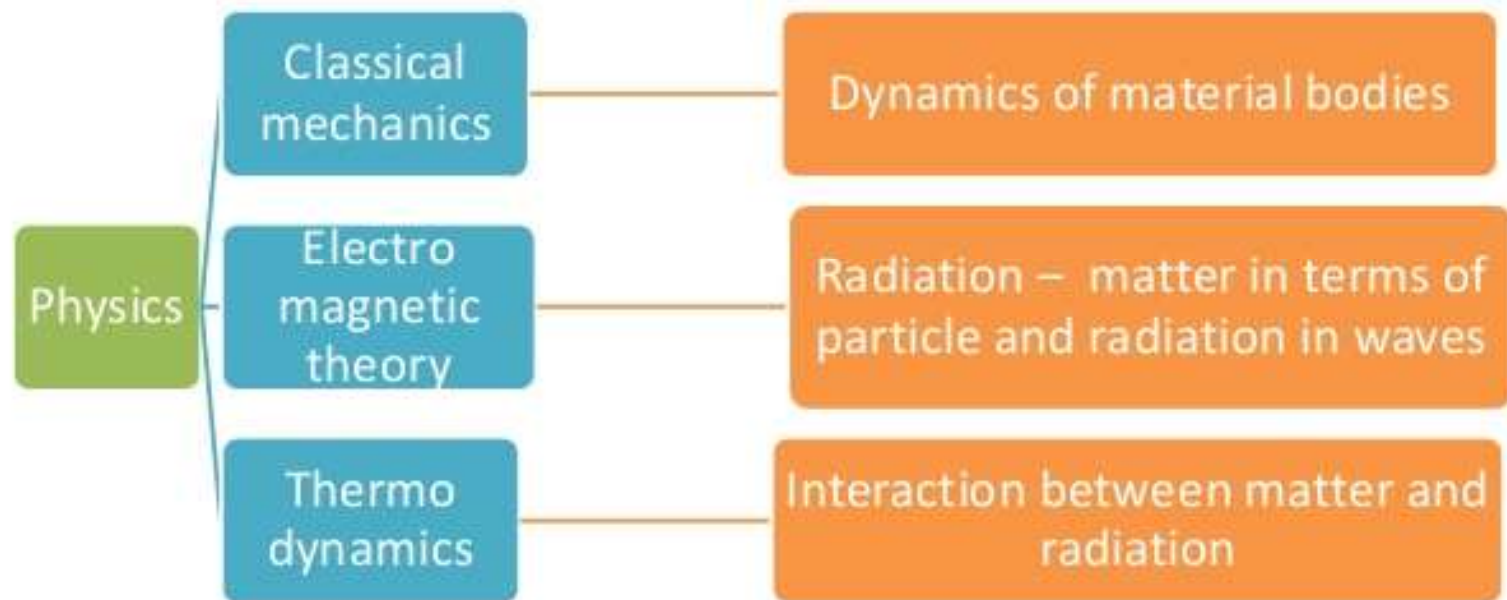


ORIGIN OF QUANTUM MECHANICS

End of 19th century - 1885



Ultimate description of nature...!!!!!!!

Classical Mechanics

- Used to predict the dynamics of *material bodies*
- *Maxwell's electromagnetism provided the proper framework to study radiation*
- *Matter and radiation were described in terms of particles and waves, respectively.*

Classical theory of electromagnetism, and thermodynamics—made people believe that the ultimate description of nature had been achieved.



At the turn of the 20th, however, classical physics, which had been quite unassailable, was seriously challenged on two major fronts:

1. Relativistic domain

Einstein's 1905 theory of relativity showed that the validity of Newtonian mechanics ceases at very high speeds (i.e., at speeds comparable to that of light).

2. Microscopic domain

As soon as new experimental techniques were developed to the point of probing atomic and subatomic structures, it turned out that classical physics fails miserably in providing the proper explanation for several newly discovered phenomena.

Failures of Classical Physics

Microscopic phenomena's such as

- ❑ Blackbody Radiation
- ❑ Photoelectric effect
- ❑ Atomic stability
- ❑ Atomic spectroscopy

The first real breakthrough came in 1900 when Max Planck introduced the concept of the *quantum of energy*.

➤ Explained the phenomenon of **Blackbody radiation**

□ First he postulated the phenomena of radiation “*as the energy exchange between radiation and its surroundings takes place in discrete, or quantized, amounts*”.

□ He argued that the energy exchange between an *electromagnetic wave of frequency (ν) and matter* occurs only in integer multiples of *$h\nu$* , which he called the energy of a quantum, where *h* is a fundamental constant called *Planck's constant*.

Planck's radiation law

- Planck assumed that the radiation in the cavity was emitted (and absorbed) by some sort of "oscillators" contained in the walls. He used Boltzmann's statistical methods to arrive at the following formula:

$$I(\lambda, T) = \frac{2\pi c^2 h}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}$$

Planck's radiation law

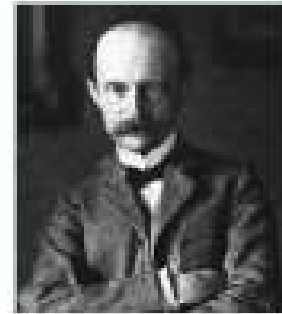
- Planck made two modifications to the classical theory:
 - 1) The oscillators (of electromagnetic origin) can only have certain discrete energies determined by $E_n = nh\nu$, where n is an integer, ν is the frequency, and h is called Planck's constant.

$$h = 6.6261 \times 10^{-34} \text{ J}\cdot\text{s}$$

- 2) The oscillators can absorb or emit energy in discrete multiples of the fundamental quantum of energy given by

$$\Delta E = h\nu$$

Max Planck and the blackbody problem



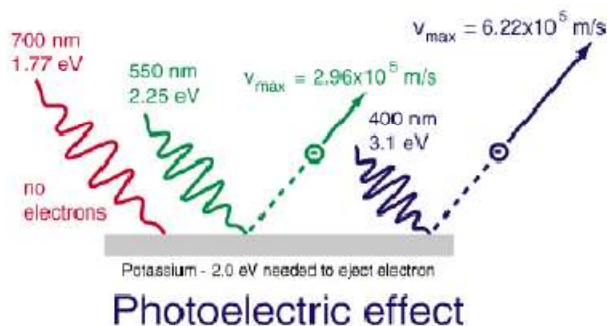
- **Max Planck** 1858-1947
 - Expert in thermodynamics and statistical mechanics
 - Around 1900: Proposes first an empirical formula (based on real physics) to reproduce both the high and low wavelength parts of the emission spectrum
 - Remarkable agreement with experimental results
 - Then, works on a theoretical basis of the formula

1918 Nobel Prize

Later Planks quantum theory prompted to introduce many concepts

Photoelectric effect

In 1905 Einstein provided a powerful consolidation to Planck's quantum concept. In trying to **understand the photoelectric effect**, Einstein recognized that Planck's idea of the quantization of the *electromagnetic waves must be valid for light as well*.



Light can eject electrons from a metal, but only if its frequency is above a threshold frequency (characteristic for each metal).

Light itself is made of discrete bits of energy (or tiny particles), called photons each of energy $h\nu$, ν being the frequency of the light.

Classically, for light as a wave, its energy is proportional to the square of its amplitude.

For particles, energy is proportional to frequency

Einstein (1905) proposed that light has particle nature (as well as wave nature).

light is quantized (photons).

□ The number of electrons emitted by a surface is proportional to the number of incident photons.

□ An electron is emitted as soon as a photon reaches the surface.

$$h\nu = h\nu_0 + \frac{1}{2} mV^2$$

$\phi = h\nu_0 =$ Work function of the material.

$\frac{1}{2} mV^2 =$ Maximum kinetic energy

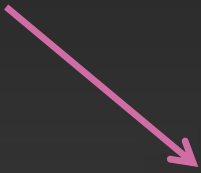
Threshold Frequency(ν_0)

$$h\nu_0 = \phi \text{ (work function)}$$

$$\frac{hc}{\lambda_0} = \phi$$

λ_0 = Threshold wavelength

c = speed of light



The minimum amount of energy that has to be given to an electron to release it from the surface of the material and varies depending on the material.

The introduction of the photon concept enabled Einstein to give an elegantly accurate explanation to the photoelectric problem, which had been waiting for a solution ever since its first experimental observation by Hertz in 1887.



- ⊙ UV light causes electrons to be released from the surface of the zinc.
- ⊙ Emission of electrons commences at the instant the surface is irradiated.
- ⊙ The frequency of the radiation must exceed the threshold frequency.
- ⊙ Intensity of radiation has no effect.

Prob.1

Copper has a work function of 4.5 eV. Therefore, the cut-off frequency and wavelength for light ejecting electrons from copper?

Work function (Φ) = $h \nu_o = h \nu_{\text{cutoff}}$

$h \nu_{\text{cutoff}} = 4.5 \text{ eV}$, or

$$\nu_{\text{cutoff}} = 4.5 \times (1.6 \times 10^{-19} \text{ C}) / 6.63 \times 10^{-34} \text{ J-sec}$$

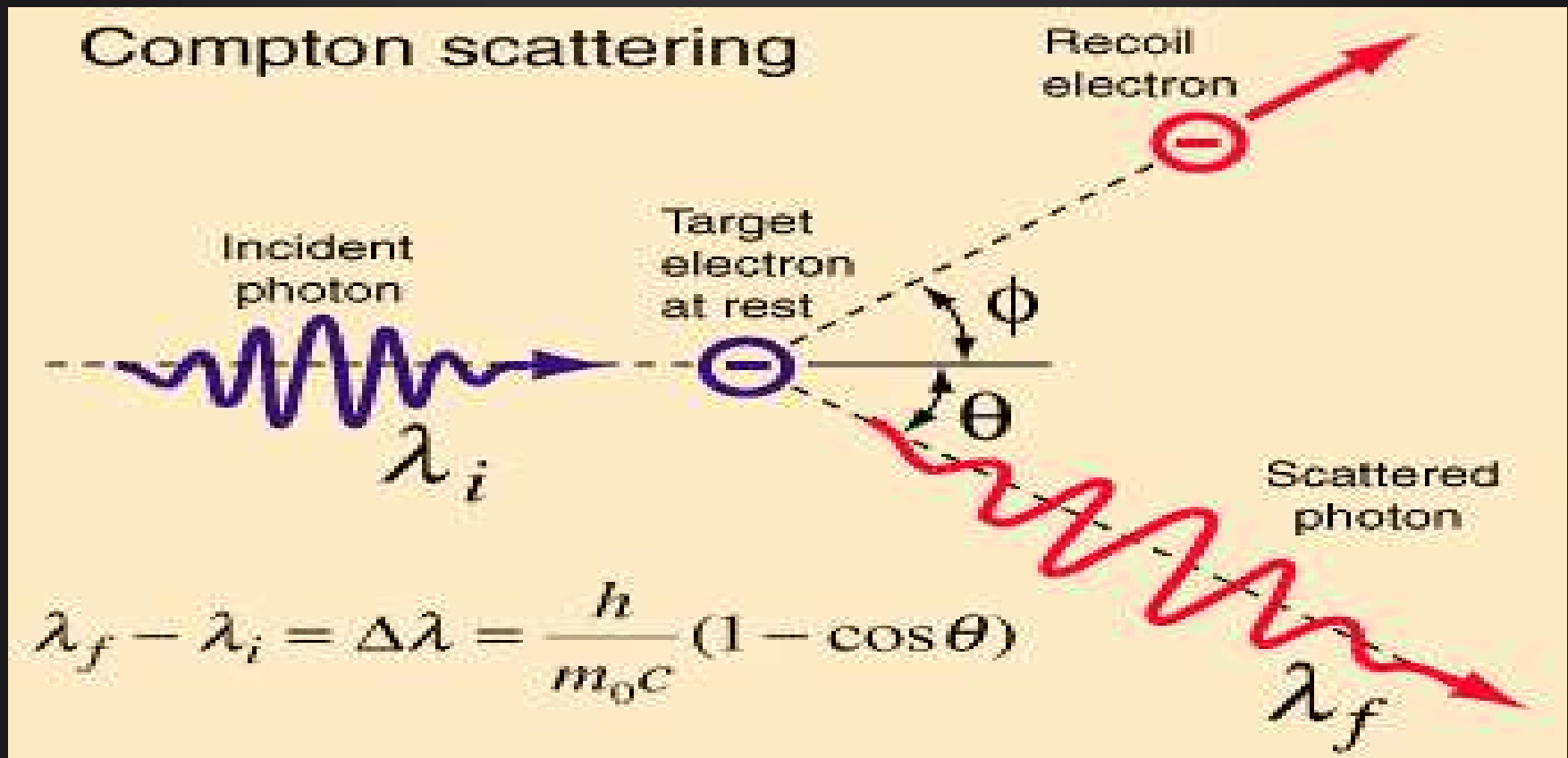
$$\nu_{\text{cutoff}} = 1.09 \times 10^{15} \text{ Hz.}$$

Since $\lambda f = c$, $\lambda_{\text{cutoff}} = c / \nu_{\text{cutoff}}$, or

$$\begin{aligned} \lambda_{\text{cutoff}} &= (3 \times 10^8 \text{ m/s}) / (1.09 \times 10^{15} \text{ cycles/sec}) \\ &= 276 \text{ nm (in the UV range)} \end{aligned}$$

COMPTON SCATTERING

When light encounters charged particles, the particles will interact with the light and cause some of the light to be scattered.



Compton Effect

Statement:

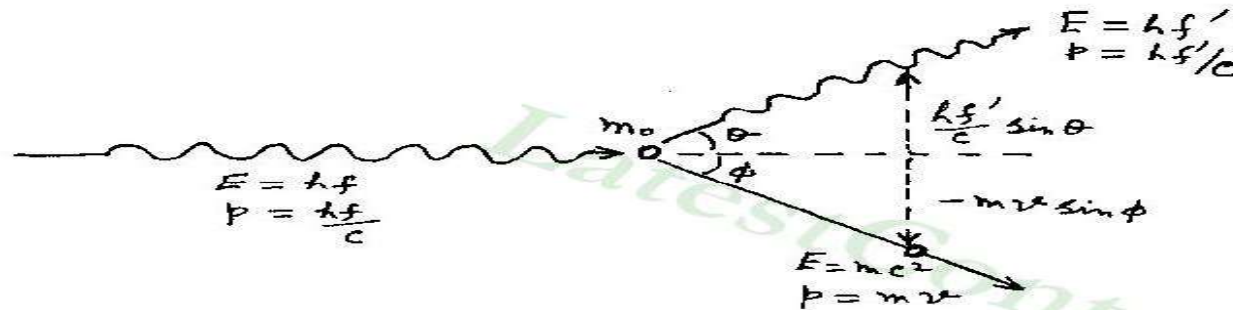
"The phenomenon in which an x-ray photon is scattered from an electron, the scattered photon having the smaller frequency than the incident photon"

Explanation:

According to the classical theory, the wavelength of x-rays scattered by electrons must be equal to the wavelength of primary x-rays. But a change in wavelength has been observed by experiments. This is called the Compton effect.

Illustration:

Suppose an x-ray photon of energy hf collides with an electron at rest and is then changed in direction and frequency as shown in the figure.



Applying Law of Conservation of Energy, we get

$$\begin{aligned} E_{\text{initial}} &= E_{\text{final}} \\ E + m_0 c^2 &= E' + E_e \\ \text{or } hf + m_0 c^2 &= hf' + m c^2 \\ \text{or } hf - hf' &= (m - m_0) c^2 \end{aligned}$$



.....(1)

Applying Law of Conservation of Linear momentum in the direction of the incident photon, we have

$$\begin{aligned} (p_x)_{\text{initial}} &= (p_x)_{\text{final}} \\ \text{or } \frac{hf}{c} + 0 &= \frac{hf'}{c} \cos \theta + mv \cos \phi \end{aligned} \quad \text{..... (2)}$$

Applying Law of Conservation of Linear Momentum in the direction at right angle to the incident photon,

$$\begin{aligned} (p_y)_{\text{initial}} &= (p_y)_{\text{final}} \\ \text{or } 0 &= \frac{hf'}{c} \sin \theta - mv \sin \phi \end{aligned} \quad \text{..... (3)}$$

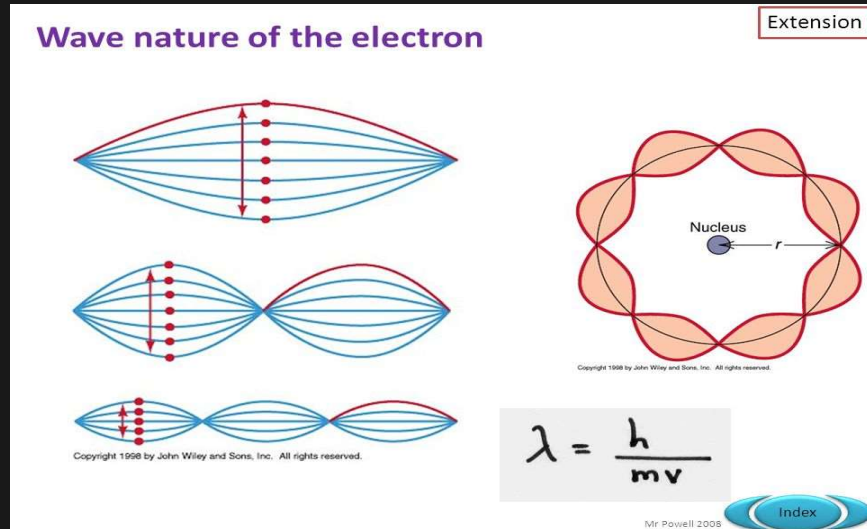
Compton shift in wavelength

$$\Delta\lambda = \lambda_{\text{scattered}} - \lambda_{\text{incident}} = (h/mc)[1 - \cos(\theta)]$$

θ = scattering angle of scattered photon from
the original direction of incoming photon

The scattered photons will have less energy and less momentum after collision with electrons, and so should have a larger wavelength according to the formula

Matter waves (de Broglie hypothesis)



□ Prince Louis V. de Broglie suggested that massive particles (i.e. matter) should have wave properties similar to electromagnetic radiation.

□ The energy can be written analogous to photons

What applies to mass less particles $E = pc = hf$, i.e. photons, also applies to massive particles.

$$hf = pc = p\lambda f$$

- The wavelength of a matter wave is called the de Broglie wavelength,

$$\lambda = \frac{h}{p}$$

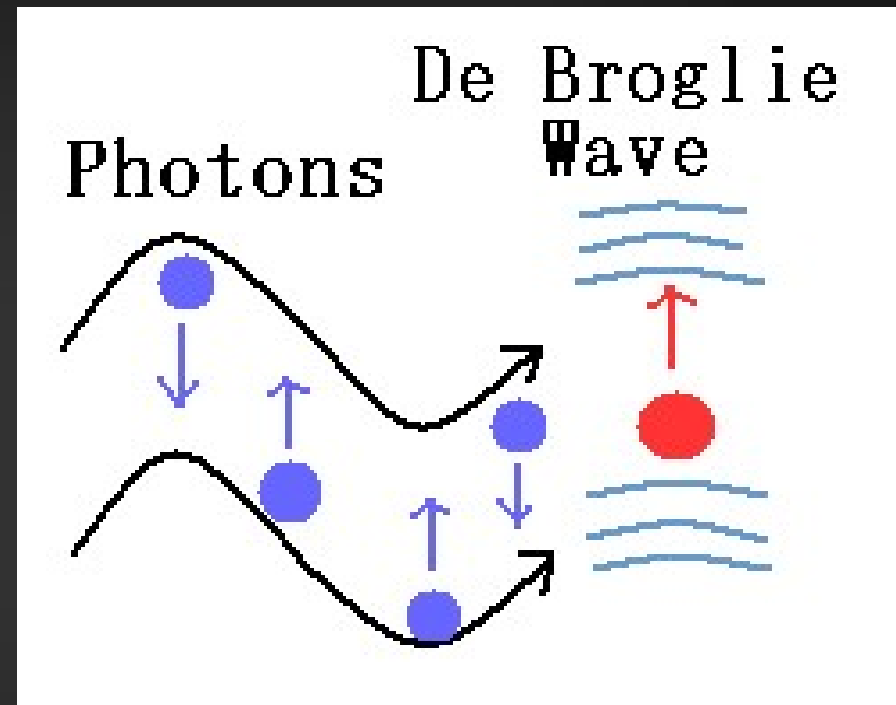
$$K = \frac{1}{2}mv^2 = \frac{1}{2} \frac{(mv)^2}{m} = \frac{p^2}{2m}$$

$$\therefore \quad p = \sqrt{2mK}$$

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mK}}$$

For same energy $\lambda \propto \frac{1}{\sqrt{m}}$

$$\therefore \quad \frac{\lambda_p}{\lambda_\alpha} = \sqrt{\frac{m_\alpha}{m_p}} = \sqrt{\frac{4m_p}{m_p}} = \frac{2}{1}$$



PROPERTIES OF MATTER WAVES

- ✓ Matter waves are not electromagnetic in nature
- ✓ Matter-wave represents the probability of finding a particle in space.
- ✓ Matter waves are independent of the charge on the material particle.
- ✓ Electron microscope works on the basis of de-Broglie waves.
- ✓ Matter waves can propagate in a vacuum, hence they are not mechanical wave.
- ✓ The number of de-Broglie waves associated with n th orbital is n .
- ✓ The phase velocity of matter waves can be greater than the speed of light.
- ✓ The number of de-Broglie waves associated with the n th orbital electron is n .

POSTULATE 1: STATE SPACE

- ❖ Any isolated physical space is associated with a complex vector space (Hilbert space) with inner product called the *State Space* of the system.
- ❖ The system is completely described by a *state vector*, a unit vector, pertaining to the state space.
- ❖ The state space describes all possible states the system can be in. Postulate 1 does NOT tell us either what the state space is or what the state vector is.

$|\Psi(t)\rangle$ = Contains (and serves as the basis to extract) all the needed information about the system. Any superposition of state vectors is also a state vector.

- ❖ *Wave functions that are physically acceptable must, along with their first derivatives must be finite, continuous, and single-valued everywhere.*

Probability Density

Only the square of its norm, $|\Psi(\mathbf{r}, t)|^2$ has meaning. According to Born's probabilistic interpretation, the square of the norm of $\Psi(\mathbf{r}, t)$

$$P(\mathbf{r}, t) = |\Psi(\mathbf{r}, t)|^2$$

represents a position probability density;

$$\int |\psi(\vec{r}, t)|^2 d^3r = \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dy \int_{-\infty}^{+\infty} |\psi(\vec{r}, t)|^2 dz = 1.$$

A wave function $\psi(\vec{r}, t)$ satisfying this relation is said to be *normalized*.

This condition on the wave function follows directly from the fact that the particle must be somewhere, so the total probability of finding it anywhere in space must add up to unity.

The Superposition Principle

If $\Psi_1(\mathbf{r}, t)$ and $\Psi_2(\mathbf{r}, t)$ separately satisfy the Schrödinger equation, then the wave function $\Psi(\mathbf{r}, t) = \alpha_1 \Psi_1(\mathbf{r}, t) + \alpha_2 \Psi_2(\mathbf{r}, t)$, where α_1 and α_2 are complex numbers, also satisfies the Schrödinger equation.

$$|\psi\rangle = \sum_i \alpha_i |\psi_i\rangle,$$

The probability for this superposition.

$$P = \left| \sum_i \alpha_i |\psi_i\rangle \right|^2 = \sum_i |\alpha_i|^2 = P_1 + P_2 + P_3 + \cdots,$$

Consider a system whose state is given in terms of an orthonormal set of three vectors: $|\phi_1\rangle$, $|\phi_2\rangle$, $|\phi_3\rangle$ as

$$|\psi\rangle = \frac{\sqrt{3}}{3}|\phi_1\rangle + \frac{2}{3}|\phi_2\rangle + \frac{\sqrt{2}}{3}|\phi_3\rangle.$$

(a) Verify that $|\psi\rangle$ is normalized. Then, calculate the probability of finding the system in any one of the states $|\phi_1\rangle$, $|\phi_2\rangle$, and $|\phi_3\rangle$. Verify that the total probability is equal to one.

(b) Consider now an ensemble of 810 identical systems, each one of them in the state $|\psi\rangle$. If measurements are done on all of them, how many systems will be found in each of the states $|\phi_1\rangle$, $|\phi_2\rangle$, and $|\phi_3\rangle$?

Solution

(a) Using the orthonormality condition $\langle \phi_j | \phi_k \rangle = \delta_{jk}$ where $j, k = 1, 2, 3$, we can verify that $|\psi\rangle$ is normalized:

$$\langle \psi | \psi \rangle = \frac{1}{3} \langle \phi_1 | \phi_1 \rangle + \frac{4}{9} \langle \phi_2 | \phi_2 \rangle + \frac{2}{9} \langle \phi_3 | \phi_3 \rangle = \frac{1}{3} + \frac{4}{9} + \frac{2}{9} = 1. \quad (3.11)$$

Since $|\psi\rangle$ is normalized, the probability of finding the system in $|\phi_1\rangle$ is given by

$$P_1 = |\langle \phi_1 | \psi \rangle|^2 = \left| \frac{\sqrt{3}}{3} \langle \phi_1 | \phi_1 \rangle + \frac{2}{3} \langle \phi_1 | \phi_2 \rangle + \frac{\sqrt{2}}{3} \langle \phi_1 | \phi_3 \rangle \right|^2 = \frac{1}{3}, \quad (3.12)$$

since $\langle \phi_1 | \phi_1 \rangle = 1$ and $\langle \phi_1 | \phi_2 \rangle = \langle \phi_1 | \phi_3 \rangle = 0$.

Similarly, from the relations $\langle \phi_2 | \phi_2 \rangle = 1$ and $\langle \phi_2 | \phi_1 \rangle = \langle \phi_2 | \phi_3 \rangle = 0$, we obtain the probability of finding the system in $|\phi_2\rangle$:

$$P_2 = |\langle \phi_2 | \psi \rangle|^2 = \left| \frac{2}{3} \langle \phi_2 | \phi_2 \rangle \right|^2 = \frac{4}{9}. \quad (3.13)$$

As for $\langle \phi_3 | \phi_3 \rangle = 1$ and $\langle \phi_3 | \phi_1 \rangle = \langle \phi_3 | \phi_2 \rangle = 0$, they lead to the probability of finding the system in $|\phi_3\rangle$:

$$P_3 = |\langle \phi_3 | \psi \rangle|^2 = \left| \frac{\sqrt{2}}{3} \langle \phi_3 | \phi_3 \rangle \right|^2 = \frac{2}{9}. \quad (3.14)$$

As expected, the total probability is equal to one:

$$P = P_1 + P_2 + P_3 = \frac{1}{3} + \frac{4}{9} + \frac{2}{9} = 1. \quad (3.15)$$

(b) The number of systems that will be found in the state $|\phi_1\rangle$ is

$$N_1 = 810 \times P_1 = \frac{810}{3} = 270. \quad (3.16)$$

Likewise, the number of systems that will be found in states $|\phi_2\rangle$ and $|\phi_3\rangle$ are given, respectively, by

$$N_2 = 810 \times P_2 = \frac{810 \times 4}{9} = 360, \quad N_3 = 810 \times P_3 = \frac{810 \times 2}{9} = 180. \quad (3.17)$$

Postulate 2: Observables and operators

To every physically measurable quantity A , called an observable or dynamical variable, there corresponds a linear Hermitian operator $\hat{A}$ whose eigenvectors form a complete basis.

Observable	Corresponding operator
$\vec{r}$	$\hat{\vec{R}}$
$\vec{p}$	$\hat{\vec{P}} = -i\hbar\vec{\nabla}$
$T = \frac{p^2}{2m}$	$\hat{T} = -\frac{\hbar^2}{2m}\nabla^2$
$E = \frac{p^2}{2m} + V(\vec{r}, t)$	$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(\hat{\vec{R}}, t)$
$\vec{L} = \vec{r} \times \vec{p}$	$\hat{\vec{L}} = -i\hbar\hat{\vec{R}} \times \vec{\nabla}$

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = E \psi(\vec{r}, t).$$

$$-i\hbar \vec{\nabla} \psi(\vec{r}) = \vec{p} \psi(\vec{r})$$

Postulate 3: Measurements and eigenvalues of operators

The measurement of an observable A may be represented formally by the action of $\hat{A}$ on a state vector $|\Psi(t)\rangle$

The only possible result of such a measurement is one of the eigenvalues a_n (which are real) of the operator $\hat{A}$.

$$\hat{A}|\psi(t)\rangle = a_n|\psi_n\rangle$$

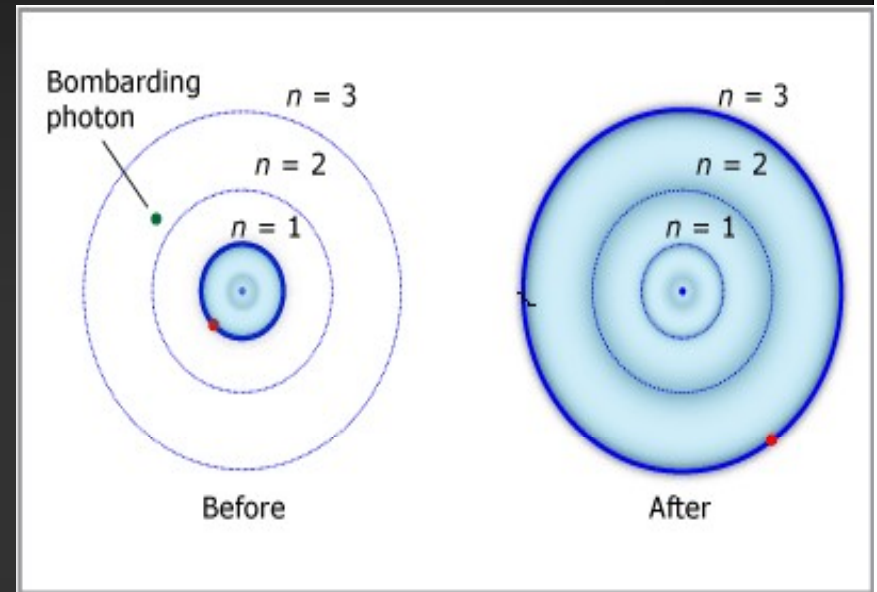
Postulate - 4

- ❑ In classical physics it is possible to perform measurements on a system without disturbing it significantly. In quantum mechanics, however, the measurement process perturbs the system significantly.
- ❑ While carrying out measurements on classical systems, this perturbation does exist, but it is small enough that it can be neglected. In atomic and subatomic systems, however, the act of measurement induces non-negligible or significant disturbances.

Example.....

- The electronic orbit is of the order of 10^{-10}
- we must use a radiation whose wavelength is smaller than 10^{-10}
- We need to bombard the electron with photons of energies higher than

$$h\nu = h\frac{c}{\lambda} = h\frac{3 \times 10^8}{10^{-10}} \sim 10^4 \text{ eV.}$$



When such photons strike the electron, not only will they perturb it, they will knock it completely off its orbit; recall that the ionization energy of the hydrogen atom is about 13.5 eV. Thus, the mere act of measuring the position of the electron disturbs it appreciably.

The act of measurement generally changes the **state of the system**.

$$|\psi\rangle = \sum_n |\psi_n\rangle \langle \psi_n | \psi \rangle = \sum_n a_n |\psi_n\rangle.$$

We do not know in advance with certainty in which eigen state, among the various states , **$|\Psi(t)\rangle$** a system will be after the measurement, only a probabilistic outcome is possible.

$$P_n = \frac{|\langle \psi_n | \psi \rangle|^2}{\langle \psi | \psi \rangle}.$$

Expectation Values

The expectation value $\langle \hat{A} \rangle$ of $\hat{A}$ with respect to a state $|\Psi(t)\rangle$ is defined by

$$\langle \hat{A} \rangle = \frac{\langle \psi | \hat{A} | \psi \rangle}{\langle \psi | \psi \rangle}.$$

For instance, the energy of a system is given by the expectation value of the Hamiltonian:

It does not mean that if one measures the position of one particle over and over again, the average of the results will be given by,

$$E = \langle \hat{H} \rangle = \langle \psi | \hat{H} | \psi \rangle / \langle \psi | \psi \rangle.$$

The position expectation may also be written as:

$$\langle x \rangle = \int_{-\alpha}^{+\alpha} x \psi^* \psi dx = \int_{-\alpha}^{+\alpha} \psi^* x \psi dx$$

Postulate -5

Time Evolution of the System's State

Time-dependent Schrödinger equation.....

$$i\hbar \frac{\partial}{\partial t} \left(\hat{U}(t, t_0) |\psi(t_0)\rangle \right) = \hat{H} \left(\hat{U}(t, t_0) |\psi(t_0)\rangle \right)$$

- **WAVE FUNCTION AND IT'S PHYSICAL SIGNIFICANCE (ψ)**



Max Born

The physical significance or interpretation of $|\psi|^2$ or $\psi \psi^*$ was given by Max Born in 1927.

1. ψ^2 or $\psi \psi^*$ represents probability per unit volume, of finding a particle described by a wave function at a particular point (x,y,z) at time 't' in that volume.

i.e. $\psi^2 = \frac{p}{dV}$

IMPORTANT CHARACTERISTICS OF A WAVE FUNCTION ASSOCIATED WITH WAVE

1. Wave function should be normalised. i.e. it should satisfy the following condition:

$$\iiint_{-\infty}^{\infty} \psi^2 dx dy dz = 1$$

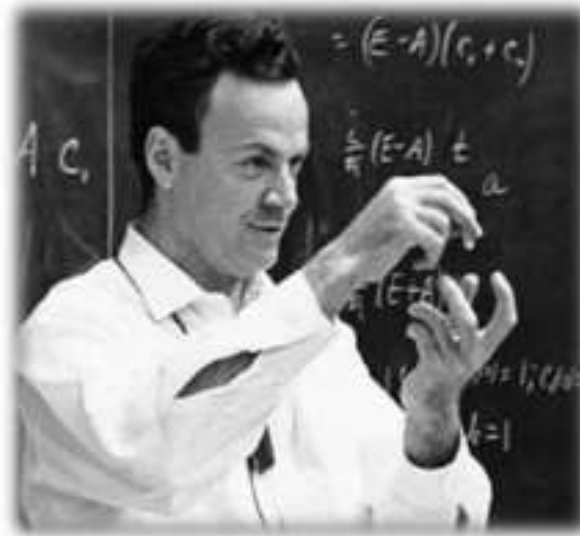
2. Wave function should be finite. ∞ probability has no meaning.
3. It should have a single value. (as at particular point probability can have only one value.)



“I think I can safely say that nobody understands quantum mechanics.”

Ch. 6, “Probability and Uncertainty”

–Richard Feynman



HEISENBERG REALISED THAT ...

- ⊙ In the world of very small particles, one cannot measure any property of a particle without interacting with it in some way.
- ⊙ This introduces an unavoidable uncertainty into the result.
- ⊙ One can never measure all the properties exactly.



Werner Heisenberg (1901-1976)

Heisenberg's Principle

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

$\downarrow$ position $\downarrow$ Momentum

Δx	$\uparrow$	Δp	$\downarrow$
Δp	$\uparrow$	Δx	$\downarrow$

□ Holds Good for microscopic particles.

□ Also apply for angular momentum (ΔJ) and angle ($\Delta\theta$).

Heisenberg Uncertainty Relationships

$$\Delta x \cdot \Delta p \sim \hbar$$

$$\Delta E \cdot \Delta t \sim \hbar$$

Heisenberg realized that ...

- In the world of very small particles, one cannot measure any property of a particle without interacting with it in some way
- This introduces an unavoidable uncertainty into the result
- One can never measure all the properties exactly.



Werner Heisenberg (1901-1976)

Problem : An electron is travelling along x- axis with a uniform velocity 2×10^6 m/s . If the velocity has been calculated with the precession of 0.15%. Calculate the maximum accuracy with which the position of the electron could be measured at the same instant of time assume mass of the electron $m_e = 9.1 \times 10^{-31}$ kg.

Apply Heisenberg Uncertainty principle

$$\Delta x \Delta p_x = h/2\pi$$

$$\Delta x = ?$$

Heisenberg's Matrix Mechanics

1924: de Broglie suggests particles are waves



Mid-1925: Werner Heisenberg introduces Matrix Mechanics

- Semi-philosophical, it only considers observable quantities
- It used matrices, which were not that familiar at the time
- It refused to discuss what happens between measurements
- In 1927 he derives uncertainty principles



Late 1925: Erwin Schrödinger proposes wave mechanics

- Used waves, more familiar to scientists at the time.
- Initially, Heisenberg's and Schrödinger's formulations were competing.
- Eventually, Schrödinger showed they were equivalent; different descriptions which produced the same predictions.



Both formulations are used today, but Schrödinger is easier to understand