\hat{A} + \hat{B})^\dagger = \hat{A}^\dagger + \hat{B}^\dagger \quad (8.34b)$$

$$\text{iii) } (\lambda \hat{A})^\dagger = \lambda^* \hat{A}^\dagger \quad (8.34c)$$

We now write down the result for the adjoint of the product of any two operators $\hat{A}$ and $\hat{B}$ (see margin remark for proof):

$$(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger \quad (8.34d)$$

This result is also true for Hermitian operators. Since Hermitian operators are self-adjoint, for any two Hermitian operators $\hat{A}$ and $\hat{B}$, we can write:

$$(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger = (\hat{A}\hat{B})^\dagger = \hat{B}\hat{A} \quad (8.34e)$$

To get this result we used the property of a Hermitian operator specified in Eq. (8.33) to write $\hat{A}^\dagger = \hat{A}$ and $\hat{B}^\dagger = \hat{B}$. Recollect that the entire discussion on Hermitian operators was initiated with the idea that Hermitian operators have real expectation values. Let us now prove it in the following example.

For $\hat{D} = \hat{A}\hat{B}$, using Eq. (8.32) we can write:

$$\begin{aligned} \int \phi^* (\hat{A}\hat{B}\psi) d\tau \\ = \int \left[(\hat{A}\hat{B})^\dagger \phi \right]^* \psi d\tau \end{aligned}$$

The LHS of this equation is:

$$\begin{aligned} \int \phi^* (\hat{A}\hat{B}\psi) d\tau \\ = \int \phi^* \hat{A}(\hat{B}\psi) d\tau \\ = \int (\hat{A}^\dagger \phi)^* (\hat{B}\psi) d\tau \\ = \int (\hat{B}^\dagger \hat{A}^\dagger \phi)^* \psi d\tau \end{aligned}$$

On comparing this with the RHS of the equation we can write:

$$(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger$$

EXAMPLE 8.6: HERMITIAN OPERATORS HAVE REAL EXPECTATION VALUES

Show that a Hermitian operator $\hat{A}$ has a real expectation value.

SOLUTION ■ From Eq. (8.28) the expectation value of $\hat{A}$ is:

$$\langle A \rangle = \iiint \psi^* \hat{A} \psi d\tau \quad (i)$$

The complex conjugate of this equation is:

$$\langle A \rangle^* = \iiint \psi [\hat{A} \psi]^* d\tau \quad (ii)$$

Since $\hat{A}$ is Hermitian, using $\phi = \psi$ in Eq. (8.29), we can write:

$$\iiint \psi^* [\hat{A} \psi] d\tau = \iiint [\hat{A} \psi]^* \psi d\tau \quad (iii)$$

Comparing Eqs.(i) and (ii) with Eq. (iii), we can write: $\langle A \rangle = \langle A \rangle^*$ which means that $\langle A \rangle$ is real.

Since Hermitian operators have real expectation values, we are justified in representing all quantum mechanical observables by Hermitian operators. To summarise:

HERMITIAN OPERATORS

- A Hermitian operator $\hat{D}$ is defined as:

$$\iiint \phi^* (\hat{D} \psi) d\tau = \iiint (\hat{D} \phi)^* \psi d\tau \quad (8.29)$$

where ϕ and ψ are any two states of the system.

- Hermitian operators have real expectation values.
- All quantum mechanical observables are represented by Hermitian operators.
- The Hermitian conjugate $\hat{D}^\dagger$ of an operator $\hat{D}$ is defined as:

$$\int \phi^* (\hat{D} \psi) d\tau = \int (\hat{D}^\dagger \phi)^* \psi d\tau \quad (8.32)$$

- For a Hermitian operator: $\hat{D} = \hat{D}^\dagger$ (8.33)

We will now introduce you to another interesting feature arising out of the discussion so far: representing the Schrödinger equation as an eigenvalue equation.

8.3.2 Eigenfunctions and Eigenvalues

So far you have studied that, in general, when an operator $\hat{D}$ operates upon function ψ we get a new function χ ($\hat{D}\psi = \chi$). However, under special circumstances χ may just be a multiple of ψ , say, $\chi = d\psi$. In that case the operator equation becomes:

$$\hat{D}\psi = d\psi \quad (8.35)$$

where d is (in general) a complex number. Note that in Eq. (8.35), when the operator $\hat{D}$ operates on a function ψ , the result is the product of a constant d and the function (ψ) itself. Such an equation is called **an eigenvalue equation for the operator $\hat{D}$** . The constant d is called the **eigenvalue** of the operator $\hat{D}$ and ψ is called its **eigenfunction**.

Now recall the time independent Schrödinger equation, which we have written as an operator equation earlier in this unit [Eq. (8.8)]:

$$\hat{H}\psi(x) = E\psi(x) \quad (8.36)$$

Now this equation has the form of an eigenvalue equation. So, the time independent Schrödinger equation is an eigenvalue equation for the Hamiltonian operator $\hat{H}$. It tells us that $\hat{H}$ operating on a special class of wave functions gives back the same wave functions multiplied by the eigenvalue E of $\hat{H}$. Now since E has the dimensions of energy, Eq. (8.36) would give us the value of the energy of the quantum mechanical system corresponding to the wave function $\psi(x)$. **We already know that $\hat{H}$ is a Hermitian operator.** We can show that Hermitian operators actually have real eigenvalues. Let us see this in the following example.

EXAMPLE 8.7: HERMITIAN OPERATORS HAVE REAL EIGENVALUES

Show that a Hermitian operator $\hat{A}$ has real eigenvalues.

SOLUTION ■ The eigenvalue equation for the Hermitian operator $\hat{A}$ can be written as:

$$\hat{A}\psi = a\psi \quad (i)$$

where ψ is the eigenfunction and a is the eigenvalue of the operator.

Since $\hat{A}$ is Hermitian, using $\phi = \psi$ in Eq. (8.29), we can write:

$$\iiint \psi^* [\hat{A}\psi] d\tau = \iiint [\hat{A}\psi]^* \psi d\tau \quad (ii)$$

Using Eq.(i) in Eq.(ii) we get:

$$\iiint \psi^* [a\psi] d\tau = \iiint [a\psi]^* \psi d\tau \quad (iii)$$

Since a is a constant, Eq. (iii) is:

$$a \iiint \psi^* \psi d\tau = a^* \iiint \psi^* \psi d\tau \Rightarrow (a - a^*) \iiint \psi^* \psi d\tau = 0 \quad (\text{iv})$$

Since, in general, $\iiint \psi^* \psi d\tau \neq 0$, we can write $a - a^* = 0 \Rightarrow a = a^*$

This means that the eigenvalue a of the Hermitian operator $\hat{A}$ is always real.

The expectation value $\langle \hat{A} \rangle$ is equal to the eigenvalue a itself, which is real.

So, basically, suppose that a system is in a state ψ , which is the eigenfunction of a operator $\hat{A}$ corresponding to an observable of the system. Then the measured value of the observable will be the eigenvalue of the operator corresponding to that eigenfunction. This value can be calculated from the eigenvalue equation.

Let us summarise what you have learnt in this section.

EIGENFUNCTIONS AND EIGENVALUES

- The eigenvalue equation for an operator $\hat{D}$ acting on a state ψ is

$$\hat{D}\psi = d\psi \quad (8.35)$$

The constant d is the eigenvalue of the operator and ψ is called the eigenfunction of the operator.

- All Hermitian operators have real eigenvalues.
- The time independent Schrödinger equation for a quantum mechanical system is:

$$\hat{H}\psi(x) = E\psi(x) \quad (8.36)$$

The solutions of this equation are the energy eigenvalues E of the system corresponding to the eigenfunctions $\psi(x)$, which are also the stationary states of the system.

We have seen that each observable of the system is connected to an operator and the measured value to the eigenvalue of the operator. What if you now wish to measure more than one observable for the quantum system?

You have studied in Unit 6, that quantum mechanics imposes a limit to the accuracy with which certain pairs of dynamical variables can be measured for a quantum system.

Let us now understand how that translates in the language of operators.

8.3.3 Commuting and Non-Commuting Operators

As you have learnt, the measurement process is the operator acting on the wave function. Consider any **two commuting operators** $\hat{A}$ and $\hat{B}$, which correspond to any two observables of the system. Suppose the state ψ is a non-degenerate eigenfunction (read the margin remark) of $\hat{A}$ with an eigenvalue a . So, we can write: $\hat{A}\psi = a\psi$.

So, a measurement of the observable corresponding to $\hat{A}$ would give us the value a . Now, suppose then we try to carry out a measurement of the observable corresponding to $\hat{B}$ on the same state ψ after the operator $\hat{A}$ operates on it. This is equivalent to the operator $\hat{B}$ acting on the state $\hat{A}\psi$:

$$\hat{B}(\hat{A}\psi) = a(\hat{B}\psi) = a\chi \quad \text{where } \chi = (\hat{B}\psi) \quad (8.37)$$

Now let us assume that the operators $\hat{A}$ and $\hat{B}$ commute with each other. Then we have

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0 \quad \Rightarrow \quad \hat{A}\hat{B} = \hat{B}\hat{A} \quad (8.38)$$

Operating both sides of Eq. (8.38) on the wave function ψ , and using $\hat{A}\psi = a\psi$, we get

$$\hat{A}(\hat{B}\psi) = \hat{B}(\hat{A}\psi) = a(\hat{B}\psi) \quad (8.39)$$

Eq. (8.39) looks like an eigenvalue equation for the operator $\hat{A}$ with the same eigenvalue a , except that now the eigenfunction is not ψ , but the function $\hat{B}\psi$. However, in the beginning we stated that eigenfunction ψ is non degenerate. Therefore, the function $\hat{B}\psi$ must be a multiple of ψ . So let us write:

$$\hat{B}\psi = b\psi \quad (8.40)$$

Since b is a constant, Eq. (8.40) is the eigenvalue equation for the operator $\hat{B}$, with an eigenvalue b and the **same eigenfunction** ψ as $\hat{A}$.

So, **two commuting operators** $\hat{A}$ and $\hat{B}$ **have simultaneous eigenfunctions**.

We can say that the state of the system does not change when either the operator $\hat{A}$ or the operator $\hat{B}$ acts on it. This implies that these two observables can be exactly measured simultaneously. By extension, the observables represented by two **operators that do not commute cannot be measured simultaneously**. For example, the operators $\hat{x}$ and $\hat{p}_x$ do not commute, since $[\hat{x}, \hat{p}_x] = i\hbar$ and so x and p_x cannot be measured simultaneously with arbitrary accuracy.

The uncertainty in the measured value of an observable associated with the operator $\hat{A}$ is expressed in terms of the expectation values of $\hat{A}$ and $\hat{A}^2$ for specific wave functions as follows:

$$\Delta A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2} \quad (8.41)$$

If there is just one eigenfunction corresponding to an eigenvalue of the operator, that eigenfunction of the operator is called a **non-degenerate eigenfunction** of the operator for that eigenvalue. If there are more than one eigenfunctions, which correspond to one particular eigenvalue of the operator, then this set of eigenfunctions are the **degenerate eigenfunctions** of the operator corresponding to that eigenvalue. You will study this in Sec. 8.3.4.

EXAMPLE 8.8: CALCULATING Δx

$$\begin{aligned} & \frac{2}{L} \int_0^L x^2 \sin^2 \frac{\pi x}{L} dx \\ &= \frac{1}{L} \int_0^L x^2 \left(1 - \cos \frac{2\pi x}{L} \right) dx \\ & \frac{1}{L} \int_0^L x^2 dx = \frac{1}{L} \\ &= \left[\frac{x^3}{3} \right]_0^L = \frac{L^2}{3} \\ & \frac{1}{L} \int_0^L x^2 \left(\cos \frac{2\pi x}{L} \right) dx \\ &= \left[\frac{x^2}{2\pi} \sin \frac{2\pi x}{L} \right. \\ & \quad \left. + \frac{L}{2\pi^2} x \cos \frac{2\pi x}{L} \right]_0^L \\ &= \left[\frac{L^2}{4\pi^3} \sin \frac{2\pi x}{L} \right]_0^L \\ &= \frac{L^2}{2\pi^2} \end{aligned}$$

Calculate Δx for the quantum particle whose state is described by the wave function:

$$\psi(x) = \begin{cases} \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) & \text{for } 0 < x < L \\ 0 & \text{elsewhere} \end{cases}$$

SOLUTION ■ We use Eq. (8.41).

From Eq. (8.41) we can write: $\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$

Using Eq. (8.26) with $\hat{D} = \hat{x}^2 = x^2$, we can write (read the margin remark):

$$\langle x^2 \rangle = \int_0^L \left[\sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \right]^* x^2 \left[\sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \right] dx = \frac{2}{L} \int_0^L x^2 \sin^2 \frac{\pi x}{L} dx = \left[\frac{L^2}{3} - \frac{L^2}{2\pi^2} \right]$$

In SAQ 4, you have already calculated that $\langle x \rangle = \frac{L}{2}$

$$\therefore \Delta x = \sqrt{\left(\frac{L^2}{3} - \frac{L^2}{2\pi^2} \right) - \left(\frac{L}{2} \right)^2} = L \sqrt{\frac{1}{12} - \frac{1}{2\pi^2}}$$

Using the concepts presented so far, we would like to introduce an important class of eigenfunctions, namely, eigenfunctions which are normalised to unity and satisfy the orthogonality property. Such eigenfunctions are called **orthonormal eigenfunctions**. In this connection, we will also introduce another useful concept of the **degeneracy** of eigenfunctions.

8.3.4 Orthonormal Eigenfunctions

Suppose for a system there are more than one eigenfunctions of an operator having the **same eigenvalue**. Then all such functions are called **degenerate eigenfunctions**. For example, let ϕ_1 and ϕ_2 be two different eigenfunctions of an operator $\hat{D}$, which have the same eigenvalue say, d , i.e.,

$$\hat{D}\phi_1 = d\phi_1$$

and $\hat{D}\phi_2 = d\phi_2$

Then ϕ_1 and ϕ_2 are the **degenerate eigenfunctions** of the operator $\hat{D}$, having the same eigenvalue d .

Eigenfunctions of an operator having different eigenvalues are called **non-degenerate eigenfunctions**. For example, if ψ_1 and ψ_2 are two different eigenfunctions of an operator $\hat{D}$, which have eigenvalue say, d_1 and d_2 , respectively, that is:

$$\hat{D}\psi_1 = d_1\psi_1 \quad (8.42a)$$

$$\text{and} \quad \hat{D}\psi_2 = d_2\psi_2 \quad (8.42b)$$

Then we say that ψ_1 and ψ_2 are the **non-degenerate** eigenfunctions of the operator $\hat{D}$.

Let us further assume that $\hat{D}$ is a Hermitian operator and also that these non-degenerate eigenfunctions ψ_1 and ψ_2 are normalised to unity, that is, $(\psi_1, \psi_1) = (\psi_2, \psi_2) = 1$. Then using the definition for Hermitian operators [Eq. (8.29)], we can write:

$$\iiint \psi_1^* (\hat{D}\psi_2) d\tau = \iiint (\hat{D}\psi_1)^* \psi_2 d\tau \quad (8.43)$$

Using Eqs. (8.42a) and (8.42b) we can write:

$$\iiint \psi_1^* (d_2\psi_2) d\tau = \iiint (d_1\psi_1)^* \psi_2 d\tau \quad (8.44)$$

which is

$$d_2 \iiint \psi_1^* \psi_2 d\tau = d_1 \iiint \psi_1^* \psi_2 d\tau \Rightarrow (d_2 - d_1) \iiint \psi_1^* \psi_2 d\tau \quad (8.45)$$

Here we have used the condition that the eigenvalues of a Hermitian operator are real and therefore, $d_1^* = d_1$. Since we started by assuming that d_1 and d_2 are not equal, therefore, from Eq. (8.45) we must have:

$$\iiint \psi_1^* \psi_2 d\tau = 0 \quad (8.46)$$

Such eigenfunctions whose inner product is equal to zero are said to be **orthogonal** to each other. Hence, ψ_1 and ψ_2 are **orthogonal eigenfunctions**.

We can generalise this statement: If $\psi_1, \psi_2, \psi_3, \dots, \psi_n$ are non-degenerate eigenfunctions of a Hermitian operator, normalised to unity, then they satisfy the following **orthonormality conditions**:

$$(\psi_i, \psi_j) = 0 \quad \text{for } i \neq j, \quad i = 1, 2, \dots, n, \quad j = 1, 2, \dots, n \quad (8.47a)$$

$$(\psi_i, \psi_j) = 1 \quad \text{for } i = j \quad (8.47b)$$

Thus, the eigenfunctions are normalised to unity, and all eigenfunctions ψ_i, ψ_j satisfy the orthogonality property (Eq. 8.47a) for $i \neq j$. These conditions can be represented in an elegant, compact form using the Kronecker delta symbol δ_{ij} which is defined as follows:

$$\delta_{ij} = 0 \quad \text{for } i \neq j \quad (8.48a)$$

$$\delta_{ij} = 1 \quad \text{for } i = j \quad (8.48b)$$

Now the orthonormality conditions can be written as:

$$(\psi_i, \psi_j) = \delta_{ij}, \quad i = 1, 2, \dots, n, \quad j = 1, 2, \dots, n \quad (8.49)$$

Eigenfunctions of an operator which satisfy Eq. (8.49) are called **orthonormal functions** and form an **orthonormal set**.

Let us use these ideas to prove another important property.

EXAMPLE 8.9: PARITY OF EIGEN FUNCTIONS

If an operator $\hat{A}$ commutes with the parity operator $\hat{P}$, show that the non-degenerate eigenfunctions of $\hat{A}$ have definite parity.

SOLUTION ■ We use Eq. (8.38) and the definition of the parity operator.

The eigenvalue equation for the operator $\hat{A}$ is:

$$\hat{A}\psi(x) = a\psi(x) \quad (i)$$

Since $\hat{P}$ commutes with $\hat{A}$, we have:

$$[\hat{P}, \hat{A}] = 0 \quad \Rightarrow \quad \hat{P}\hat{A} = \hat{A}\hat{P} \quad (ii)$$

$$\therefore \hat{A}[\hat{P}\psi(x)] = \hat{P}[\hat{A}\psi(x)] = \hat{P}[a\psi(x)] = a[\hat{P}\psi(x)] \quad (iii)$$

So, $\psi(x)$ and $[\hat{P}\psi(x)]$ are eigenfunctions of $\hat{A}$ with the same eigenvalue.

Since $\psi(x)$ is non-degenerate, the two functions $\psi(x)$ and $[\hat{P}\psi(x)]$ can differ at the most by a constant. Hence,

$$\hat{P}\psi(x) = p\psi(x) \quad (iv)$$

Thus $\psi(x)$ is an eigenfunction of the parity operator with p as the eigenvalue. Let us now try to determine the value of p . Applying once again the parity operator we get:

$$\hat{P}[\hat{P}\psi(x)] = p[\hat{P}\psi(x)] = p^2\psi(x) \quad (v)$$

But $\psi(x)$ and $\hat{P}^2\psi(x)$ have to be identical. Hence,

$$p^2 = 1 \quad \Rightarrow \quad p = \pm 1 \quad (vi)$$

The eigenvalues of the parity operator are therefore ± 1 . So, the eigenfunctions of $\hat{A}$ have a definite parity. For degenerate eigenfunctions it is possible to take linear combinations of $\psi(x)$ and $\psi(-x)$ to obtain eigenfunctions of definite parity.

We shall use this property in the next block to obtain eigenfunctions and eigenvalues of some simple systems. We end this discussion with an exercise for you.

SAQ 6 - Eigenfunctions and eigenvalues

Show that the functions $\exp(-x^2/2)$ and $x \exp(-x^2/2)$ are eigenfunctions of the operator $(-d^2/dx^2 + x^2)$ and calculate the eigenvalues.

PROPERTIES OF EIGENFUNCTIONS

- Eigenfunctions of an operator having **different eigenvalues** are called **non-degenerate eigenfunctions**.
- If $\psi_1, \psi_2, \psi_3, \dots, \psi_n$ are non-degenerate eigenfunctions of a Hermitian operator, normalised to unity, then they satisfy the following **orthonormality conditions**:

$$(\psi_i, \psi_j) = 0 \quad \text{for } i \neq j, \quad i = 1, 2, \dots, n, \quad j = 1, 2, \dots, n \quad (8.47a)$$

$$(\psi_i, \psi_j) = 1 \quad \text{for } i = j \quad (8.47b)$$

- If an operator $\hat{A}$ **commutes with the parity operator** $\hat{P}$, the non-degenerate eigenfunctions of $\hat{A}$ have definite parity.
- Two commuting operators $\hat{A}$ and $\hat{B}$ have simultaneous eigenfunctions.
- The observables represented by two operators that do not commute cannot be measured simultaneously with arbitrary accuracy.

In the last section of this unit, we establish a correspondence between the quantum mechanical and classical concepts. Remember that in quantum mechanics, we have operators and in classical mechanics, there are only dynamical variables. So, we have to consider the expectation values of operators to establish this correspondence. Now, according to the correspondence principle, we expect that the motion of a quantum object, represented by ψ , should agree with that of a classical particle whenever the distances and momenta become so large that we can ignore the uncertainty principle. When we try to explore this point, we arrive at the Ehrenfest theorem.

8.4 EHRENFEST THEOREM

Let us consider the rate of change of an operator $\hat{D}$ associated with an observable D . We assume that $\hat{D}$ does not depend explicitly on time. We can write the expectation value of $\hat{D}$ in the normalized state ψ as [Eq. (8.28)]:

$$\langle D \rangle = \iiint \psi^* \hat{D} \psi d\tau \quad (8.28)$$

The rate of change of $\langle D \rangle$ with time can be written as:

$$\frac{d}{dt} \langle D \rangle = \frac{d}{dt} \left[\iiint \psi^* \hat{D} \psi d\tau \right] \quad (8.50)$$

We can take the derivative of each term in the integrand separately to get:

$$\frac{d}{dt} \langle D \rangle = \iiint \left[\left(\frac{\partial \psi^*}{\partial t} \right) \hat{D} \psi + \psi^* \hat{D} \left(\frac{\partial \psi}{\partial t} \right) \right] d\tau \quad (8.51)$$

Now recall the time dependent Schrödinger equation of Unit 7 [Eq. (7.50)]:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = i\hbar\frac{\partial\psi}{\partial t} \Rightarrow \hat{H}\psi = i\hbar\frac{\partial\psi}{\partial t} \quad (8.52)$$

The Hamiltonian operator can also be written as:

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

So, we can write:

$$\frac{\partial\psi}{\partial t} = \left(\frac{1}{i\hbar}\right)\hat{H}\psi \quad (8.53)$$

In this equation, the operator $\hat{H}$ is the Hamiltonian operator in three dimensions:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V} \quad (8.54)$$

We now write the complex conjugate of Eq. (8.52) and remember that $\hat{H}$ is a Hermitian operator:

$$\psi^*\hat{H} = -i\hbar\frac{\partial\psi^*}{\partial t} \quad (8.55)$$

So, we can write Eq. (8.55) as:

$$\frac{\partial\psi^*}{\partial t} = \left(-\frac{1}{i\hbar}\right)\psi^*\hat{H} \quad (8.56)$$

Using Eqs. (8.53 and 8.56) in Eq. (8.51), we get

$$\frac{d}{dt}\langle D \rangle = \frac{1}{i\hbar} \iiint \left[-\psi^*\hat{H}\hat{D}\psi + \psi^*\hat{D}\hat{H}\psi \right] d\tau \quad (8.57)$$

So, we can write:

$$\frac{d}{dt}\langle D \rangle = \frac{1}{i\hbar} \iiint \psi^* [\hat{D}\hat{H} - \hat{H}\hat{D}] \psi d\tau \quad (8.58)$$

For an operator $\hat{D}$ that depends explicitly on time, the equation changes to:

$$\frac{d}{dt}\langle D \rangle = \left\langle \frac{\partial\hat{D}}{\partial t} \right\rangle + \frac{1}{i\hbar} \langle [\hat{D}, \hat{H}] \rangle$$

This equation is known as the Heisenberg's equation of motion.

Identifying the quantity in the bracket as the commutator of the operators $\hat{D}$ and $\hat{H}$ we can write:

$$\frac{d}{dt}\langle D \rangle = \frac{1}{i\hbar} \iiint \psi^* [\hat{D}, \hat{H}] \psi d\tau = \frac{1}{i\hbar} \langle [\hat{D}, \hat{H}] \rangle \quad (8.59)$$

This equation relates the rate of change of the expectation value of an operator with the expectation value of the commutator of the operator with the Hamiltonian operator. This equation is for an operator $\hat{D}$ that does not depend explicitly on time (read the margin remark).

We now use Eq. (8.59) to obtain the rate of change of the expectation values of the operators $\hat{x}$ and $\hat{p}_x$ using the following expression for $\hat{H}$:

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \hat{V}(x)$$

So, we can write:

$$\frac{d}{dt}\langle x \rangle = \frac{1}{i\hbar} \langle [\hat{x}, \hat{H}] \rangle = \frac{1}{i\hbar} \left\langle \left[\hat{x}, \left(\frac{\hat{p}_x^2}{2m} + \hat{V}(x) \right) \right] \right\rangle = \frac{1}{i\hbar} \left\langle \frac{1}{2m} [\hat{x}, \hat{p}_x^2] + [\hat{x}, \hat{V}(x)] \right\rangle \quad (8.60)$$

Now using Eq. (8.19d) we get

$$[\hat{x}, \hat{p}_x^2] = \hat{p}_x [\hat{x}, \hat{p}_x] + [\hat{x}, \hat{p}_x] \hat{p}_x \quad (8.61)$$

Since we know that $[\hat{x}, \hat{p}_x] = i\hbar$, Eq. (8.61) reduces to:

$$[\hat{x}, \hat{p}_x^2] = 2i\hbar \hat{p}_x \quad (8.62)$$

Also since $V(x)$ is a function of x alone, and an operator always commutes with itself, we have:

$$[\hat{x}, \hat{V}(x)] = 0 \quad (8.63)$$

Substituting $[\hat{x}, \hat{p}_x^2]$ and $[\hat{x}, \hat{V}(x)]$ from Eqs. (8.62 and 8.63) in Eq. (8.60), we get:

$$\frac{d}{dt}\langle x \rangle = \frac{1}{i\hbar} \left\langle \frac{1}{2m} (2i\hbar p_x) + 0 \right\rangle = \frac{1}{m} \langle p_x \rangle \quad (8.64a)$$

You can see that this relation is similar to the following equation in Newtonian mechanics:

$$\frac{dx}{dt} = \frac{p_x}{m} \quad (\because p_x = mv_x = m \frac{dx}{dt}) \quad (8.64b)$$

Next, let us consider the rate of change of the expectation value of the linear momentum operator $\hat{p}_x$:

$$\frac{d}{dt}\langle p_x \rangle = \frac{1}{i\hbar} \langle [\hat{p}_x, \hat{H}] \rangle = \frac{1}{i\hbar} \left\langle \left[\hat{p}_x, \left(\frac{\hat{p}_x^2}{2m} + \hat{V}(x) \right) \right] \right\rangle = \frac{1}{i\hbar} \left\langle \frac{1}{2m} [\hat{p}_x, \hat{p}_x^2] + [\hat{p}_x, \hat{V}(x)] \right\rangle \quad (8.65)$$

Now, since an operator always commutes with itself, the first term in the RHS of Eq. (8.65) is zero: $[\hat{p}_x, \hat{p}_x^2] = 0$. Next, let us evaluate $[\hat{p}_x, \hat{V}(x)]$. We put

$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$ and $\hat{V}(x) = V(x)$ and use the standard method for evaluating a

commutator. We operate the commutator on a function $f(x)$ to get:

$$\begin{aligned} [\hat{p}_x, \hat{V}(x)]f(x) &= \hat{p}_x[V(x)f(x)] - V(x)[\hat{p}_x f(x)] \\ &= -i\hbar \frac{d}{dx} [V(x)f(x)] - V(x) \left[-i\hbar \frac{df(x)}{dx} \right] \end{aligned} \quad (8.66)$$

Notice that since $V(x)$ and $f(x)$ are functions of only x , we have replaced the partial derivative $\partial/\partial x$ by the ordinary derivative d/dx . So, we get:

$$[\hat{p}_x, \hat{V}(x)]f(x) = -i\hbar \frac{dV(x)}{dx} f(x) \quad (8.67)$$

And since the function $f(x)$ is arbitrary, we can write:

$$[\hat{p}_x, \hat{V}(x)] = -i\hbar \frac{\partial V(x)}{\partial x} \quad (8.68)$$

Replacing from Eq. (8.68) into Eq. (8.65), we get, finally for the rate of change of the expectation value of the linear momentum

$$\frac{d}{dt} \langle p_x \rangle = \frac{1}{i\hbar} \left\langle 0 + \left[-i\hbar \frac{dV(x)}{dx} \right] \right\rangle \quad (8.69)$$

$$\text{or} \quad \frac{d}{dt} \langle p_x \rangle = - \left\langle \frac{dV(x)}{dx} \right\rangle \quad (8.70a)$$

You are familiar with a similar expression in classical mechanics:

$$\frac{dp_x}{dt} = - \frac{dV(x)}{dx} \quad (8.70b)$$

Now, compare Eqs. (8.64a) and (8.70a) with their classical counterparts, Eqs. (8.64b) and (8.70b), respectively. You can see that in quantum mechanics, the dynamical variables are replaced by their corresponding expectation (or average) values.

For a macroscopic system there is hardly any difference between x , p_x and dV/dx and their average values. However, for microscopic systems they are quite different. As a matter of fact, you have seen that for a microscopic system the precise values of x and p_x do not exist simultaneously but their average values can be obtained. Eqs. (8.64a and 8.70a) constitute the **Ehrenfest theorem**, which shows the correspondence as well as a basic difference between classical and quantum mechanics. Let us give the formal statement of the theorem.

EHRENFEST THEOREM

- The rate of change of an operator $\hat{D}$ associated with an observable D which does not depend explicitly on time is given by:

$$\frac{d}{dt} \langle D \rangle = \frac{1}{i\hbar} \int \psi^* [\hat{D}, \hat{H}] \psi d\tau = \frac{1}{i\hbar} \langle [\hat{D}, \hat{H}] \rangle \quad (8.59)$$

where $\hat{H}$ is the Hamiltonian operator for the system.

- The **Ehrenfest theorem** for a system defined by $\hat{H} = \frac{\hat{p}_x^2}{2m} + \hat{V}(x)$ is the following set of equations:

$$\frac{d}{dt} \langle x \rangle = \frac{1}{m} \langle p_x \rangle \quad (8.64a)$$

$$\frac{d}{dt} \langle p_x \rangle = - \left\langle \frac{dV(x)}{dx} \right\rangle \quad (8.70a)$$

- When an operator commutes with the Hamiltonian, the expectation value of the observable associated with it is a constant of motion.

You may like to apply these ideas and make use of Eq. (8.59) to arrive at an interesting result.

SAQ 7 - Ehrenfest theorem

Show that when an operator commutes with the Hamiltonian, the expectation value of the observable associated with it is a constant of motion.

8.5 SOME POSTULATES OF QUANTUM MECHANICS

As you have studied so far, the mathematical framework of quantum mechanics has been developed based on a small set of fundamental **assumptions or postulates**. The postulates themselves cannot be derived.

They are deemed to be correct when the consequences deduced from these postulates are verified experimentally. You may come across various statements of the postulates in text books; they may be presented in a different form and the total number of postulates may also differ, depending on how they are presented.

Here we summarise for you, only those postulates that you have studied so far in Units 7 and 8, for a quick reference.

Postulate 1

The state of a quantum mechanical system is completely specified by a function $\psi(x, y, z, t)$ that depends on the spatial coordinates and time. This function is called the **wave function** of the system. All possible information about the system can be derived from the wave function.

Postulate 2

Every physical observable of the system is associated with a Hermitian operator which acts on the wave function.

Postulate 3

The only possible result of the measurement of the observable associated with an operator $\hat{D}$ is one of the eigenvalues of $\hat{D}$, which can be derived from the eigenvalue equation:

$$\hat{D}\psi(x) = d\psi$$

Postulate 4

If a system is in a state described by a normalized wave function, then the average measured value of the observable corresponding to the operator $\hat{D}$ is given by:

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

Postulate 5

The wave function of the system evolves in time according to the time dependent Schrödinger equation:

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

With this we complete our study of the basic concepts and mathematical framework of quantum mechanics. In the next block, you will study a few applications of quantum mechanics to simple systems.

We now summarise the concepts you have studied in this unit.

8.6 SUMMARY

Concept	Description
Operators in quantum mechanics	■ Every physical observable in quantum mechanics is associated with an operator, which operates on the wave function. When a quantum mechanical operator $\hat{O}$ operates on a wave function ψ, we get: $\hat{O}\psi = \chi$ where χ is some other function. The quantum mechanical operators associated with the position and momentum variables, x and p_x, are defined in the following way: $\hat{x}\psi = x\psi \Rightarrow \hat{x} = x$ $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$ To construct the operator for any other dynamical variable we write the classical expression for it in terms of the position and momentum variables and replace these variables by their corresponding operator forms.
The parity operator	■ The parity operator is a space inversion operator. The parity operation is equivalent to transforming a right-handed system of coordinates into a left-handed one. For a one-dimensional system the action of the parity operator is defined as follows: $\hat{P}\psi(x,t) = \psi(-x,t)$ and $\hat{P}A\left(x, -i\hbar \frac{\partial}{\partial x}, t\right) = A\left(-x, i\hbar \frac{\partial}{\partial x}, t\right)$

Properties of Operators

- For any two operators $\hat{A}$ and $\hat{B}$ operating on a wave function ψ :

$$(\hat{A} + \hat{B})\psi = \hat{A}\psi + \hat{B}\psi$$

$$(\hat{A} - \hat{B})\psi = \hat{A}\psi - \hat{B}\psi$$

$$\hat{A}\hat{B}\psi = \hat{A}(\hat{B}\psi)$$

In general, $\hat{A}\hat{B}\psi \neq \hat{B}\hat{A}\psi$

If for all ψ , $\hat{A}\psi = \hat{B}\psi$, the operators $\hat{A}$ and $\hat{B}$ are equal.

The identity operator $\hat{I}$ leaves the wave function unchanged: $\hat{I}\psi = \psi$

Commutators and their properties

- The **commutator** of the two operators $\hat{A}$ and $\hat{B}$ denoted by the commutator bracket $[\hat{A}, \hat{B}]$ is defined as:

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

For operators $\hat{A}$, $\hat{B}$ and $\hat{C}$, we can write:

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

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

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

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

An **operator always commutes with its own power**:

$$[\hat{A}^n, \hat{A}] = 0; \quad n = 0, 1, 2, 3, \dots$$

An operator always commutes with a constant:

$$[\hat{C}, \hat{A}] = 0 \quad \text{where } \hat{C} = C \text{ (a constant).}$$

For the position and momentum operators we have:

$$[\hat{x}, \hat{p}_x] = i\hbar; \quad [\hat{y}, \hat{p}_y] = i\hbar; \quad [\hat{z}, \hat{p}_z] = i\hbar$$

Expectation values

- The **expectation value** of the operator $\hat{D}$ corresponding to the dynamical variable D is the average of the measured value of D in any quantum mechanical system in a state described by a wave function $\psi(x, y, z, t)$. It is defined as:

$$\langle D \rangle = \iiint \psi^*(x, y, z, t) \hat{D} \psi(x, y, z, t) d\tau \quad (\psi \text{ is normalized})$$

For a one-dimensional system:

$$\langle D \rangle = \int \psi^*(x, t) \hat{D} \psi(x, t) dx$$

Hermitian operators

- A **Hermitian operator** $\hat{D}$ is defined as:

$$\iiint \phi^* (\hat{D}\psi) d\tau = \iiint (\hat{D}\phi)^* \psi d\tau$$

where ϕ and ψ are any two states of the system. **Hermitian operators have real expectation values. All quantum mechanical observables are represented by Hermitian operators.**

The Hermitian conjugate $\hat{D}^\dagger$ of an operator $\hat{D}$ is defined as:

$$\int \phi^* (\hat{D}\psi) d\tau = \int (\hat{D}^\dagger \phi)^* \psi d\tau$$

For a Hermitian operator: $\hat{D} = \hat{D}^\dagger$

Eigenfunctions and eigenvalues

- The **eigenvalue equation** for an operator $\hat{D}$ acting on a state ψ is:

$$\hat{D}\psi = d\psi$$

The constant d is the **eigenvalue** of the operator and ψ is called the **eigenfunction** of the operator.

All Hermitian operators have real eigenvalues.

The time independent Schrödinger equation for a quantum mechanical system is:

$$\hat{H}\psi(x) = E\psi(x)$$

The solutions of this equation are the energy eigenvalues E of the system corresponding to the eigenfunctions $\psi(x)$, which are also the stationary states of the system.

Properties of Eigenfunctions

- Eigenfunctions of an operator having **different eigenvalues** are called **non-degenerate eigenfunctions**. If $\psi_1, \psi_2, \psi_3, \dots, \psi_n$ are non-degenerate eigenfunctions of a Hermitian operator, normalised to unity, then they satisfy the following **orthonormality conditions**:

$$(\psi_i, \psi_j) = 0 \quad \text{for } i \neq j, \quad i = 1, 2, \dots, n, \quad j = 1, 2, \dots, n$$

$$(\psi_i, \psi_j) = 1 \quad \text{for } i = j$$

If an operator $\hat{A}$ **commutes with the parity operator** $\hat{P}$, the non-degenerate eigenfunctions of $\hat{A}$ have definite parity.

Two commuting operators $\hat{A}$ and $\hat{B}$ have simultaneous eigenfunctions. The observables represented by two operators that do not commute cannot be measured simultaneously with arbitrary accuracy.

Ehrenfest theorem

- The rate of change of an operator $\hat{D}$ associated with an observable D , which does not depend explicitly on time is given by:

$$\frac{d}{dt} \langle D \rangle = \frac{1}{i\hbar} \int \psi^* [\hat{D}, \hat{H}] \psi d\tau = \frac{1}{i\hbar} \langle [\hat{D}, \hat{H}] \rangle$$

where $\hat{H}$ is the Hamiltonian operator for the system. The **Ehrenfest theorem** for a system defined by $\hat{H} = \frac{\hat{p}_x^2}{2m} + \hat{V}(x)$ is the following set of equations:

$$\frac{d}{dt}\langle x \rangle = \frac{1}{m}\langle p_x \rangle$$

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

When an operator commutes with the Hamiltonian, the expectation value of the observable associated with it is a constant of motion.

8.7 TERMINAL QUESTIONS

1. If for two operators $\hat{A}$ and $\hat{B}$, $[\hat{A}, \hat{B}] = 1$, show that

$$[\hat{A}^2, \hat{B}^2] = 2(\hat{A}\hat{B} + \hat{B}\hat{A})$$

2. If two non-commuting operators $\hat{A}$ and $\hat{B}$ commute with their commutator $[\hat{A}, \hat{B}]$, then show that $[\hat{A}, \hat{B}^n] = n\hat{B}^{n-1}[\hat{A}, \hat{B}]$ where n is an integer. Hence, obtain the value of $[e^{\hat{A}}, \hat{B}]$.
3. Determine whether the parity operator $\hat{P}$ is Hermitian or not.
4. Calculate $[\hat{x}\hat{p}_x, \hat{H}]$ for $\hat{H} = \frac{\hat{p}_x^2}{2m} + \hat{V}(x)$.
5. Show that $[\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y$.
6. Suppose $\psi(x) = \sum_i c_i \phi_i(x)$, where $\phi_i(x)$ are eigenfunctions of a Hermitian operator $\hat{D}$ with eigenvalues d_i and $(\phi_i, \phi_j) = \delta_{ij}$. Show that $(\psi, D\psi) = \sum_i d_i |c_i|^2$.
7. The eigenvalues and eigenfunctions of a quantum mechanical operator $\hat{A}$ are denoted by a_n and ψ_n , respectively. If $f(x)$ denotes a function that can be expanded in the powers of x , show that:

$$f(\hat{A})\psi_n = f(a_n)\psi_n$$

8. An operator A is defined as $\hat{A} = a\hat{x} + ib\hat{p}_x$ where a and b are constants. Calculate the commutators $[\hat{A}, \hat{x}]$ and $[\hat{A}, \hat{A}]$.
9. Show that $[\hat{x}, \hat{p}_x^n] = in\hbar\hat{p}_x^{n-1}$

If $f(p_x)$ is a dynamical variable which can be expanded in powers of p_x , use this result to prove that:

$$[\hat{x}, f(\hat{p}_x)] = i\hbar \frac{\partial}{\partial \hat{p}_x} f(\hat{p}_x)$$

10. The normalized wave function for a particle of mass m is :

$$\psi(x) = \left(\frac{2\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2} \quad \text{for } -\infty < x < \infty$$

Calculate the expectation value of the kinetic energy of the particle.

11. An electron has the following wave function:

$$\psi(x) = \sqrt{6}e^{-x}(1 - e^{-x}), \text{ for } 0 \leq x \leq \infty$$

Determine the expectation value of x .

12. Show that the parity operator $\hat{P}$ commutes with

$$\hat{A} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + ax^2 + bx^4$$

8.8 SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. Using Eq. (8.11) : $\hat{P}\psi_1(x) = \hat{P}(Ae^{ikx}) = Ae^{-ikx}$ (changing x to $-x$)

So, $\psi_2(x) = Ae^{-ikx}$

$$\hat{P}[\psi(x)] = \hat{P}[\psi_1(x) + \psi_2(x)] = \hat{P}[Ae^{ikx} + Ae^{-ikx}] = [Ae^{-ikx} + Ae^{+ikx}]$$

$$= \psi_2(x) + \psi_1(x) = \psi(x)$$

$$\Rightarrow \hat{P}\psi(x) = \psi(x)$$

So $\psi(x)$ has even parity.

2. Remember that to determine the value of a commutator of operators, we determine the action of the commutator on an arbitrary function, let us say, ψ . We use the expressions derived in Example 8.1 for $\hat{p}_y$ and $\hat{p}_z$:

$$\begin{aligned} \text{a) } [\hat{y}, \hat{p}_y]\psi &= \hat{y}(\hat{p}_y\psi) - \hat{p}_y(\hat{y}\psi) = y\left(-i\hbar \frac{\partial\psi}{\partial y}\right) + i\hbar \frac{\partial}{\partial y}(y\psi) \\ &= -i\hbar y \frac{\partial\psi}{\partial y} + i\hbar y \frac{\partial\psi}{\partial y} + i\hbar\psi = i\hbar\psi \Rightarrow [\hat{y}, \hat{p}_y] = i\hbar \end{aligned}$$

$$\begin{aligned} \text{b) } [\hat{z}, \hat{p}_y]\psi &= \hat{z}(\hat{p}_y\psi) - \hat{p}_y(\hat{z}\psi) = z\left(-i\hbar \frac{\partial\psi}{\partial z}\right) + i\hbar \frac{\partial}{\partial z}(z\psi) \\ &= -i\hbar z \frac{\partial\psi}{\partial z} + i\hbar z \frac{\partial\psi}{\partial z} + i\hbar\psi = i\hbar\psi \Rightarrow [\hat{z}, \hat{p}_y] = i\hbar \end{aligned}$$

$$\begin{aligned} \text{c) } [\hat{x}, \hat{p}_y]\psi &= \hat{x}(\hat{p}_y\psi) - \hat{p}_y(\hat{x}\psi) = x\left(-i\hbar \frac{\partial\psi}{\partial y}\right) + i\hbar \frac{\partial}{\partial y}(x\psi) \\ &= -i\hbar x \frac{\partial\psi}{\partial y} + i\hbar x \frac{\partial\psi}{\partial y} = 0 \Rightarrow [\hat{x}, \hat{p}_y] = 0 \end{aligned}$$

$$\begin{aligned} \text{d) } [\hat{x}, \hat{p}_z]\psi &= \hat{x}(\hat{p}_z\psi) - \hat{p}_z(\hat{x}\psi) = x\left(-i\hbar \frac{\partial\psi}{\partial z}\right) + i\hbar \frac{\partial}{\partial z}(x\psi) \\ &= -i\hbar x \frac{\partial\psi}{\partial z} + i\hbar x \frac{\partial\psi}{\partial z} = 0 \Rightarrow [\hat{x}, \hat{p}_z] = 0 \end{aligned}$$

3. To prove Eq. (8.19a) we let the commutator act on a wave function ψ :

$$\begin{aligned} [\hat{A}, \hat{B}] \psi &= \hat{A}(\hat{B} \psi) - \hat{B}(\hat{A} \psi) = -[\hat{B}(\hat{A} \psi) - \hat{A}(\hat{B} \psi)] \\ &= -[\hat{B}\hat{A} - \hat{A}\hat{B}] \psi = -[\hat{B}, \hat{A}] \psi \end{aligned}$$

So, we get: $[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]$

To prove Eq. (8.19d) we have to show that:

$$[\hat{A}, \hat{B}\hat{C}] \psi = \hat{B}[\hat{A}, \hat{C}] \psi + [\hat{A}, \hat{B}] \hat{C} \psi \quad (\text{i})$$

The RHS of Eq. (i) is

$$\begin{aligned} \hat{B}[\hat{A}, \hat{C}] \psi + [\hat{A}, \hat{B}] \hat{C} \psi &= \hat{B}[\hat{A}\hat{C} - \hat{C}\hat{A}] \psi + [\hat{A}\hat{B} - \hat{B}\hat{A}] \hat{C} \psi \\ &= \hat{B}\hat{A}\hat{C}\psi - \hat{B}\hat{C}\hat{A}\psi + \hat{A}\hat{B}\hat{C}\psi - \hat{B}\hat{A}\hat{C}\psi = \hat{A}\hat{B}\hat{C}\psi - \hat{B}\hat{C}\hat{A}\psi \\ &= [\hat{A}, (\hat{B}\hat{C}) - (\hat{B}\hat{C})\hat{A}] \psi = [\hat{A}\hat{B}, \hat{C}] \psi \end{aligned}$$

which is equal to the LHS of Eq. (i). Hence, Eq. (8.19d) is proved. To prove Eq. (8.19e), we first see the action of the commutator of an operator with itself. So,

$$[\hat{A}, \hat{A}] \psi = \hat{A}(\hat{A}\psi) - \hat{A}(\hat{A}\psi) = 0 \quad (\text{ii})$$

Now, using Eq. (8.19c) and Eq. (ii) we can write:

$$[\hat{A}^2, \hat{A}] = \hat{A}[\hat{A}, \hat{A}] + [\hat{A}, \hat{A}]\hat{A} = 0$$

In the same way,

$$[\hat{A}^3, \hat{A}] = [\hat{A}(\hat{A}^2), \hat{A}] = \hat{A}[\hat{A}^2, \hat{A}] + [\hat{A}, \hat{A}]\hat{A}^2 = 0$$

So, in general, $[\hat{A}^n, \hat{A}] = 0$

4. We use Eq. (8.26) with $\psi^*(x) = \psi(x)$ and $\hat{x} = x$. So,

$$\begin{aligned} \langle x \rangle &= \int_0^L \left(\sqrt{\frac{2}{L}} \sin \frac{\pi x}{L} \right) x \left(\sqrt{\frac{2}{L}} \sin \frac{\pi x}{L} \right) dx = \frac{2}{L} \int_0^L x \sin^2 \frac{\pi x}{L} dx \\ &= \frac{1}{L} \int_0^L x \left(1 - \cos \frac{2\pi x}{L} \right) dx \quad (\text{see the margin remark}) \end{aligned}$$

$$\therefore \langle x \rangle = \frac{1}{L} \left[\frac{L^2}{2} \right] = \frac{L}{2}$$

$$\begin{aligned} &\int_0^L x \left(1 - \cos \frac{2\pi x}{L} \right) dx \\ &= \int_0^L x dx - \int_0^L x \cos \frac{2\pi x}{L} dx \\ &\int_0^L x dx = \left[\frac{x^2}{2} \right]_0^L = \frac{L^2}{2} \\ &\int_0^L x \cos \frac{2\pi x}{L} dx \\ &= \frac{L}{2\pi} \left[x \sin \frac{2\pi x}{L} \right]_0^L \\ &+ \frac{L^2}{4\pi^2} \left[\frac{\cos 2\pi x}{L} \right]_0^L = 0 \end{aligned}$$

5. a) To show that $\hat{x}$ is Hermitian we have to show that $\hat{x}$ satisfies

Eq. (8.29). Using $\hat{D} = \hat{x}$ in Eq. (8.29) and taking $\phi = \phi(x)$ and $\psi = \psi(x)$, we get:

$$\begin{aligned} \int_{-\infty}^{\infty} \phi^*(x) \psi dx &= \int_{-\infty}^{\infty} \phi^* x \psi dx = \int_{-\infty}^{\infty} x \phi^* \psi dx = \int_{-\infty}^{\infty} (\hat{x} \phi)^* \psi dx \\ &(\text{because } x \text{ is real, } x^* = x) \end{aligned}$$

So, $\hat{x}$ is a Hermitian operator. $\hat{V}(\hat{x})$ is a function of the Hermitian operator $\hat{x}$ and so, we can write $\hat{V}(\hat{x}) = V(x)$. Substituting $\hat{D} = \hat{V}(\hat{x})$ in Eq. (8.29), we get:

$$\int \phi^* \hat{V}(\hat{x}) \psi dx = \int \phi^* V(x) \psi dx = \int V(x) \phi^* \psi dx = \int (V\phi)^* \psi dx$$

Since x is real, $V(x)^* = V(x)$. Hence, $\hat{V}(\hat{x})$ is also a Hermitian operator.

b) To check if $\hat{T} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$ is Hermitian, we evaluate the integral.

$$\int_{-\infty}^{\infty} \phi^* \hat{T} \psi dx = \int_{-\infty}^{\infty} \phi^* \left[-\frac{\hbar^2}{2m} \left(\frac{d^2}{dx^2} \psi \right) \right] dx$$

Integrating the RHS of the above equation by parts, we get:

$$\int_{-\infty}^{\infty} \phi^* \left[-\frac{\hbar^2}{2m} \left(\frac{d^2 \psi}{dx^2} \right) \right] dx = -\frac{\hbar^2}{2m} \left(\phi^* \frac{d\psi}{dx} \Big|_{-\infty}^{\infty} \right) + \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \frac{d\phi^*}{dx} \frac{d\psi}{dx} dx$$

The first term on the RHS above goes to zero, since the wave function for a system goes to zero at $x = \pm\infty$. Once again, integrating the 2nd term by parts, we get,

$$\begin{aligned} \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \frac{d\phi^*}{dx} \frac{d\psi}{dx} dx &= \frac{\hbar^2}{2m} \left[\left(\frac{d\phi^*}{dx} \psi(x) \right) \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \frac{d^2 \phi^*}{dx^2} \psi(x) dx \right] \\ &= -\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \frac{d^2 \phi^*}{dx^2} \psi(x) dx = \int_{-\infty}^{\infty} \left(-\frac{\hbar^2}{2m} \frac{d^2 \phi}{dx^2} \right)^* \psi dx = \int_{-\infty}^{\infty} (\hat{T}\phi)^* \psi dx \end{aligned}$$

So, $\int_{-\infty}^{\infty} \phi^* \hat{T} \psi dx = \int_{-\infty}^{\infty} (\hat{T}\phi)^* \psi dx$ and $\hat{T}$ is a Hermitian operator.

So, the Hamiltonian operator $\hat{H} = -\frac{\hbar^2}{2m} \hat{p}_x^2 + \hat{V}(\hat{x})$ is Hermitian because both the terms in it are Hermitian.

6. We have to show that each function $f(x)$ satisfies the equation

$$\left(-\frac{d^2}{dx^2} + x^2 \right) f(x) = \lambda f(x) \text{ and calculate } \lambda, \text{ the eigenvalue.}$$

$$\text{For } f(x) = \exp\left(-\frac{x^2}{2}\right)$$

$$\left(-\frac{d^2}{dx^2} + x^2 \right) \exp\left(-\frac{x^2}{2}\right) = e^{-x^2/2} - x^2 \exp\left(-\frac{x^2}{2}\right) + x^2 \exp\left(-\frac{x^2}{2}\right) = e^{-x^2/2}$$

So, the eigenvalue $\lambda = 1$. For $f(x) = x \exp\left(-\frac{x^2}{2}\right)$

$$\left(-\frac{d^2}{dx^2} + x^2\right)\left(xe^{-x^2/2}\right) = \left[3xe^{-x^2/2} - x^3e^{-x^2/2} - x^3e^{-x^2/2}\right] = 3xe^{-x^2/2}$$

So the eigenvalue is $\lambda = 3$

7. In Eq. (8.59), we set $[\hat{D}, \hat{H}] = 0$. So, we get:

$$\frac{d}{dt}\langle D \rangle = 0 \Rightarrow \langle D \rangle \text{ is a constant of motion.}$$

Terminal Questions

1. $[\hat{A}^2, \hat{B}^2] = \hat{A}[\hat{A}, \hat{B}^2] + [\hat{A}, \hat{B}^2]\hat{A}$ (using Eq. (8.19c))
 $= \hat{A}\{\hat{B}[\hat{A}, \hat{B}] + [\hat{A}, \hat{B}]\hat{B}\} + \{\hat{B}[\hat{A}, \hat{B}] + [\hat{A}, \hat{B}]\hat{B}\}\hat{A}$
 $= \hat{A}\hat{B} + \hat{A}\hat{B} + \hat{B}\hat{A} + \hat{B}\hat{A} \quad \because [\hat{A}, \hat{B}] = 1$
2. For $n=1$, the given equation is true because: $[\hat{A}, \hat{B}] = (1)\hat{B}^{1-1}[\hat{A}, \hat{B}]$

For $n=2$, the given equation is also true:

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

$$\because [\hat{B}, [\hat{A}, \hat{B}]] = 0, \quad \hat{B}[\hat{A}, \hat{B}] = [\hat{A}, \hat{B}]\hat{B}$$

Let us assume then that the relation holds for an arbitrary value of n :

$$[\hat{A}, \hat{B}^n] = n\hat{B}^{n-1}[\hat{A}, \hat{B}] \quad (i)$$

Hence, using Eq. (8.19d), we have:

$$\begin{aligned} [\hat{A}, \hat{B}^{n+1}] &= [\hat{A}, \hat{B}^n \hat{B}] = \hat{B}[\hat{A}, \hat{B}^n] + [\hat{A}, \hat{B}^n]\hat{B} \\ &= n\hat{B}^n[\hat{A}, \hat{B}] + [\hat{A}, \hat{B}]\hat{B}^n \quad \text{using Eq. (i)} \\ &= (n+1)\hat{B}^n[\hat{A}, \hat{B}] \end{aligned}$$

Hence, if Eq. (i) is true for n it is also true for $n+1$. Thus, Eq. (i) is true for any value of n (read the margin remark). Now, you know that

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!}$$

$$\begin{aligned} \therefore [e^{\hat{x}}, \hat{p}_x] &= \sum_{n=0}^{\infty} \frac{1}{n!} [\hat{x}^n, \hat{p}_x] = - \sum_{n=0}^{\infty} \frac{1}{n!} [\hat{p}_x, \hat{x}^n] \\ &= - \sum_{n=1}^{\infty} \frac{1}{(n-1)!} \hat{x}^{n-1} [\hat{p}_x, \hat{x}] \quad (\text{see the margin remark}) \\ &= - \sum_{n=1}^{\infty} \frac{1}{(n-1)!} \hat{x}^{n-1} [\hat{p}_x, \hat{x}] = i\hbar \sum_{n=1}^{\infty} \frac{\hat{x}^{n-1}}{(n-1)!} = i\hbar e^{\hat{x}}. \end{aligned}$$

This is the method of induction which you have studied in your school mathematics courses.

You can use Eq. (i) for calculating this commutator because

$$[\hat{x}, [\hat{p}_x, \hat{x}]] = [\hat{x}, -i\hbar] = 0;$$

$$[\hat{p}_x, [\hat{p}_x, \hat{x}]] = [\hat{p}_x, -i\hbar] = 0;$$

3. We define the expectation value of the parity operator $\hat{P}$ using Eq. (8.26):

$$\begin{aligned}\int_{-\infty}^{\infty} \psi^*(x) \hat{P} \psi(x) dx &= \int_{-\infty}^{\infty} \psi^*(x) \psi(-x) dx = - \int_{-\infty}^{\infty} \psi^*(-x') \psi(x') dx' \\ &\quad (\text{where } x' = -x) \\ &= \int_{-\infty}^{\infty} \{\hat{P} \psi(x')\}^* \psi(x') dx'\end{aligned}$$

Hence, $\hat{P}$ is a Hermitian operator.

4. Now using Eq. (8.19a), we can write:

$$[\hat{x}\hat{p}_x, \hat{H}] = [\hat{x}\hat{p}_x, \hat{p}_x^2/2m + \hat{V}(x)] = \frac{1}{2m} [\hat{x}\hat{p}_x, \hat{p}_x^2] + [\hat{x}\hat{p}_x, \hat{V}(x)] \quad (i)$$

Using Eqs (8.19b and 8.68), we get

$$[\hat{x}\hat{p}_x, \hat{p}_x^2] = \hat{x}[\hat{p}_x, \hat{p}_x^2] + [\hat{x}, \hat{p}_x^2]\hat{p}_x = 0 + \hat{p}_x[\hat{x}, \hat{p}_x]\hat{p}_x + [\hat{x}, \hat{p}_x]\hat{p}_x^2 = 2i\hbar\hat{p}_x^2 \quad (ii)$$

$$[\hat{x}\hat{p}_x, \hat{V}(x)] = \hat{x}[\hat{p}_x, \hat{V}(x)] + [\hat{x}, \hat{V}(x)]\hat{p}_x = \hat{x}\left[-i\hbar\frac{dV(x)}{dx}\right] + 0 \quad (iii)$$

Substituting from Eqs. (ii) and (iii) into Eq. (i), we get

$$[\hat{x}\hat{p}_x, \hat{H}] = \frac{1}{2m} (2i\hbar\hat{p}_x^2) - i\hbar\hat{x}\left[\frac{dV(x)}{dx}\right] = i\hbar\left[\frac{\hat{p}_x^2}{m} - \hat{x}\frac{dV(x)}{dx}\right]$$

5. We define $[\hat{L}_z, \hat{L}_x] = \hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z$

From Example 8.1(b) we can write:

$$L_x = yp_z - zp_y; L_y = zp_x - xp_z; L_z = xp_y - yp_x$$

$$\text{Hence, } [\hat{L}_z, \hat{L}_x] = [\hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \hat{y}\hat{p}_z - \hat{z}\hat{p}_y]$$

Using Eq. (8.19b), we get

$$[\hat{L}_z, \hat{L}_x] = [\hat{x}\hat{p}_y, \hat{y}\hat{p}_z] - [\hat{x}\hat{p}_y, \hat{z}\hat{p}_y] - [\hat{y}\hat{p}_x, \hat{y}\hat{p}_z] + [\hat{y}\hat{p}_x, \hat{z}\hat{p}_y]$$

$$\begin{aligned}[\hat{x}\hat{p}_y, \hat{y}\hat{p}_z] &= \hat{x}[\hat{p}_y, \hat{y}\hat{p}_z] + [\hat{x}, \hat{y}\hat{p}_z]\hat{p}_y \\ &= \hat{x}\hat{y}[\hat{p}_y, \hat{p}_z] + \hat{x}[\hat{p}_y, \hat{y}]\hat{p}_z + \hat{y}[\hat{x}, \hat{p}_z]\hat{p}_y + [\hat{x}, \hat{y}]\hat{p}_z\hat{p}_y \\ &= 0 - i\hbar\hat{x}\hat{p}_z + 0 + 0 = -i\hbar\hat{x}\hat{p}_z\end{aligned}$$

$$\begin{aligned}[\hat{x}\hat{p}_y, \hat{z}\hat{p}_y] &= \hat{x}[\hat{p}_y, \hat{z}\hat{p}_y] + [\hat{x}, \hat{z}\hat{p}_y]\hat{p}_y \\ &= \hat{x}\hat{z}[\hat{p}_y, \hat{p}_y] + \hat{x}[\hat{p}_y, \hat{z}]\hat{p}_y + \hat{z}[\hat{x}, \hat{p}_y]\hat{p}_y + [\hat{x}, \hat{z}]\hat{p}_y^2 = 0\end{aligned}$$

Similarly,

$$[\hat{y}\hat{p}_x, \hat{y}\hat{p}_z] = 0 \text{ and } [\hat{y}\hat{p}_x, \hat{z}\hat{p}_y] = i\hbar\hat{z}\hat{p}_x$$

$$\therefore [\hat{L}_z, \hat{L}_x] = -i\hbar\hat{x}\hat{p}_z - 0 - 0 + i\hbar\hat{z}\hat{p}_x = i\hbar(\hat{z}\hat{p}_x - \hat{x}\hat{p}_z) = i\hbar\hat{L}_y$$

6. Since $\psi(x) = \sum_i c_i \phi_i(x)$, we can write :

$$\langle D \rangle = \sum_i \sum_j c_i^* c_j d_j (\phi_i, \phi_j) = \sum_i \sum_j c_i^* c_j d_j \delta_{ij} = \sum_i |c_i|^2 d_i$$

since only those terms of the series will survive for which $j = i$.

7. We can write $\hat{A}\psi_n = a_n\psi_n$

$$\begin{aligned} f(\hat{A}) &= b_0 + b_1\hat{A} + b_2\hat{A}^2 + \dots + a_n\hat{A}^n \\ \therefore f(\hat{A})\psi_n &= [b_0 + b_1\hat{A} + b_2\hat{A}^2 + \dots + b_n\hat{A}^n]\psi_n \\ &= b_0\psi_n + b_1(\hat{A}\psi_n) + b_2(\hat{A}^2\psi_n) + \dots + b_n(\hat{A}^n\psi_n) \end{aligned} \quad (i)$$

$$\text{Now } \hat{A}^2\psi_n = \hat{A}(\hat{A}\psi_n) = \hat{A}(a_n\psi_n) = a_n(\hat{A}\psi_n) = a_n^2\psi_n$$

$$\hat{A}^3\psi_n = \hat{A}(\hat{A}^2\psi_n) = a_n^2(\hat{A}\psi_n) = a_n^3\psi_n$$

So, we can write: $\hat{A}^n\psi_n = a_n^n\psi_n$.

$$\text{And Eq. (i) is: } f(\hat{A})\psi_n = [b_0 + b_1a_n + b_2a_n^2 + \dots + b_na_n^n]\psi_n = f(a_n)\psi_n$$

$$\begin{aligned} 8. \quad (i) \quad [\hat{A}, \hat{x}] &= [a\hat{x} + ib\hat{p}_x, \hat{x}] = a[\hat{x}, \hat{x}] + ib[\hat{p}_x, \hat{x}] \\ &= a \cdot 0 - ib[\hat{x}, \hat{p}_x] = -ib(i\hbar) = b\hbar \end{aligned}$$

$$\begin{aligned} (ii) \quad [\hat{A}, \hat{A}] &= [a\hat{x} + ib\hat{p}_x, a\hat{x} + ib\hat{p}_x] \\ &= a^2[\hat{x}, \hat{x}] + iab[\hat{p}_x, \hat{x}] + iab[\hat{x}, \hat{p}_x] - b^2[\hat{p}_x, \hat{p}_x] \\ &= 0 + iab(-i\hbar) + iab(i\hbar) - 0 = 0 \end{aligned}$$

9. Using the results of TQ 2, we can write:

$$[\hat{A}, \hat{B}], [\hat{A}, \hat{B}^n] = n\hat{B}^{n-1}[\hat{A}, \hat{B}] \text{ where } n \text{ is an integer.}$$

For $\hat{A} = \hat{x}$ and $\hat{B} = \hat{p}_x$, we can use this result:

$$\text{because } [\hat{x}, [\hat{x}, \hat{p}_x]] = [\hat{x}, i\hbar] = 0 \text{ and } [\hat{p}_x, [\hat{x}, \hat{p}_x]] = [\hat{p}_x, i\hbar] = 0$$

We can write (see also the margin remark):

$$[\hat{x}, \hat{p}_x^n] = n\hat{p}_x^{n-1}[\hat{x}, \hat{p}_x] = i\hbar n\hat{p}_x^{n-1} \quad (i)$$

(To obtain these results from first principles, you can follow the steps of Terminal Question 2).

We can write a function $f(p_x)$ as :

$$f(p_x) = a_0 + a_1p_x + a_2p_x^2 + a_3p_x^3 + \dots + a_np_x^n$$

$$\text{So: } \hat{f}(\hat{p}_x) = a_0 + a_1\hat{p}_x + a_2\hat{p}_x^2 + \dots + a_n\hat{p}_x^n$$

where $a_0, a_1, \dots, a_n$ are constants. So we can write,

$$[\hat{x}, \hat{f}(\hat{p}_x)] = [\hat{x}, a_0] + a_1[\hat{x}, \hat{p}_x] + a_2[\hat{x}, \hat{p}_x^2] + \dots + a_n[\hat{x}, \hat{p}_x^n] \quad (ii)$$

Using the results of Eq. (i) in Eq. (ii), we get

$$[\hat{x}, \hat{f}(\hat{p}_x)] = 0 + a_1(i\hbar) + 2a_2(i\hbar)\hat{p}_x + \dots + a_n(i\hbar)n\hat{p}_x^{n-1} = i\hbar \frac{\partial}{\partial \hat{p}_x} f(\hat{p}_x)$$

$$10. \text{ Using Eq. (8.26) with } \hat{T} = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} \text{ and } \psi(x) = \left(\frac{2\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2}, \text{ we get:}$$

$$\begin{aligned}\frac{d}{dx}e^{-\alpha x^2} &= -2\alpha x e^{-\alpha x^2} \\ \frac{d^2(e^{-\alpha x^2})}{dx^2} &= \frac{d}{dx}(-2\alpha x e^{-\alpha x^2}) \\ &= -2\alpha e^{-\alpha x^2} \\ &\quad + 4\alpha^2 x^2 e^{-\alpha x^2} \\ &= -2\alpha(1 - 2\alpha x^2)e^{-\alpha x^2}\end{aligned}$$

Using Table 7.1(4)

$$\int_{-\infty}^{\infty} e^{-2\alpha x^2} dx = \left(\frac{\pi}{2\alpha}\right)^{1/2}$$

and

$$\int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} dx = \frac{1}{2} \left(\frac{\pi}{8\alpha^3}\right)^{1/2}$$

$$\begin{aligned}\langle T \rangle &= (2\alpha/\pi)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha x^2} \left[-\frac{\hbar^2}{2m} \left(\frac{d^2}{dx^2} e^{-\alpha x^2} \right) \right] dx \\ &= (2\alpha/\pi)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha x^2} \left[-\frac{\hbar^2}{2m} (-2\alpha(1 - 2\alpha x^2)e^{-\alpha x^2}) \right] dx \\ &= -\frac{\hbar^2}{2m} (2\alpha/\pi)^{1/2} \left[-\int_{-\infty}^{\infty} 2\alpha e^{-\alpha x^2} dx + \int_{-\infty}^{\infty} 4\alpha^2 x^2 e^{-\alpha x^2} dx \right] \\ &= -\frac{\hbar^2}{2m} \left(\frac{2\alpha}{\pi}\right)^{1/2} \left[-2\alpha \left(\frac{\pi}{2\alpha}\right)^{1/2} + \frac{4\alpha^2}{4\alpha} \left(\frac{\pi}{2\alpha}\right)^{1/2} \right] = \frac{1}{2} \left(\frac{\alpha \hbar^2}{m} \right)\end{aligned}$$

(see the details of the calculation in the margin remark).

11. Using Eq. (8.26) for $\hat{D} = \hat{x}$ and $\psi(x) = \sqrt{6}e^{-x}(1 - e^{-x})$, we get

$$\begin{aligned}\langle x \rangle &= 6 \int_0^{\infty} x e^{-2x} (1 - e^{-x})^2 dx = 6 \int_0^{\infty} (x e^{-2x} + x e^{-4x} - 2x e^{-3x}) dx \\ &= 6 \left[\frac{1}{2^2} + \frac{1}{4^2} - \frac{2}{3^2} \right] = \frac{13}{24} \quad [\text{Using Table 7.1(2)}]\end{aligned}$$

12. Now $\hat{A} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + ax^2 + bx^4$

Since $\hat{A}(-x) = \hat{A}(x)$

$$\hat{P}[\hat{A}(x)\psi(x)] = \hat{A}(-x)\psi(-x) = \hat{A}(x)[\hat{P}\psi(x)] \Rightarrow [\hat{P}\hat{A}(x) - \hat{A}(x)\hat{P}]\psi(x) = 0$$

Since $\psi(x)$ is arbitrary,

$$[\hat{P}\hat{A}(x) - \hat{A}(x)\hat{P}] = 0 \Rightarrow \hat{A} \text{ commutes with } \hat{P}.$$

FURTHER READINGS

1. Quantum Physics of Atoms, Molecules, Solids, Nuclei and Particles, Robert Eisberg and Robert Resnick, Wiley Student Edition (2006).
2. Modern Physics, Raymond Serway, Clement Moses and Curt Moyer, 3rd Edition, Cengage Learning (2012).

TABLE OF PHYSICAL CONSTANTS

Symbol	Quantity	Value
c	Speed of light in vacuum	$2.998 \times 10^8 \text{ ms}^{-1}$
μ_0	Permeability of free space	$1.257 \times 10^{-6} \text{ NA}^{-2}$
ϵ_0	Permittivity of free space	$8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$
$1/4\pi\epsilon_0$		$8.988 \times 10^9 \text{ Nm}^2\text{C}^{-2}$
e	Charge of the proton	$1.602 \times 10^{-19} \text{ C}$
$-e$	Charge of the electron	$1.602 \times 10^{-19} \text{ C}$
h	Planck's constant	$6.626 \times 10^{-34} \text{ Js}$
$\hbar$	$h / 2\pi$	$1.054 \times 10^{-34} \text{ Js}$
m_e	Electron rest mass	$9.109 \times 10^{-31} \text{ kg}$
$-e/m_e$	Electron charge to mass ratio	$1.759 \times 10^{-19} \text{ Ckg}^{-1}$
m_p	Proton rest mass	$1.673 \times 10^{-27} \text{ kg}$
m_n	Neutron rest mass	$1.675 \times 10^{-27} \text{ kg}$
a_0	Bohr radius	$5.292 \times 10^{-11} \text{ m}$
N_A	Avogadro constant	$6.022 \times 10^{23} \text{ mol}^{-1}$
R	Universal gas constant	$8.315 \text{ J mol}^{-1}\text{K}^{-1}$
k_B	Boltzmann constant	$1.381 \times 10^{-23} \text{ JK}^{-1}$
G	Universal gravitational constant	$6.673 \times 10^{-11} \text{ Nm}^2\text{kg}^{-2}$

LIST OF BLOCKS AND UNITS: BPHET-141

BLOCK 1: THE SPECIAL THEORY OF RELATIVITY

- | | |
|--------|----------------------------------|
| Unit 1 | Postulates of Special Relativity |
| Unit 2 | Relativistic Kinematics |
| Unit 3 | Relativistic Dynamics |

BLOCK 2: INTRODUCTION TO QUANTUM MECHANICS

- | | |
|--------|--|
| Unit 4 | Birth of Quantum Physics |
| Unit 5 | Wave-Particle Duality |
| Unit 6 | The Uncertainty Principle and its Consequences |
| Unit 7 | Schrödinger Equation |
| Unit 8 | Observables and Operators |

BLOCK 3: APPLICATIONS OF QUANTUM MECHANICS TO SIMPLE SYSTEMS

- | | |
|---------|-----------------------|
| Unit 9 | Particle in a Box |
| Unit 10 | Step Potential |
| Unit 11 | Barrier Potential |
| Unit 12 | Finite Potential Well |

BLOCK 4: NUCLEAR PHYSICS

- | | |
|---------|-------------------------|
| Unit 13 | Radioactivity |
| Unit 14 | The Atomic Nucleus |
| Unit 15 | Applied Nuclear Science |

Special Theory of Relativity: Constancy of Speed of Light, Postulates of Special Theory of Relativity, Lorentz Transformation, Length Contraction, Time Dilation, Examples, Velocity Addition Theorem, Doppler Effect, Variation of Mass with Velocity, Energy-Mass Equivalence, Relativistic Energy and Momentum.

An Introduction to Quantum Mechanics: Birth of Quantum Physics, Blackbody Radiation, Planck's Quantum Hypothesis, Planck's constant and light as a collection of photons; Photo-electric effect and Compton scattering. Problems with Rutherford model – instability of atoms and observation of discrete atomic spectra; Bohr Model, Bohr's quantization rule and atomic stability; calculation of energy levels for hydrogen like atoms and their spectra.

de-Broglie hypothesis and matter waves; Davisson-Germer experiment, Wave-Particle Duality, Matter waves and wave amplitude, Wave Packet, Group Velocity.

The Uncertainty Principle and its Consequences, Thought Experiments: Position measurement – gamma ray microscope thought experiment; Two slit interference experiment with photons, atoms and particles; Complementarity; Estimating minimum energy of a confined particle using uncertainty principle; Energy-time uncertainty principle.

Postulates of Quantum Mechanics, Time Dependent and Time Independent Schrödinger Equation in One Dimension, Statistical Interpretation of Wave Function, Probability Current Density and Continuity Equation, Normalization of Wave Functions, Wave Function in Momentum Space; Observables and Operators, Linear Momentum and Energy Operators; Parity Operator and its Eigenvalues; Commutation Relations, Expectation Values.

Applications of Quantum Mechanics: One Dimensional Infinitely Rigid Box – energy eigenvalues and eigenfunctions, normalization, quantum dot as an example, Particle in a Box, Free Particle, Step Potential and Rectangular Potential Barrier, Quantum mechanical scattering and Tunneling; One Dimensional Potential Well and barrier.

Nuclear Physics: Radioactivity: Stability of nucleus; Law of Radioactive Decay, Mean life and half-life; Radioactive Equilibria, Natural Radioactive Series, Law of α decay, β decay – energy released, spectrum and Pauli's prediction of neutrino; γ -ray emission. General Properties of Nuclei: Size and structure of atomic nucleus and its relation with atomic weight; Impossibility of an electron being in the nucleus as a consequence of the uncertainty principle. Nature of nuclear force, NZ graph, semi-empirical mass formula and binding energy; Stability of Nuclei: Binding Energy Curve. Fission and fusion – mass defect, generation of energy; Fission – nature of fragments and emission of neutrons. Nuclear reactor: slow neutrons and their interactions with Uranium 235; Fusion and thermonuclear reactions.