1. OLD QUANTUM THEORY :—

1.1 What's wrong with our favourite Classical Mechanics?

As we continue to expand our knowledge in the domain of observations, we must constantly check whether the existing laws of physics can explain the new phenomena, if they do not, we must try to find new laws that do! In this section, we will see how some experiments/observations betray the inadequacy of the classical scheme.

- What we now call "Classical Physics" is the result of the scientific evolution of the sixteenth and seventeenth centuries that culminated in Newtonian mechanics. [By "classical physics", we mainly mean three theories —— (i) Newton's law of physics, (ii) Maxwell's theory of electro-magnetic field and (iii) Einstein's theory of general relativity]. The core of this physics is "Newton's laws" describing the motion of particles of matter.

- **Particles and Waves in Classical Physics :**

In classical physics, there exist two distinct entities: particles and waves.

(i) Particles are localized bundles of energy and momentum. They are described at any instant by the "state parameters"— for example, position (q) and velocity $(\dot{q})$ (or momentum $p = m\dot{q}$). (remember Lagrangian & Hamiltonian formalism). These two parameters evolve in time according to some equations of motion — "Newton's 2nd Law" — $m\frac{d^2q}{dt^2} = -\frac{dV}{dq}$, where $q(t)$ is the position of a particle of mass m at some time t, $\dot{q}(t) \equiv \frac{dq}{dt}$ is the velocity and that particle is assumed to move under influence of some potential $V(q)$.

Given the initial values for $q(t_i)$ and $\dot{q}(t_i)$ at some initial time t_i, the trajectory $q(t)$ can be determined from this equation of motion (Newton's 2nd Law) for all future times.
[OR, in Lagrangian formalism, $\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j}\right) - \frac{\partial L}{\partial q_j} = 0 \; (j = 1, \ldots, n)$ where $L(\dot{q}_j, q_j, t) = T - V$.

Or, in Hamiltonian formalism, $\frac{\partial H}{\partial p_j} = \dot{q}_j$, $-\frac{\partial H}{\partial q_j} = \dot{p}_j$.

where the generalized momenta $p_i = \frac{\partial L}{\partial \dot{q}_i}$ and the Ha[illegible] is defined as, $H(p,q,t) = \sum_j p_j \dot{q}_j - L(\dot{q},q,t) = T$[illegible]

— In all these formalism, we have to solve a 2nd order diff[illegible] equation using two boundary conditions for $q(t_i)$ and $\dot{q}(t_i)$ in order to determine the trajectory of that particle in motion [illegible] all future times.]

(ii) A wave, in contrast, is a disturbance spread o[illegible] It is described by a wave function, say $\psi(\vec{r},t)$ which [illegible] the disturbance at the 3D point $\vec{r}$ at time t — it could be a sound wave or electromagnetic wave. The analogs of q and $\dot{q}$ for a wave are ψ and $\dot{\psi}$ at each point $\vec{r}$, assuming ψ obeys a second-order wave equation in time, such as —

$$\nabla^2\psi = \frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2}$$

which describes waves propagating at the speed of light c. Given $\psi(\vec{r},0)$ and $\dot{\psi}(\vec{r},0)$, one can get the wave function $\psi(\vec{r},t)$ for all future times by solving the above wave eq^n.

<u>Special case</u> : "<u>Plane Waves</u>" — waves that are periodic in space & time.

In one-dimension, the plane wave may be written as —

$$\boxed{\psi(x,t) = A\exp\left[i\left(\frac{2\pi}{\lambda}x - \frac{2\pi}{T}t\right)\right] \equiv A\exp[i\phi].}$$

At some given time t, the wave is periodic in space with a period λ (called its "<u>wave length</u>"). Likewise, at a given point x, it is periodic in time t with a period T (called its "<u>time period</u>") — [show that, $\psi(x+\lambda, t+T) = \psi(x,t)$, from the above eq^n — use the fact that, $e^{i2\pi} = 1$]

Instead of λ and T, we'll often use two related quantities — $\boxed{k = 2\pi/\lambda}$ — called the "<u>wave number</u>"

& $\boxed{\omega = 2\pi/T}$ — called the "<u>angular frequency</u>".

So, 1-D plane wave —

$$\boxed{\psi(x,t) = A\exp[i(kx-\omega t)] \equiv A\exp[i\phi]}$$

ϕ is called "phase". This wave travels at a speed $\boxed{v = \omega/k}$

The overall scale factor A is called the "amplitude". For any wave, the "intensity" is defined as $I = |\psi|^2$. For a plane wave, this is constant $I = |A|^2$. [If ψ describes an electromagnetic wave, the intensity is a measure of the energy and momentum carried by the wave.]

Plane wave in 3-dim. —

$$\psi(\vec{r},t) = A e^{i(\vec{k}\cdot\vec{r}-\omega t)}, \quad \omega = |\vec{k}|v$$

where each component k_i gives the phase changes per unit length along i^{th} axis. The quantity $\vec{k}$ is called the "wave vector."

- **A Classical experiment with Waves & Particles:**

Waves exhibit a phenomenon called "interference", which is peculiar to them and is not exhibited by particles in classical mechanics. Waves and particles are independent paradigms of classical physics: a particle is not a wave and a wave is not a particle! But this conception of natural world started to change at the beginning of twentieth century, as new experimental evidence was provided by the study of the black-body radiation, of the photo-electric effect, of the Compton effect, or of the diffraction and interference properties of electrons.

In this section, we will describe mainly the interference phenomenon by a simple classical example/experiment.

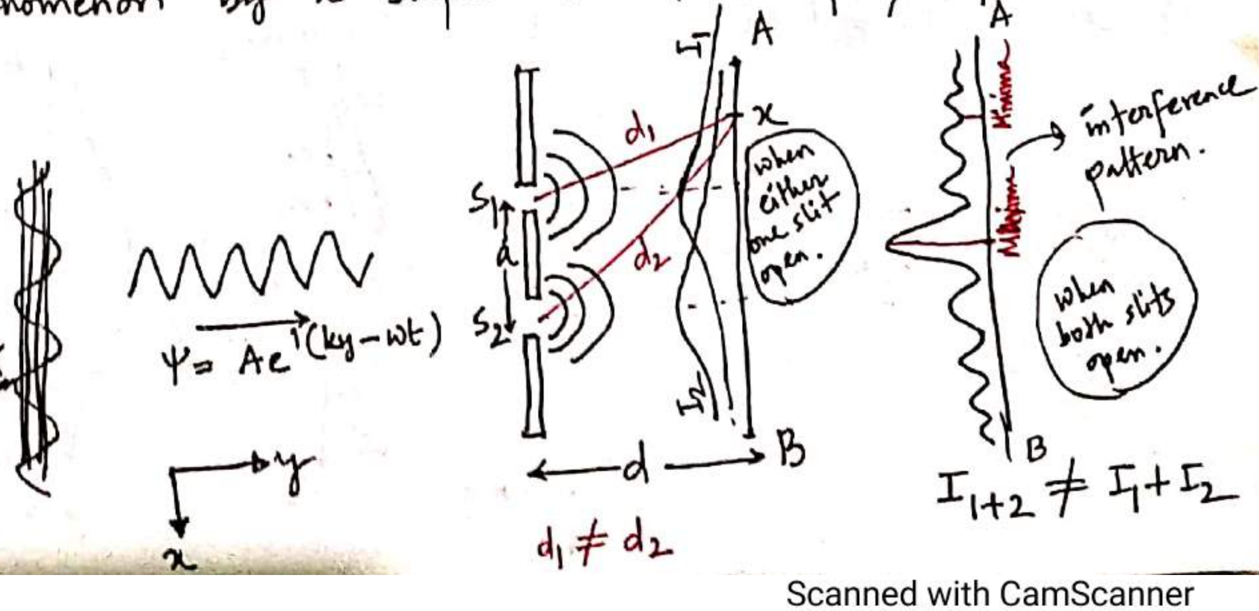


Fig. 1 Wave experiment

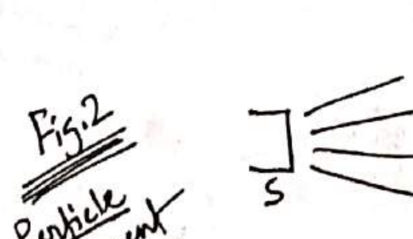
Let a wave $\psi = Ae^{i(ky-\omega t)}$ be incident normally on a screen with slits S_1 & S_2, which are a distance "a" apart. At a distance d parallel to it, is a detector that measures the intensity as a function of the position x measured along the path AB (Fig. 1.).

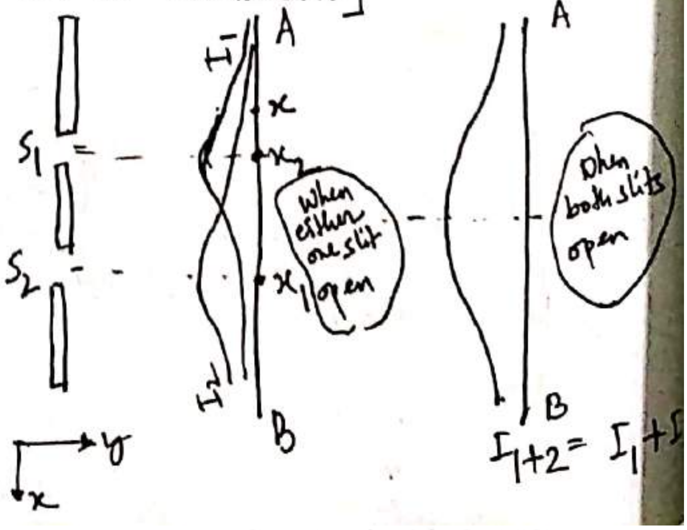
If we first keep only S_1 open, the incident wave will come out of S_1 and propagate radially outward. One may think of S_1 as the virtual source of this wave ψ_1, which has the same frequency and wavelength (or same k and ω) as the incident wave. The detector will register the intensity pattern as $I_1 = |\psi_1|^2$. Similarly, if we keep only S_2 open instead of S_1, the wave ψ_2 produces the pattern $I_2 = |\psi_2|^2$.

Now, if both S_1 and S_2 are opened, both waves ψ_1 and ψ_2 are present and they together produce an intensity pattern of $I_{1+2} = |\psi_1 + \psi_2|^2$.

The interesting thing is that, $I_{1+2} \neq I_1 + I_2$, but rather it shows the "interference pattern," as shown in the right-side of the figure 1. The ups and downs in this pattern are due to the fact that the waves ψ_1 and ψ_2 have to travel different distances d_1 and d_2 to arrive at some given point x, and thus are not always in step. Whereas, the maxima occurs when the waves arrive exactly in step.

[Maxima correspond to the case $d_2 - d_1 = n\lambda$ (n is an integer) & Minima correspond to the case $d_2 - d_1 = (2n+1)\lambda/2$ when the waves are exactly out of step. In terms of phases, ϕ_1 and ϕ_2, $\phi_2(x) - \phi_1(x) = 2n\pi$ at a maximum and $\phi_2(x) - \phi_1(x) = (2n+1)\pi$ at a minimum.]





Now, consider the same experiment with particles. The source of the incident plane waves is replaced by a source of particles that shoots them toward the screen with varying direction but with fixed energy (Fig. 2). The intensity $I(x)$ is defined by the number of particles arriving per second at any given x.

If either S_1 or S_2 is open, the intensity patterns I_1 and I_2 will look very much like the corresponding pattern for the wave.

What if both S_1 and S_2 are opened ??

Classical mechanics has an unambiguous prediction: $I_{1+2} = I_1 + I_2$. The reason for this: each particle travels along a definite trajectory that passes via S_1 or S_2 to the destination x. To a particle headed for S_1, it doesn't matter whether S_2 is open or closed. Being localized in space, it has no way of knowing whether S_2 is open or closed. Thus the number of particle coming via S_1 at x is independent of whether S_2 is open or not and vice-versa. It follows that, $I_{1+2} = I_1 + I_2$ — this is true even if we keep sending one particle at a time.

So, in classical physics, the prediction for particles and waves are very different.

- **Double-Slit Experiment with Light:**

Consider now what happens when we perform the same experiment with light to check the classical physics notion that light is an electromagnetic wave phenomenon.

We first set up the double-slit experiment as in Fig. 1 ~~ahp~~ with a row of light-sensitive detectors along AB and send a light beam in a direction perpendicular to the screen — same as Fig. 1. We find that, with either S_1 or S_2 open we get patterns I_1 and I_2, and with both slits open we get an interference pattern I_{1+2} exactly the same as we found earlier in Fig. 1. This might convince us that the light is a purely wave phenomenon. But the following experiment will change this belief!

We repeat the experiment with a slight change — we start with S_1 open and cut down the intensity of light — A very strange thing happens!

We find that the energy is not arriving continously, but in sudden bursts, a burst here, a burst there, etc. If we further cut down the intensity so that only one detector gets activated at a given time, we will find each burst occurs at some x along AB. We then collect all the data and plot the histogram — we see the envelope of that histogram becoms the pattern I_1.

So, we have made an important discovery: light energy is not continuous — it comes in bundles (called "photons"). We did not see / cannot see this discrete nature of light when we send light as a beam, because the bundles then come in so fast and spread all over the line AB, that the energy seems to be continous in space and time.

Now, if the light is made of particle, should it behave the same way in the experiment like Fig. 2 ?? This is where the classical physics fail to explain the observed behaviour of light. If we open both slits S_1 and S_2, and still keep the intensity so low that only one photon is shot at a time, we find that $I_{1+2} \neq I_1 + I_2$ — it clearly shows an interference pattern. This behaviour is in contradiction with the classical physics, where we saw $I_{1+2} = I_1 + I_2$ for classical particles. This result completely rules out the possiblity that photon may be a classical particle — it clearly shows a very different physics — introduction of Quantum Mechanics.

⇒ From these facts, Born drew the following interpretation: with each photon is associated a wave ψ, called the "probability amplitude", whose modulus squared $|\psi(x)|^2$ gives the probability of finding the particle at x.

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- The entire experiment may be understood in terms of this hypothesis ——

→ Every incoming photon of energy E and momentum p has a wave function ψ associated with it, which is a plane wave with $\omega = E/\hbar$ and $k = p/\hbar$ (where $\hbar = h/2\pi$ is a constant. The constant h is called "Planck's constant", and has dimensions of erg sec — same dim. of angular momentum — Its value is $\hbar = h/2\pi \simeq 10^{-27}$ erg sec.). This wave interferes with itself and forms the oscillating pattern $|\psi(x)|^2$ along AB, which gives the probability that the given photon will arrive at x. A given photon arrives at some definite x and does not reveal the probability distribution alone. If, however, we wait till several photons, all described by the same ψ, have arrived, the number at any x will become proportional to the probability function $|\psi(x)|^2$.
Likewise, if an intense (macroscopic) monochromatic beam is incident, many photons, all described by the same wave fn. and hence same probability distribution, arrive at the same time and all along the line AB. Then the intensity distribution assumes the shape of the probability distribution right away and the energy flow seems to be continuous and in agreement with the predictions of classical electromagnetic theory.

Point to note: a wave is associated not with a beam of photons, but with each photon.

→ This hypothesis is known as "wave-particle duality" (see next)

- Matter Waves (de Broglie Waves) :—

The idea that the light, which one thought as a pure wave phenomenon, should consist of photons, prompted de Broglie to conjecture that entities like the electrons, which are belived to be particles, should also exhibit wavelike behaviour.

More specifically, he (1924) conjectured that, in analogy with photons, particles of momentum p will produce an interference pattern corresponding to a wave number $k = p/\hbar$ in the double-slit experiment. This prediction was verified for electrons by Davisson and Germer, shortly thereafter (19... (See the Davisson-Germer experiment below).

It is now widely accepted that all particles are described by probability amplitudes $\psi(x)$, and that the assumption that they move in definite trajectories (i.e. the concept of Classical Physics) is ruled out by experiment.

→ So, does that mean our old classical theory is wrong??

→ What about our common sense which says that billiard balls or cricket balls travel along definite trajectories?

→ How did classical mechanics survive for three centuries?

The answer is that, the wave nature of matter is not apparent for macroscopic phenomena since $\hbar$ is so small!

To understand this statement, let us set up a hypothetical double-slit experiment with bullets of mass 1g, moving at 1 cm/sec speed. The wavelength associated with these bullets is —

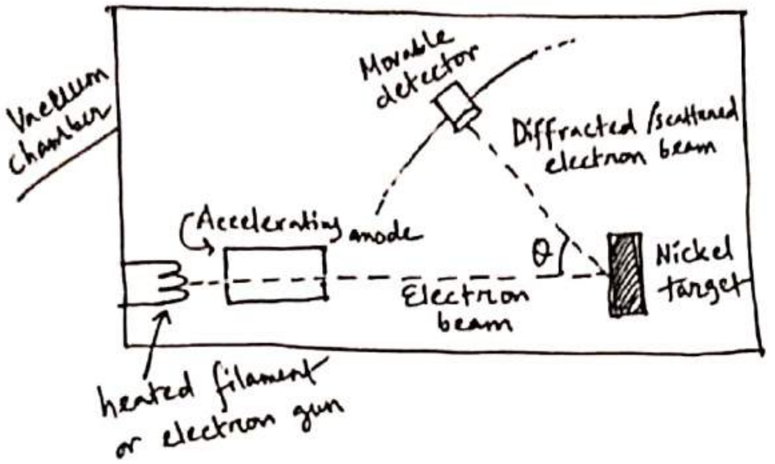
$$\lambda = \frac{2\pi}{k} = \frac{h}{p} \simeq 10^{-26} \text{ cm}.$$

which is 10^{-13} times smaller than the radius of the proton! For any reasonable values of the parameters a and d (see Fig. 1), the interference pattern would be so dense in x that our intruments will only measure the smooth average, which will obey $I_{1+2} = I_1 + I_2$ as predicted classically.

- Short note on the wave-particle duality:

We found that, entities such as the electron are particles in the classical sense — when detected they seem to carry all their energy, momentum, charge etc. in localized form. At the same time they are not particle-like when the assumption that they move along definite trajectories leads to conflict with experiment. It appears that, each particle has associated with it a wave function $\psi(x,t)$, such that $|\psi(x,t)|^2$ gives the probability of finding it at a point x at time t. This is called "wave-particle duality". In 1924, de Broglie first proposed this idea that all matter should display the wave-particle duality nature like photons.

• Davisson – Germer Experiment :—



In 1927, Davisson and Germer carried out an experiment, popularly known as Davisson – Germer experiment, to explain the wave nature of electrons through electron diffraction.

⇒ Experimental set up: The experiment included an "electron gun" which is basically a heated filament that releases thermally excited electrons. These electrons then were accelerated through a potential difference from a high voltage power supply, giving them a desired velocity. These emitted electrons or electron beam were/was made to fall on the surface of a nickel crystal. This produced scattering of electrons in various directions. To avoid the collisions of electrons with other molecules on their way towards the surface, the whole experiment was conducted in a vacuum chamber. To measure the number of electrons that were scattered at different angles, a movable electron detector (which can only move on an arc path about the crystal) was used.

⇒ Results: (i) By varying accelerating potential difference, they obtained the variation of the intensity (I) of the scattered electrons with the angle of scattering θ. The accelerated voltage was varied from 44V to 68V.

(ii) A strong peak was noticed in the intensity (I) of the scattered beam for a voltage of 54V at a scattering angle $\theta = 50^\circ$.

(iii) The peak can only be explained as a result of the constructive interference of electrons which were scattered.

(iv) The wavelength was measured to be 0·165 nm. ($1\text{nm} = 10^{-9}\text{m}$)

⇒ Using the de Broglie hypothesis, one can get this value to be

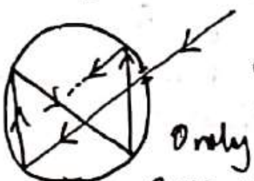
$\lambda = h/p = \frac{1{\cdot}227}{\sqrt{54}} = 0{\cdot}167\ \text{nm}$ ⟹ Confirms the wave nature of electrons & de Broglie relation.

1.2 Some Historical Motivations for Quantum Theory:

In the early years of the tweentieth century, Max Planck, Albert Einstein, Louis de Broglie, Neils Bohr, Werner Heisenberg, Erwin Schrödinger, Max Born, Paul Dirac and others created the theory now known as quantum mechanics. We have already established the fact that the behavior of quantum system is very different forom the macroscopic systems of Classical Mechanics. In this section, we will consider many historical motivations for quantum mechanics before we proceed to develop the mathematical formalism: Roughly speaking the history is as follows:

1. Planck's Black Body Theory (1900): —

One of the major challenges of theoretical physics towards the end of the nineteeth century was to derive an expression for the spectrum of electro-magnetic energy emitted by an object in thermal equilibrium at some temperature T. Such an object is known as a black body, so named because it absorbs light of any frequency falling on it. However, in nature, we have no such bodies which absorb all the radiation falling upon them — no perfect or ideal black body exists in nature. But we may approximate it very closely for both theoretical and experimental purposes by making a very small hole in the side of a closed hollow container.



If a ray of radiant energy enters through the small hole of the container (hollow and closed), a large part of the radiation is absorbed as it strikes the inside of this container. Only a very small fraction of this diffusely reflected energy goes out through the hole, the rest being completely absorbed by successive reflections. When, likewise, such container is heated, the inside walls radiate, an some of this radiation passes out through the hole. That is to say, the "black body" may radiate as well as absorb energy. Such radiation is called "black body radiation".

- **Stefan-Boltzmann Law:** — (1884)

The total energy of black body radiation:

$$\boxed{E(T) = V\int d\nu\, \rho(\nu, T) = aVT^4}$$

Where, $\rho(\nu, T)$ is the spectral density or the energy per unit volume per unit time of radiation from the black body at temperature T and volume V, ν is the corresponding frequency. a is some constant.

- **Wein displacement law** :— (1893) [Wein's displacement law : $\lambda_{max} T = \text{const.}$ Wein's law/formula : $\rho(\nu,T) = \alpha \nu^3 e^{-\beta\nu/T}$]

Wein derived that, $\rho(\nu,T) = \nu^3 f\left(\frac{\nu}{T}\right)$

$= \nu^3$ times some function of the ratio of ν to T

Higher the temperature T, the shorter the wavelength λ_{max} at which maximum energy occurs : $\boxed{\lambda_{max} T = \text{const.}}$

$$\Rightarrow \boxed{\rho(\nu,T) = \alpha \nu^3 e^{-\beta\nu/T}} \rightarrow \text{(conjecture/guess)}$$

where α & β are two unknown constants to be determined by data.

→ At higher frequency range, the experimental data are in excellent agreement with this law/formula.

- **Rayleigh-Jeans Law** :— (1900)

Using arguments from classical physics (or precisely statistical Mechanics), one can obtain the formula for $\rho(\nu,T)$ as:

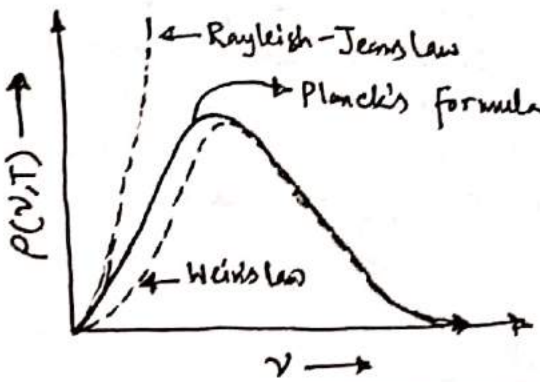
$$\boxed{\rho(\nu,T) = \frac{8\pi\nu^2}{c^3} k_B T}$$

Where, k_B is the Boltzmann constant → 1.38×10^{-16} erg K^{-1}

→ This formula worked well at low frequency range, but struggle to match the data at higher frequencies — obviously incorrect and indicates a deep flaw in classical physics.

- **Planck's law** :— (1900)

In an attempt to understand the form of the spectrum of the electromagnetic radiation emitted by a black body i.e. $\rho(\nu,T)$, Planck proposed a formula which he obtained by looking for a formula that fitted Wein's law at high frequencies, and also fitted the low frequency experimental results (which happens to be given by the Rayleigh-Jeans formula, but Planck was not aware of that at that time).



Planck proposed that, the atoms making up the black body object, absorbed and emitted light of frequency ν in multiples of a fundamental unit of energy, or "quanta" of energy, $E = h\nu$.

On basis of this assumption, he ~~derived~~ obtained:

$$\boxed{\rho(\nu,T) = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/k_B T} - 1}}$$

where h is known as Planck's constant and could be determined from the data.

$h = 6.6218 \times 10^{-34}$ J-sec $= 6.6218 \times 10^{-27}$ erg-sec.

⇒ Planck was now in a situation which is not very uncommon for theoretical physicist, he had a formula that fits the data, but did not have a proof! He then proceeded to try to derive this law. He modeled the black body as a set of charges that were attached to harmonic oscillators. The acceleration of these particles then produced radiation (as accelerating charge radiates). The assumption was that these oscillators were in thermal equilibrium with the radiation. In obtaining his proof, he did two things which were not consistent with classical physics, he used a counting law for determining the probability of various configurations that was not consistent with classical statistical mechanics and he was required to assume that these oscillators in the walls of the black body could only radiate at a specific energy: $\underline{E = h\nu}$. He referred to these bundles of energy as "quanta".

This is a very radical departure from classical mechanics, because according to electrodynamics the energy of the radiation should be determined by the magnitude of the oscillations and be independent of the frequency. Planck assumed that, there must be some unknown physics associated with the production of radiation of the oscillators! This is historically the "beginning of quantum mechanics."

2. The Photoelectric Effect (1905):—

Although Planck ~~believed~~ believed that the rule for the absorption and emission of light quanta applied only to black body radiation, and was a property of the atoms, rather than the property of radiation, Einstein saw it as a property of electromagnetic radiation, whether it was black body radiation or of any other origin. He applied this idea in his work on the photoelectric effect in 1905.

The "photoelectric effect" was first observed by H. Hertz in 1887 and then studied by many experimentalists in the following years: "~~matter (~~metals ~~and non-metallic solids, liquid and gases)~~ emits electrons as consequence of the absorption of incident electromagnetic radiation, or light, whose frequency lies in the visible or ultraviolet spectrum."

Experimentally, this phenomenon exhibits the following behavior:—

- The effect occurs only when the frequency ν of the incoming radiation is higher than a threshold frequency ν_0, which depends on the material.
- The number of electrons emitted per unit of time is proportional to the intensity of the incoming radiation. But doesn't change the electron's energy! — contradiction to Classical Theory!!!
- The maximum kinetic energy T_{max} of the emitted electrons satifies the relation: $T_{max} = h(\nu - \nu_0)$, $h \approx 6.6 \times 10^{-34}$ J-sec.

It is difficult to explain these features using classical physics — it predicts a threshold for the electromagnetic flux but not for the frequency; it predicts that the energy absorbed by the photo-electrons increases with the intensity but not with the frequency of the incident radiation. Both features are in contrast with the experiment!

Einstein's proposal was to assume that, electromagnetic energy is exchanged between radiation and electrons in "packets", all carrying the same energy related to the radiation frequency as follows:

$$E_\nu = h\nu$$

Denoting by W, "work function" — the energy necessary to pull out an electron from the metal, one can deduce that the maximum kinetic energy of the emitted electron is

$$\boxed{T_{max} = h\nu - W = h(\nu - \nu_0)}$$, where $\nu_0 = \frac{W}{h}$ in agreement with the experimental result.

3. Bohr's Model of the Hydrogen Atom (1913):—

Niels Bohr then made use of Einstein's idea in an attempt to understand why hydrogen atoms do not self destruct, as according to the laws of classical electrodynamic theory, they ~~should~~ should! ⟶ because: as implied by the Rutherford scattering experiments (1908 – 1913), a hydrogen atom consists of a positively charged nucleus (a proton) around which circulates a very light (relative to the proton's mass) negatively charged particle, an electron. Classical electromagnetism says that, as the electron is accelerating in its circular path, it should be radiating away energy in the form of electromagnetic waves, and do so on a very short time-scale of $\sim 10^{-12}$ sec, during which time the electron would spiral into the proton and the hydrogen atom would cease to exist. This obviously does not occur! [Classically, accelerated electrons radiate energy at a rate of $\frac{2}{3} e^2/c^3 \times |\ddot{x}|^2$]

Bohr proposed that, the angular momentum of the electrons orbiting around the nucleus in an atom can be just an integer multiple of $\hbar \,(= h/2\pi)$ (now known as "quantization condition"):

$$\boxed{L = mvr = n\hbar} \quad (n = 1, 2, 3, \ldots)$$

where v ~~is~~ and m are the speed and mass of the electrons respectively. Now n is refferred to as "a quantum number". The orbit which satisfies this condition would be "stable" and the atom is said to be in a "stationary state."

He further assumed that, electrons do not emit continuous radiation if not in a transition between different orbits. Actually, it is known that electrons stop radiating energy long before they could fall into nucleus! This fact strongly suggests that there should or rather must be a minimum energy possible in the atom:—

This lowest possible energy corresponds to the lowest discrete quantized state of energy and that radiation stops when this state is reached. This is known as ~~stationary state~~ "Ground state".

On the basis of this proposal, Bohr showed that the hydrogen atom could only have energies given by the formula

$$\boxed{E_n = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{2a_0}\frac{1}{n^2}} \quad [n = 1, 2, \cdots]$$

where $\boxed{a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.0529 \text{ nm}}$ $[1\text{ nm} = 10^{-9}\text{ m}]$

is known as the Bohr radius, and roughly speaking gives an indication of the size of an atom as determined by the rules of quantum mechanics.

Derivation:

Classically, the energy of hydrogen atom:

$$E = T + V = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\epsilon_0 r} \quad \left[\text{where P.E. } V = -\frac{e^2}{4\pi\epsilon_0 r}\right]$$

We know that, for a circular orbit, the attractive force (or ~~Coulomb's~~ Coulomb's force) balancing the outward centrifugal force [here centrifugal force $= \frac{mv^2}{r}$ and ~~coulomb~~ coulomb force $F = -\frac{\partial V}{\partial r} = \frac{e^2}{4\pi\epsilon_0 r^2}$]

$$\frac{mv^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2}$$

$$\Rightarrow mv^2 r = \frac{e^2}{4\pi\epsilon_0} \quad \text{——(i)}$$

$$\text{or} \quad mv^2 = \frac{e^2}{4\pi\epsilon_0 r}. \quad \text{——(ii)}$$

Now, according to Bohr's postulate, $mvr = n\hbar$ $(n = 1, 2, \cdots)$

$$\Rightarrow mv^2 r = vn\hbar$$

$$\Rightarrow \frac{e^2}{4\pi\epsilon_0} = vn\hbar \quad (\text{using eq}^n \text{ (i)})$$

$$\Rightarrow v = \frac{e^2}{4\pi\epsilon_0}\frac{1}{n\hbar} \quad \text{——(iii)}$$

Furthermore, we obtain the Energy

$$E = -\frac{1}{2}mv^2 \quad \left(\text{as } \frac{e^2}{4\pi\epsilon_0 r} = mv^2 \text{ from eq}^n \text{ (ii)}\right)$$

$$= -\frac{1}{2}m\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\left(\frac{1}{n\hbar}\right)^2 \quad (\text{using eq}^n \text{ (iii)})$$

$$\Rightarrow \boxed{E = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{2a_0}\frac{1}{n^2}}$$

where $\frac{1}{a_0} = \frac{me^2}{4\pi\epsilon_0\hbar^2}$

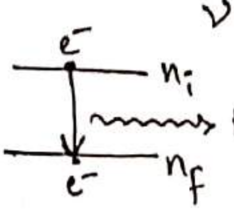
One can also define a new dimensionless constant:

$$\boxed{\alpha = \frac{e^2}{\hbar c} \simeq \frac{1}{137}}$$

and rewrite it as $E_n = -\frac{1}{4\pi\epsilon_0}\frac{\alpha^2 mc^2}{2n^2}$

Using the Einstein's work on photon quanta ($E = h\nu$), Bohr further proposed that the hydrogen atom emits or absorbs light quanta by jumping between the energy levels. The frequency ν of the photon emitted in a downward transition from the stationary state with quantum number n_i to another stationary state of lower energy with quantum number n_f would be —

$$\nu = \frac{E_{n_i} - E_{n_f}}{h} = \frac{1}{4\pi\epsilon_0} \cdot \frac{e^2}{2a_0 h}\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]$$



With this, Bohr explained the results of the experiments by Balmer (1885) that the hydrogen atom emits a discrete group of frequencies. Since each frequency leads to a corresponding line in the spectrum of the atom, this result means that the spectrum is discrete, whereas classical physics predicts a continous spectrum and fails to match the experimental results. Bohr proposed that, if there were a set of discrete energy levels then, according to the relation $\Delta E = h\nu$, one could easily explain the emission of discrete frequencies.

Although Bohr's theory was quite successful for the hydrogen atom, it was an utter failure when applied to more complex atoms, even for helium atom! None theless, this theory is considered as one of the successful theory towards the old quantum theory.

- Bohr and Sommerfeld extended the quantization condition to more general mechanical systems by re-formulating it using the "action variable" (remember the classical mechanics — least action principle):

$$\boxed{\oint p\,dq = nh}, \quad n = 1, 2, 3, \ldots \longrightarrow$$

"Wilson–Sommerfeld or Bohr – Sommerfeld quantization formula" (1915)

where p is the momentum canonically conjugated with the position coordinate q of the particle. The integral is taken over the path actually covered by the particle during a single period of oscillation. Such integral is known as "phase integral".

⟹ Example: A particle moving in a plane with a polar angle ϕ and with a definite angular momentum p_ϕ (or L). If the potential is spherically symmetrical, this angular momentum is known to be a constant of the motion. The coordinate conjugate to p_ϕ is ϕ itself. During a period, ϕ goes from 0 to 2π, so that,

$$\oint p\,dq = \int_0^{2\pi} p_\phi\, d\phi = p_\phi \int_0^{2\pi} d\phi = 2\pi p_\phi = 2\pi L$$

So, using quantization formula,

$$2\pi L = nh \Rightarrow L = n\hbar$$

1.3. More about Wave Aspects of Matter: Group & Phase velocities :—

We've already seen that the investigations on the nature of light showed the wave–particle duality nature: depending on the kind of experiment performed, light must be described by electromagnetic waves or by particles (photons). The wave aspect appeared in the context of diffraction and interference phenomena, whereas the particle-like aspect shows up in black-body radiation or in the photoelectric effect. Likewise, de Broglie assigned the same duality nature to matter, transferring the relations known from light to material particle. What is true for photons should be valid for any type of particle.

According to the particle-like aspect, we generally assign to a particle, for example an electron with mass m, propagating uniformly with velocity $\vec{v}$ through field-free space with an energy E and a momentum $\vec{p}$. In the wave picture, the particle is described by a frequency ν and a wave vector $\vec{k}$. Now, since these two different aspects are assigned to the same particle, the following relations should ~~must~~ be valid: (this is our speculation!)

$$\boxed{E = h\nu = \hbar\omega} \quad \text{and} \quad \boxed{\vec{p} = \hbar\vec{k} = \frac{h}{\lambda}\frac{\vec{k}}{|\vec{k}|}} \rightarrow$$ should these ~~always~~ also be valid for matter?

We have already seen in the previous sections that these equations are true for the photon (electromagnetic field), now they are postulated or assumed to be valid for all particles! Then to every "free" particle, a plane wave can be assigned in a same way we did for electromagnetic wave:

$$\psi(\vec{r},t) = A\exp[i(\vec{k}\cdot\vec{r} - \omega t)] \equiv A\exp[i\underbrace{\phi}_{\text{"phase" }(\phi)}]$$

or using the above relations:

$$\psi(\vec{r},t) = A\exp[i(\vec{p}\cdot\vec{r} - Et)/\hbar]$$

following de Broglie, the plane wave connected to the particle has a wavelength of

$$\lambda = \frac{2\pi}{k} = \frac{h}{p}.$$

Now the phase $\phi = \vec{k}\cdot\vec{r} - \omega t$ of the wave $\psi(\vec{r},t)$ propagates with velocity $\vec{v}_p = \dot{\vec{r}}$ (called the "phase velocity") according to the relation

$$\frac{d\phi}{dt} = \vec{k}\cdot\dot{\vec{r}} - \omega = \vec{k}\cdot\vec{v}_p - \omega = 0$$ [as ϕ is dimensionless quantity, $\frac{d\phi}{dt} = 0$]

Hence, we get for the magnitude of the phase velocity $\vec{u}$ as: (because $\vec{k}$ and $\vec{u}$ have the same direction, $\vec{k}\cdot\vec{v}_p = k v_p$)

$$|\vec{v}_p| = \boxed{v_p = \frac{\omega}{k}.} \longleftarrow \text{phase velocity}$$

⟹ Next, we'll show that what corresponds to the ~~partic~~ particle velocity is not this phase velocity, but rather the velocity of the envelope (called "group velocity", v_g).

We know that, the relativistic energy for free particles is: (remember STR!)

$$E^2 = m_0^2 c^4 + p^2 c^2 \quad [m_0 \equiv \text{rest mass}]$$

for $v << c$, we can write –

$$E = mc^2 = \sqrt{m_0^2 c^4 + p^2 c^2} = m_0 c^2 + \frac{p^2}{2m_0} + \cdots\cdots$$

(Taylor series expansion)

Using the relation $E = \hbar\omega$, we can get the Frequency as a function of the wave number k:

$$\omega(k) = \frac{m_0 c^2}{\hbar} + \frac{\hbar k^2}{2m_0} + \cdots \quad (\text{also using } \vec{p} = \hbar\vec{k})$$

Therefore, the phase velocity $v_p = \omega/k$ in a vacuum can be written as:

$$v_p = \frac{m_0 c^2}{\hbar k} + \frac{\hbar k}{2m_0} + \cdots$$

This relation immidiately tells us that the matter waves show "dispersion" even in vacuum (in contrast to the electromagnetic waves), i.e. waves with a different wave number (wavelength) have different phase velocities.

On the other hand, v_p follows this relation –

$$v_p = \frac{\omega}{k} = \frac{\hbar\omega}{\hbar k} = \frac{E}{p} = \frac{mc^2}{mv} = \frac{c^2}{v}$$

As we know that, $c > v$, the phase velocity of matter wave is always larger than the speed of light in a vacuum! Hence, it cannot be associated with the velocity of the assigned particles. Because these are massive, they can only propagate more slowly than light does.

So, we define another quantity — the "group velocity"

$$\boxed{v_g = \frac{d\omega}{dk}} = \frac{d(\hbar\omega)}{d(\hbar k)} = \frac{dE}{dp}.$$

The variation of energy dE of the particle moving under the influence of a force $\vec{F}$ along a path $d\vec{s}$ is $dE = \vec{F}\cdot d\vec{s}$ and because $\vec{F} = \frac{d\vec{p}}{dt}$, we can write:

$$dE = \frac{d\vec{p}}{dt}\cdot d\vec{s} = d\vec{p}\cdot\vec{v}$$

Since $\vec{v}$ and $\vec{p} = m\vec{v}$ are parallel,

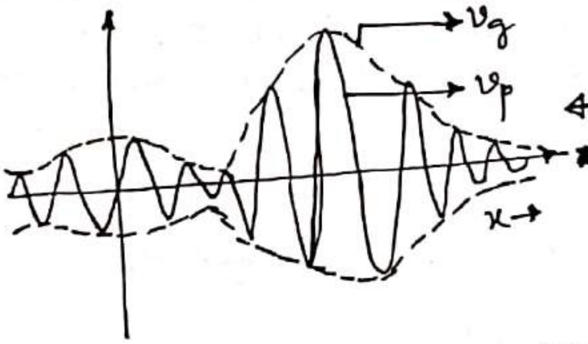
$$dE = |\vec{v}|\,|d\vec{p}| = v\,dp$$

$$\Rightarrow \frac{dE}{dp} = v$$

So, the group velocity of a matter wave is identical with the particle velocity:

$$\boxed{v_g = \frac{dE}{dp} = v}$$

Thus, the group velocity i.e. the velocity of the whole wave packet should be the correct representation of the matter wave velocity.



← A wave packet. The "envelope" travels at the group velocity v_g, whereas the individual "ripple" travels at the phase velocity v_p.

- If we assume the velocity of the free particle to be small $v << c$ (non-relativistic), we can write:

$$E = \frac{p^2}{2m_0} = \frac{\hbar^2 k^2}{2m_0} \Rightarrow \omega = \frac{\hbar k^2}{2m_0} \quad (\text{as } E = \hbar\omega)$$

then, $v_p = \frac{\omega}{k} = \frac{\hbar k}{2m_0}$

whereas, $v_g = \frac{d\omega}{dk} = \frac{\hbar k}{m_0} = \frac{p}{m_0} = v_{\text{classical}}.$ $(\text{as } |\vec{p}| = \hbar|\vec{k}|)$

So, $\boxed{v_{\text{classical}} = v_g = 2v_p.}$

Using de-Broglie relation,

$$\lambda = \frac{2\pi}{k} = \frac{2\pi\hbar}{p} = \frac{h}{p}$$

and for this case $(v << c)$, as $E = \frac{p^2}{2m_0}$, we can write

$$\boxed{\lambda = \frac{h}{\sqrt{2m_0 E}}}$$

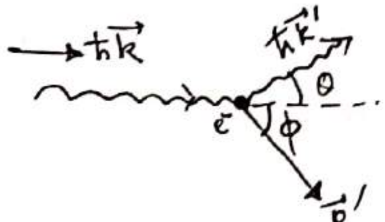
This means that, we must know the rest mass of the particle in motion in order to determine its wavelength!

- Example: An electron with kinetic energy $E = 10$ keV and rest mass $m_0 = 9.1 \times 10^{-28}$ g, calculate its miller wavelength.

Ans: Use $\lambda_e = \dfrac{h}{\sqrt{2m_0 E}} = 0.122 \times 10^{-8}$ cm $= 0.122$ Å

- Compton Scattering:

When high energy photons (X-rays or γ-rays) are scattered by electrons, a shift in frequency can be observed, the amount of this shift depends on the scattering angle. This effect was discovered by Compton in 1923 and explained on the basis of the photon picture simultaneously by Compton himself and Debye.



Assume the electron is unbound and at rest before collision. Let $\hbar\vec{k}$ be the three-momentum of the initial photon, $\hbar\vec{k}'$ be the momentum of the scattered photon ($\vec{k}'$ being wave-vector) and $\vec{p}'$ be be the momentum of the scattered electron. Also the photon scatters at an angle θ from the incident photon.

Since the electron was initially at rest, the momentum conservation requires that,

$$\hbar\vec{k} = \hbar\vec{k}' + \vec{p}' \quad \text{——— (1)}$$

and the energy conservation requires that,

$$\hbar\omega + m_0c^2 = \hbar\omega' + \sqrt{c^2p'^2 + m_0^2c^4} \quad \text{——— (2)}$$

where, m_0 is electron's rest mass. [OR some books use $\dfrac{m_0c^2}{\sqrt{1-v^2/c^2}}$, they are identical]

from eq^n (1),

$$\vec{p}' = \hbar\vec{k} - \hbar\vec{k}'$$

$$\Rightarrow |\vec{p}'|^2 = \hbar^2|\vec{k}|^2 + \hbar^2|\vec{k}'|^2 - 2\hbar^2\,\vec{k}\cdot\vec{k}'$$

$$= \hbar^2k^2 + \hbar^2k'^2 - 2\hbar^2 kk'\cos\theta$$

$$= \hbar^2\frac{\omega^2}{c^2} + \hbar^2\frac{\omega'^2}{c^2} - \frac{2\hbar^2}{c^2}\omega\omega'\cos\theta \quad [\text{As } \omega = c|\vec{k}|]$$

$$\Rightarrow c^2p'^2 = \hbar^2\omega^2 + \hbar^2\omega'^2 - 2\hbar^2\omega\omega'\cos\theta \quad \text{——— (3)}$$

Now, from eq^n (2),

$$\sqrt{c^2p'^2 + m_0^2c^4} = \hbar(\omega-\omega') + m_0c^2$$

squaring both sides,

$$c^2p'^2 + m_0^2c^4 = \hbar^2(\omega-\omega')^2 + m_0^2c^4 + 2m_0c^2\hbar(\omega-\omega')$$

$$\Rightarrow c^2p'^2 = \hbar^2(\omega-\omega')^2 + 2m_0c^2\hbar(\omega-\omega') \quad \text{——— (4)}$$

so, from eq^{n}s (3) & (4),

$$\hbar^2\omega^2 + \hbar^2\omega'^2 - 2\hbar^2\omega\omega'\cos\theta = \hbar^2\omega^2 + \hbar^2\omega'^2 - 2\hbar^2\omega\omega' + 2m_0c^2\hbar(\omega-\omega')$$

$$\Rightarrow 2\hbar^2\omega\omega'(1-\cos\theta) = 2m_0c^2\hbar(\omega-\omega')$$

$$\Rightarrow 1-\cos\theta = \frac{m_0c^2}{\hbar}\left(\frac{1}{\omega'} - \frac{1}{\omega}\right)$$

$$= \frac{m_0c^2}{h}\left(\frac{1}{\nu'} - \frac{1}{\nu}\right) \quad [\text{as } \hbar\omega = h\nu]$$

$$\Rightarrow \boxed{\lambda' - \lambda = \frac{h}{m_0c}(1-\cos\theta)} \quad \left[\text{as } \lambda = \frac{c}{\nu}\right]$$

$$= \frac{2h}{m_0c}\sin^2\theta/2$$

The scattering formula shows that the change in wavelength depends only on the scattering angle θ. During the collision the photon loses a part of its energy and thus the wavelength increases as $\lambda' > \lambda$. The constant $\frac{h}{m_0c}$ must have the dimension of length and is called the "Compton wavelength" — this can be used as a measure of the size of a particle.

The kinetic energy of the scattered electron will be:

$$T = \hbar\omega - \hbar\omega' = h\nu - h\nu'$$

$$= hc\left(\frac{1}{\lambda} - \frac{1}{\lambda'}\right)$$

$$= h\nu \frac{2\lambda_c \sin^2\theta/2}{\lambda + 2\lambda_c\sin^2\theta/2} \quad (\text{prove this!})$$

where, $\lambda_c \equiv$ Compton wavelength $= \frac{h}{m_0c}$.

Thus the energy of the scattered electron is directly proportional to the energy of the photon (which is $= h\nu$). Therefore, the Compton effect can only be observed in the domain of short wavelengths (X-rays and γ-rays).

To see the difference between this results obtained from the classical theory and this new "quanta" theory of light, just remember that, in classical electrodynamics, no alteration in frequency is permitted in the scattering of electromagnetic waves; only light quanta with momentum $\hbar k$ and energy $\hbar\omega$ make this possible! Thus the Compton effect is a further proof for the concept of photons and for the validity of momentum and energy conservation in interaction between light and matter.