

UNIT IV

QUANTUM PHYSICS

INTRODUCTION

During 20th century, scientists have studied the structure of atoms. The discovery of electrons in 1897 by J.J. Thomson proved the presence of more fundamental particles in atoms. After fourteen years, Rutherford discovered that most of the mass of an atom resides in a tiny nucleus whose radius is 10^5 times smaller than that of an atom. In the mean time, Max Planck proved that light beams were made of photons that are equivalent to particles of wave motion. Integration of these concepts and discoveries resulted in development of Quantum theory which deals with discrete nature of energy levels in microscopic systems i.e., subatomic particles as well as atoms, molecules, elements, compounds and much larger systems. In this microscopic world, the distances are measured in nanometres (10^{-9} m) or femtometer (10^{-15} m) or Fermi. The theory of relativity developed by Einstein gave a better understanding to Quantum Physics. It is an interdisciplinary subject relating Nanotechnology, Condensed Matter Physics, Quantum Chemistry, Structural Biology, Particle Physics, Electronics etc.,

BLACK BODY RADIATION

A black body is defined as an object that absorbs all incoming radiations and emits all energy at full efficiency for all wavelengths. To stay in thermal equilibrium, it must emit radiations at the same rate as it absorbs it. Sun and Planets are examples of natural black bodies.

According to Kirchhoff, if a black body having a cavity and a hole at a particular temperature absorbs and then emits equal amount of radiation. Under this condition, the energy distribution in the radiation spectrum does not depend on the material of the wall. Such a radiation was called 'absolutely black'.

Wien and Lummer suggested a test model of an ideal black body to verify Kirchhoff theory experimentally.

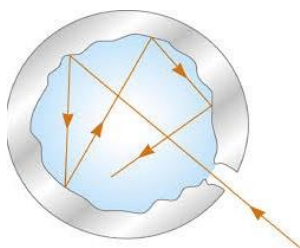


Fig 1 Experimental setup for black body radiation

Accordingly, a double walled metallic sphere was painted inside with lamp black or platinum black material can be used as a black body. Through the hole radiation (light ray) is sent into the sphere maintained at room temperature. The radiation undergoes total internal reflection and gets completely absorbed inside. When the walls of the cavity are heated, the hole will brightly shine owing to the electromagnetic radiation from inside the sphere. Using this experiment, thermal

radiation laws were verified due to fundamental spectral dependence of black body radiation on frequency and temperature.

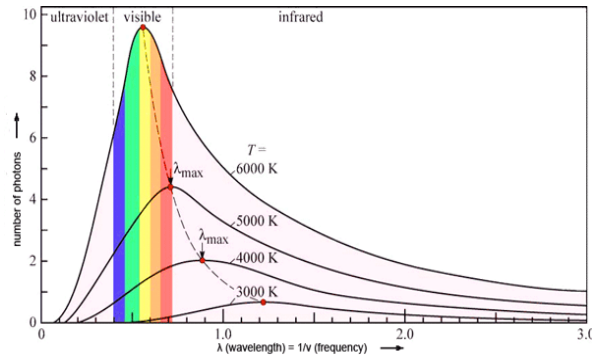


Fig 2 Black body radiation spectrum

The following important conclusions are derived by the above spectrum

- 1) The shape of the curve is the same for all temperatures
- 2) The energy is not uniformly distributed. At a given temperature the intensity of radiation increases with the increase in wavelength, attains a maximum and then decreases.
- 3) The wavelength corresponding to maximum energy (λ_m) shifts towards lower wavelengths as the temperature increases.
- 4) For all the wavelengths an increase in temperature causes increase in energy.
- 5) At any given temperature the total energy emitted is calculated by measuring the area under that particular curve.

LAWS OF BLACK BODY RADIATION

Empirical laws are framed from experimental behaviour.

STEFAN-BOLTZMANN LAW

Stefan-Boltzmann law states that the total energy(E) emitted per unit area per second increases with the fourth power of the absolute temperature of the body

$$E \propto T^4$$

$$E = \sigma T^4$$

Where the constant $\sigma = 5.67 \times 10^{-8} \text{ Wm}^{-2}\text{K}^{-4}$ is called Stefan's constant. The area under the curve represents the total energy emitted per unit area of the surface of black body per second at that particular temperature.

WIEN'S DISPLACEMENT LAW

Wien's displacement law states that the product of the peak wavelength and temperature is constant.

$$\lambda_m T = \text{constant}$$

The value of this constant is $2.898 \times 10^{-3} \text{ mK}$.

Wien also showed that the maximum energy radiated at peak wavelength is proportional to the fifth power of absolute temperature

$$E_{\lambda} \propto T^5$$

This is called Wien's radiation law. The energy density in the wavelength range λ and $\lambda+d\lambda$ is given as

$$E_{\lambda}d\lambda = C_1\lambda^{-5}e^{-C_2/\lambda T}d\lambda$$

Where C_1 and C_2 are constants and T is the temperature of the black body. **This is Wien's radiation law which holds good only for shorter wavelengths.**

RAYLEIGH-JEANS LAW

The energy density in the wavelength range λ and $\lambda+d\lambda$ is given as

$$E_{\lambda}d\lambda = \frac{8\pi k_B kT}{\lambda^4}d\lambda$$

Where k_B is the Boltzmann constant. **This law holds good only for shorter wavelengths.**

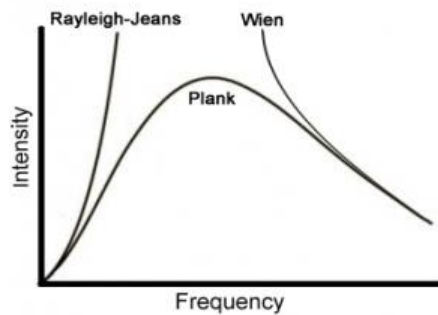


Fig 3 Radiation laws-comparison of classical and quantum concepts

From the fig 3, it is clear that Wien's law fits well at lower range of wavelengths but fail at higher range. The Rayleigh-Jeans formula agrees well with the experimental results at longer wavelength. In the shorter wavelength region however the formula predicts very high energy density and thus disagrees with the experimental results. This is called **ultraviolet catastrophe**. Thus, where the Wien's law fails, the Rayleigh-Jeans law works and vice versa.

PLANCK'S QUANTUM THEORY OF BLACK BODY RADIATION

Assumptions

- Black body contains electric oscillators of all frequencies and these oscillators are responsible for emission and absorption of radiation.
- Energy changes should take place discontinuously or discretely.
- The energy is always integral multiples of small, indivisible unit or packet called energy quantum.
- The quantum of energy is directly proportional to the frequency of the emitted radiation given by equation $E = nh\nu$ where h is called Planck's constant whose value is given by $h = 6.625 \times 10^{-34}Js$.

Let N be the number of oscillators with total energy (E_T) and the average energy of an oscillator (\bar{E}) is given by

$$\bar{E} = \frac{E_T}{N} \quad (1)$$

If $N_0, N_1, N_2, N_3, \dots, N_r$ are the atomic oscillators of energy $0, E, 2E, 3E, \dots, rE$ respectively then

$$\text{Total number of oscillators } N = N_0 + N_1 + N_2 + N_3 + \dots + N_r \quad (2)$$

The total energy of oscillators

$$E_T = 0N_0 + EN_1 + 2EN_2 + 3EN_3 + \dots + rEN_r \quad (3)$$

According to Maxwell's distribution formula, the number of oscillators having an energy rE is given by

$$N_r = N_0 e^{-rE/k_B T} \quad (4)$$

where k_B is called Boltzmann constant and $r=0,1,2,3,\dots$

The number of oscillators corresponding to various values of r can be calculated as

$$\begin{aligned} \text{a. For } r = 0 & \quad ; \quad N_0 = N_0 e^0 \\ \text{b. For } r = 1 & \quad ; \quad N_1 = N_0 e^{-E/k_B T} \\ \text{c. For } r = 2 & \quad ; \quad N_2 = N_0 e^{-2E/k_B T} \\ \text{d. For } r = 3 & \quad ; \quad N_3 = N_0 e^{-3E/k_B T} \\ \text{For } r = r & \quad ; \quad N_r = N_0 e^{-rE/k_B T} \end{aligned} \quad (5)$$

Substituting equation (5) in equation (2) we get

$$\begin{aligned} N &= N_0 e^0 + N_0 e^{-E/k_B T} + N_0 e^{-2E/k_B T} + N_0 e^{-3E/k_B T} + \dots + N_0 e^{-rE/k_B T} \\ N &= N_0 [1 + e^{-E/k_B T} + e^{-2E/k_B T} + e^{-3E/k_B T} + \dots + e^{-rE/k_B T}] \end{aligned} \quad (6)$$

We know from finite Geometric series that

$$1 + x + x^2 + x^3 + \dots + x^n = \frac{1 + x^{n+1}}{1 - x}$$

If $-1 < x < 1$ then

$$1 + x + x^2 + x^3 + \dots + x^n = \frac{1}{1-x}$$

On applying the above mathematical series equation (6) becomes

$$N = N_0 \left[\frac{1}{1 - e^{-E/k_B T}} \right] \quad (7)$$

Similarly on substituting equation (5) in equation (3) we get

$$E_T = 0N_0 e^0 + EN_0 e^{-E/k_B T} + 2EN_0 e^{-2E/k_B T} + 3EN_0 e^{-3E/k_B T} + \dots + rEN_0 e^{-rE/k_B T}$$

$$E_T = N_0 [0 + E e^{-E/k_B T} + 2E e^{-2E/k_B T} + 3E e^{-3E/k_B T} + \dots + rE e^{-rE/k_B T}]$$

$$E_T = N_0 E e^{-E/k_B T} [1 + 2e^{-E/k_B T} + 3e^{-2E/k_B T} + \dots + r e^{-(r-1)E/k_B T}] \quad (8)$$

We know from finite Geometric series that

$$1 + 2x + 3x^2 + 4x^3 + \dots + nx^{n-1} = \frac{1}{(1-x)^2} \quad \text{for } -1 < x < 1$$

On applying the above mathematical series equation (8) becomes

$$E_T = N_0 E e^{-E/k_B T} \left[\frac{1}{(1 - e^{-E/k_B T})^2} \right] \quad (9)$$

Substituting equation (7) and equation (9) in equation (1) we get

The average energy is given by

$$\begin{aligned} \bar{E} = \frac{E_T}{N} &= \frac{N_0 E e^{-E/k_B T}}{N_0 \left[\frac{1}{(1 - e^{-E/k_B T})^2} \right]} \left[\frac{1}{(1 - e^{-E/k_B T})^2} \right] \\ \bar{E} &= \frac{E e^{-E/k_B T}}{(1 - e^{-E/k_B T})} \\ \bar{E} &= \frac{E}{\left[\frac{(1 - e^{-E/k_B T})}{e^{-E/k_B T}} \right]} \\ \bar{E} &= \frac{E}{\left[\frac{1}{e^{-E/k_B T}} - 1 \right]} \\ \bar{E} &= \frac{E}{e^{E/k_B T} - 1} \end{aligned} \quad (10)$$

Since $E = h\nu$

$$\bar{E} = \frac{h\nu}{e^{h\nu/k_B T} - 1} \quad (11)$$

This equation represents the average energy of the oscillator.

The number of oscillators per unit volume within the range of frequency ν and $\nu + d\nu$ is given by $N = \frac{8\pi\nu^2}{c^3} d\nu$ (12)

$$\therefore \text{Energy density or total energy per unit volume } (E_\nu d\nu) = N \bar{E} \quad (13)$$

Substituting equation (11) and equation (12) in equation (13)

$$E_\nu d\nu = \frac{8\pi\nu^2}{c^3} d\nu \frac{h\nu}{e^{h\nu/k_B T} - 1} \quad (14)$$

$$E_\nu = \frac{8\pi h \nu^3}{c^3 (e^{h\nu/k_B T} - 1)} \quad (15)$$

This equation represents the **Planck's radiation law in terms of frequency.**

In terms of wavelength

Differentiating the relation $\nu = \frac{c}{\lambda}$ (16)

We get $d\nu = \frac{-c}{\lambda^2} d\lambda$

$$|d\lambda| = \left| \frac{-c}{\lambda^2} d\lambda \right| = \left[\frac{c}{\lambda^2} \right] d\lambda \quad (17)$$

Substituting equation (16) and equation (17) in equation (14) we get

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \left(\frac{1}{e^{hc/\lambda k_B T} - 1} \right) d\lambda$$

$$E_\lambda = \frac{8\pi hc}{\lambda^5} \left(\frac{1}{e^{hc/\lambda k_B T} - 1} \right) \quad (18)$$

This equation represents the **Planck's radiation law in terms of wavelength**. This formula agrees well with the experimental curves in the whole range of wavelengths.

From this formula, Wien's displacement law and Rayleigh-Jeans law can be deduced as follows.

(i) Wien's displacement law

This law holds good for shorter wavelengths

If λ is small, $(e^{hc/\lambda k_B T} - 1) \gg 1$ and hence 1 can be neglected from the equation (18)

\therefore Equation (18) becomes

$$E_\lambda = \frac{8\pi hc}{\lambda^5} \left(\frac{1}{e^{hc/\lambda k_B T}} \right)$$

$$E_\lambda = 8\pi hc \lambda^{-5} e^{-hc/\lambda k_B T}$$

$$E_\lambda = C_1 \lambda^{-5} e^{-C_2/\lambda T} \quad (19)$$

where C_1 and C_2 are constants whose value is given by $C_1 = 8\pi hc$ and $C_2 = \frac{hc}{k_B}$

Also, as $T \propto \frac{1}{\lambda}$ and $E_\lambda \propto \lambda^{-5}$, then

$$E_\lambda \propto T^5 \quad (20)$$

Equation (19) and equation (20) represents Wien's displacement law.

(ii) Rayleigh-Jeans law

This law holds good for longer wavelengths.

If λ is large, $\frac{hc}{\lambda k_B T} \ll 1$ and hence $e^{hc/\lambda k_B T}$ can be expanded using exponential series as

$$e^{hc/\lambda k_B T} = 1 + \frac{hc}{\lambda k_B T} + \frac{1}{2} \left[\frac{hc}{\lambda k_B T} \right]^2 + \frac{1}{6} \left[\frac{hc}{\lambda k_B T} \right]^3 + \dots$$

For larger values of λ higher powers of $\frac{hc}{\lambda k_B T}$ would be very small and hence can be neglected.

Therefore, the above equation becomes

$$e^{hc/\lambda k_B T} = 1 + \frac{hc}{\lambda k_B T} \quad (21)$$

Substituting equation (21) in equation (18), we get

$$E_\lambda = \frac{8\pi hc}{\lambda^5} \left(\frac{1}{1 + \frac{hc}{\lambda k_B T} - 1} \right)$$

$$E_\lambda = \frac{8\pi k_B T}{\lambda^4} \quad (22)$$

Equation (22) represents Rayleigh Jeans's law.

Thus Wien's displacement law and Rayleigh-Jeans law can be deduced from Planck's radiation law.

MATTER WAVES

According to the principle of wave particle duality in quantum physics, the matter and light exhibit the behaviours of both waves and particles, depending upon the circumstances of the experiment.

De Broglie concept of dual nature

1. The Universe is made of radiation and matter.
2. Light exhibits dual nature.
3. Nature loves symmetry, so an electron or any other material particles must exhibit dual nature.

Wave Particle Duality in Matter

Light functions as both a particle and a wave, depending on how the experiment is conducted and when observations are made.

The question of whether such duality also showed up in matter was tackled by the de Broglie hypothesis, which extended Einstein's work to relate the observed wavelength of matter to its momentum. Experiments confirmed the hypothesis in 1927, resulting in a 1929 Nobel prize for de Broglie.

De Broglie wavelength

From the theory of light, considering a photon as a particle the total energy of the photon is given by

$$E = mc^2 \quad (1)$$

For the photon as a wave, the total energy is given by

$$E = hv \quad (2)$$

From equations (1) and (2) we can get

$$E = mc^2 = hv \quad (3)$$

$$= pc = hv \quad (p = mc)$$

Therefore, momentum $p = \frac{hv}{c} = \frac{h}{\lambda} \quad (\lambda = \frac{c}{v})$

Now, the wavelength of photon $\lambda = \frac{h}{p}$

De Broglie suggested that the above equation for wavelength of photon can also be applied for material particles, if we take m is the mass of the particle and v is the velocity of the particle, then

De Broglie wavelength $\lambda = \frac{h}{mv}$ ($p = mv$)

The quantum mechanical “wavelength” associated with a particle, named as de Broglie wavelength after the scientist who discovered it. In quantum mechanics, **all particles also have wave characteristics, where the wavelength of a particle is inversely proportional to its momentum and the constant of proportionality is the Planck constant.**

Other forms of de Broglie wavelength

1. De Broglie wavelength in terms of energy

We know, the K.E of the matter particle $E = \frac{1}{2} mv^2$

Multiply ‘ m ’ on both sides of above equation

Then $Em = \frac{1}{2} m^2 v^2$

$$2Em = m^2 v^2 \text{ or } mv = \sqrt{2Em}$$

Therefore $\lambda = \frac{h}{\sqrt{2Em}}$

2. De Broglie wavelength in terms of voltage

If a charged particle of charge ‘ e ’ is accelerated with a potential difference ‘ V ’

Then equating energy of the particle and its K.E, we get

$$eV = \frac{1}{2} mv^2$$

Multiply ‘ m ’ on both sides of above equation

$$meV = \frac{1}{2} m^2 v^2 \text{ or } mv = \sqrt{2meV}$$

Therefore $\lambda = \frac{h}{\sqrt{2meV}}$

3. De Broglie wavelength in terms of temperature

When a particle is in thermal equilibrium at temperature T , then their K.E is

$$E_k = \frac{1}{2} mv_{rms}^2$$

Where v_{rms} is the root mean square velocity of the particle.

And also, energy $E = \frac{3}{2} kT$

Where ‘ k ’ is the Boltzmann constant.

From both the energy equations we can get

$$\frac{1}{2} mv^2 = \frac{3}{2} kT \text{ or } mv = \sqrt{3mkT}$$

Therefore $\lambda = \frac{h}{\sqrt{3mkT}}$

Significance of wave Particle Duality

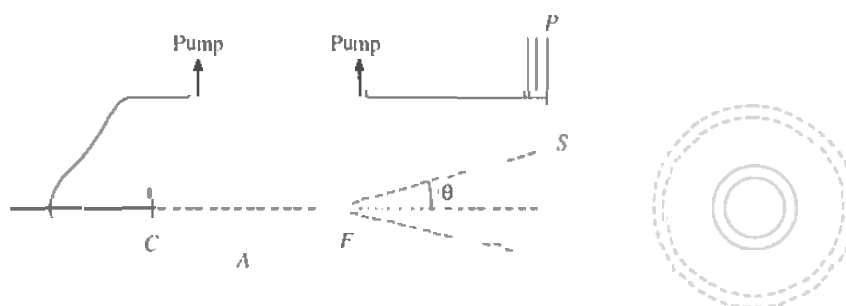
The major significance of the wave particle duality is that all behavior of light and matter can be explained through the use of a differential equation which represents a wave function, generally in the form of the Schrodinger equation. This ability to describe reality in the form of waves is the heart of quantum mechanics.

The most common interpretation is that the wave function represents the probability of finding a given particle at a given point. These probability equations can diffract, interfere, and exhibit other wave-like properties, resulting in a final probabilistic wave function that exhibits these properties as well. Particles are distributed according to the probability laws, and therefore exhibit the wave properties. In other words, the probability of a particle being in any location is a wave, but the actual physical appearance of that particle isn't.

While the mathematics, though complicated, makes accurate predictions, the physical meaning of these equations are much harder to grasp. The attempt to explain what the wave particle duality “actually means” is a key point of debate in quantum physics. Many interpretations try to explain this, but they are all bound by the same set of wave equations and ultimately, explain the same experimental observations.

EXPERIMENTAL VERIFICATION OF MATTER WAVES-G.P. THOMSON'S EXPERIMENT

Electrons from an electron source were accelerated towards a thin film made up of gold. The electron beam is accelerated by passing high voltage of about 60,000 volts. This beam is made narrow pencil of beam by passing through two slits. After passing through the gold film of thickness around $1\mu\text{m}$, the electron beam falls on the photographic film. On developing the photographic film, the resultant diffraction pattern can be seen as shown in the fig. The whole apparatus is placed in high vacuum so that electron may not lose their energy in collision with the molecules of the gas.



Thomson's experiment

a) G. P Thomson's apparatus for electron diffraction

b) Diffraction pattern of a beam of electrons by thin gold foil

The diffraction pattern was in the form of continuous, concentric, alternate black and white rings as diffraction was due to the crystalline grains which were randomly oriented at all

possible angles in the gold foil. This pattern confirms that the diffraction is only due to the presence of electrons and not due to secondary x-rays produced by the electrons while passing through the foil. If the electrons behaved as particles then they would have been scattered through a wide angle by the foil. Thus this experiment clearly proves that electron behave as waves.

SCHRÖDINGER WAVE EQUATION

Schrödinger wave equation is one of the basic equations in quantum mechanics. It can be used for both macroscopic and microscopic particles. Schrödinger derived this mathematical equation to describe the dual nature of matter waves and also to extend the idea of matter waves. He has incorporated the expression for De Broglie wavelength into the general classical wave equation to form his wave equation. This equation describes the motion of the atomic particles like electrons in an atom or metal. There are two forms of schrödinger wave equation:

1. Time dependent wave equation, and
2. Time independent wave equation.

Schrödinger time dependent wave equation

According to classical mechanics if 'x' is the position of the particle moving with the velocity 'v' then the displacement of the particle at time 't' is given by

$$Y = A e^{-i\omega(t-x/v)}$$

where ω is the angular frequency of the particle.

Similarly, in Quantum Mechanics the wave function $\Psi(x, t)$ represents the position x of a moving particle at any time 't' and is given by

$$\Psi(x, t) = A e^{-i\omega(t-x/v)} \quad (1)$$

We know the angular frequency $\omega = 2\pi\nu$

\therefore Equation (1) becomes as

$$\Psi(x, t) = A e^{-2\pi i(\nu t - \nu x/v)} \quad (2)$$

We know $E = h\nu$

$$\text{Or } \nu = \frac{E}{h} \quad (3)$$

Also, if 'v' is the velocity of the particle behaving as a wave, then the frequency $\nu = \frac{v}{\lambda}$

$$(\text{or}) \frac{\nu}{v} = \frac{1}{\lambda} \quad (4)$$

substituting equation (3) and (4) in equation (2) we get

$$\Psi(x, t) = A e^{-2\pi i \left(\frac{E}{h} t - \frac{x}{\lambda} \right)} \quad (5)$$

If 'p' is the momentum of the particle behaving as a wave, then the de – Broglie wavelength is given by

$$\lambda = \frac{h}{mv} = \frac{h}{p} \quad (6)$$

substituting equation (6) in (5) we get

$$\begin{aligned} \Psi(x, t) &= A e^{-2\pi i \left(\frac{Et}{h} - \frac{px}{h} \right)} \\ \text{(or)} \quad \Psi(x, t) &= A e^{\frac{-2\pi i}{h}(Et - px)} \end{aligned} \quad (7)$$

We can write

$$\Psi(x, t) = A e^{\frac{-i}{\hbar}(Et - px)} \quad (8)$$

where $\hbar = \frac{h}{2\pi} = 1.055 \times 10^{-34}$ Js is called reduced Planck's constant.

Differentiating equation (8) partially with respect to 'x' we get

$$\frac{\partial \Psi}{\partial x} = A e^{\frac{-i}{\hbar}(Et - px)} (ip/\hbar) \quad (9)$$

Differentiating once again partially with respect to 'x' we get

$$\frac{\partial^2 \Psi}{\partial x^2} = A e^{\frac{-i}{\hbar}(Et - px)} \left(\frac{i^2 p^2}{\hbar^2} \right) \quad (10)$$

Since $\Psi(x, t) = A e^{\frac{-i}{\hbar}(Et - px)}$ and $i^2 = -1$, we can write

$$\begin{aligned} \frac{\partial^2 \Psi}{\partial x^2} &= \Psi(x, t) \cdot \left(\frac{-p^2}{\hbar^2} \right) \\ \text{(or)} \quad p^2 \Psi &= -\hbar^2 \frac{\partial^2 \Psi}{\partial x^2} \end{aligned} \quad (11)$$

Differentiating equation (8) partially with respect to 't' we get

$$\begin{aligned} \frac{\partial \Psi}{\partial t} &= A e^{\frac{-i}{\hbar}(Et - px)} (-iE/\hbar) \\ \text{(or)} \quad \frac{\hbar}{-i} \frac{\partial \Psi}{\partial t} &= E \Psi \quad [\Psi(x, t) = A e^{\frac{-i}{\hbar}(Et - px)}] \\ \text{(or)} \quad E \Psi &= i \hbar \frac{\partial \Psi}{\partial t} \end{aligned} \quad (12)$$

A particle can behave as wave only under motion. So, it should be accelerated by a potential field (V) and kinetic energy.

Therefore the total energy $E = V + \frac{mv^2}{2}$

$$E = V + \frac{m^2 v^2}{2m}$$

$$E = V + \frac{p^2}{2m} \quad (p=mv)$$

$$E\Psi = V\Psi + \frac{p^2}{2m}\Psi \quad (13)$$

Substituting equations (11) and (12) in equations (13), we get,

$$i\hbar \frac{\partial \Psi}{\partial t} = V\Psi - \frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} \quad (14A)$$

$$\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + i\hbar \frac{\partial \Psi}{\partial t} - V\Psi = 0 \quad (14B)$$

equation (14) represents the **Schrödinger's one dimensional time dependent wave equation**. It is called time dependent wave equation because here the wave function $\Psi(x, t)$ depends both on position x and time t .

For a free particle, the potential energy $V=0$ and the equation (14B) becomes

$$\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + i\hbar \frac{\partial \Psi}{\partial t} = 0 \quad (14C)$$

The equation (14C) represents **Schrödinger's one dimensional time dependent wave equation for a free particle**.

Similarly, the three dimensional form of above equation is written as

$$\frac{\hbar^2}{2m} \nabla^2 \Psi + i\hbar \frac{\partial \Psi}{\partial t} - V\Psi = 0 \quad (15)$$

where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is the Laplacian operator

The equation (15) represents **Schrödinger's three dimensional time dependent wave equation**.

$$\frac{\hbar^2}{2m} \nabla^2 \Psi + i\hbar \frac{\partial \Psi}{\partial t} = 0 \quad (15A)$$

The equation (15A) represents **Schrödinger's three dimensional time dependent wave equation for a free particle**.

Equation (15) can be written as

$$E\Psi = H\Psi \quad (16)$$

where $\Psi(x, t) = \Psi(x, y, z, t)$

where Hamiltonian operator $H = V - \frac{\hbar^2}{2m} \nabla^2$

Schrödinger time independent wave equation

The form of equation (15) can be modified if we are not concerned with the dynamic changes of energy state. It is convenient to use the time independent wave equation rather than using time dependent wave equation for many applications.

We know that from equation (8), the splitting of RHS of this equation can be separated into two parts, viz, (1) Time dependent factor and (2) Time independent factor.

$$\text{Therefore } \Psi(x, t) = A e^{-\frac{iEt}{\hbar}} \cdot e^{\frac{ipx}{\hbar}}$$

$$\text{Or } \Psi(x, t) = A \psi(x) e^{-\frac{iEt}{\hbar}} \quad (16)$$

Where $\psi(x)$ represents the time independent wave function i.e. $\psi(x) = e^{\frac{ipx}{\hbar}}$

Differentiating equation (16) partially with respect to 't' we get

$$\frac{\partial \Psi}{\partial t} = A \psi(x) e^{-\frac{iEt}{\hbar}} \left(-\frac{iE}{\hbar}\right) \quad (17)$$

Differentiating equation (16) partially with respect to 'x' we get

$$\frac{\partial \Psi}{\partial x} = A e^{-\frac{iEt}{\hbar}} \frac{\partial \psi(x)}{\partial x} \quad (18)$$

Differentiating equation (18) partially with respect to 'x' we get

$$\frac{\partial^2 \Psi}{\partial x^2} = A e^{-\frac{iEt}{\hbar}} \frac{\partial^2 \psi(x)}{\partial x^2} \quad (19)$$

From the equation (14A) the Schrödinger one dimensional time dependent wave equation is

$$i \hbar \frac{\partial \Psi}{\partial t} = V \Psi - \frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2}$$

by substituting equations (17), (18) and (19) in above equation, we get

$$i \hbar A \psi(x) e^{-\frac{iEt}{\hbar}} \left(-\frac{iE}{\hbar}\right) = V A \psi(x) e^{-\frac{iEt}{\hbar}} - \frac{\hbar^2}{2m} A e^{-\frac{iEt}{\hbar}} \frac{\partial^2 \psi(x)}{\partial x^2} \quad (20)$$

After simplification of the equation (20), we get

$$E \psi(x) = V \psi(x) - \frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} \quad \dots\dots\dots(21)$$

Equation (21) is modified and then written as

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2} (E - V) \psi(x) = 0 \quad (22)$$

Equation (22) is called as **Schrödinger's one dimensional time independent wave equation.**

For a free particle, the potential energy $V=0$ and the equation (22) becomes

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2} E \psi(x) = 0 \quad (23)$$

Equation (23) is called as **Schrödinger's one dimensional time independent wave equation for a free particle.**

Similarly the **three dimensional Schrödinger time independent wave equation** can be written as

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0 \quad (24)$$

Where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is the Laplacian operator

For a free particle, the potential energy $V=0$ and the equation (23) becomes

$$\nabla^2 \psi + \frac{2m}{\hbar^2} E \psi = 0 \quad (25)$$

Equation (25) is called as **Schrödinger's three dimensional time independent wave equation for a free particle.**

PHYSICAL SIGNIFICANCE OF WAVE FUNCTION Ψ

- i. Wave function Ψ is a complex quantity and hence it is not a measurable quantity.
- ii. It connects the particle and its associated wave statistically.
- iii. It determines variation in the matter waves.
- iv. The square of the wave function Ψ is a measurable quantity and it is used to find the particle at a particular position. Square of the wave function Ψ is a positive quantity and it is denoted as $P(r, t)$. it is defined as

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

- v. The probability of finding the particle with in a volume $d\tau$ is

$$P = \iiint |\Psi(r, t)|^2 d\tau$$

Where $d\tau = dx.dy.dz$

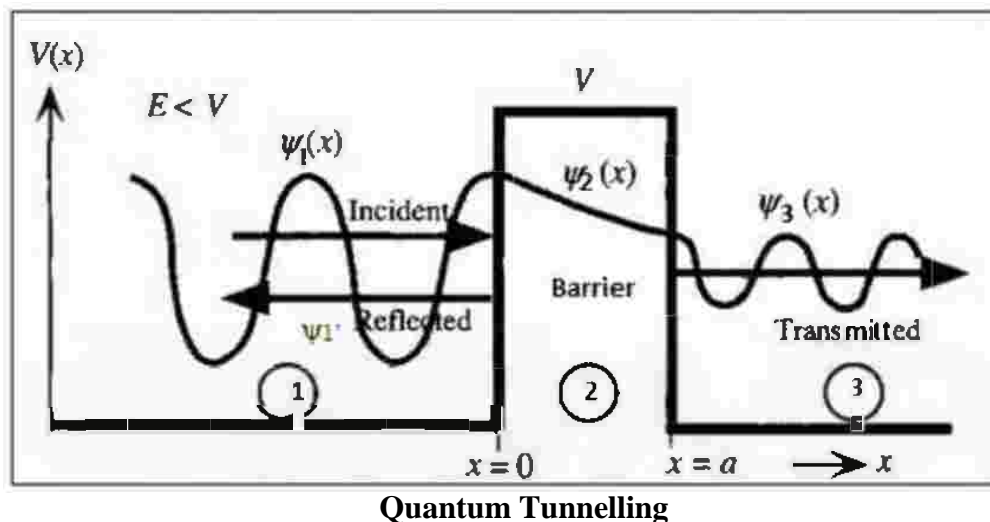
- vi. The probability of finding the particle is maximum, when it is equal to one and minimum, when it is equal to zero.
- vii. In optics, the amount of light is expressed in terms of its intensity rather than its amplitude, since intensity is a measurable physical quantity. Similarly, the wave function has no physical meaning, where as probability density has physical meaning.

TUNNELLING

In Quantum Mechanics, a particle having lesser energy (E) than the barrier potential (V) can easily cross over the potential barrier having a finite width ' l ' even without climbing over the barrier by tunnelling through the barrier. This process is called Tunnelling.

Explanation:

Let us consider a beam of particles having kinetic energy E less than the barrier potential (V), incident from the region (1) as shown in fig below.



According to Classical Mechanics, the probability for the incident particles to cross the barrier is zero, because it has very less energy (E) when compared to the barrier potential (V).

According to Quantum Mechanics, the incident wave from region -1 having the wave function ψ_1 can cross the barrier (region-2) by the process of tunnelling, represented by wave function ψ_2 and come out to the region-3, represented by ψ_3 . However based on the width of the potential barrier there is probability for the wave, represented by wave function ψ_1 , to get reflected within the same region-1 as shown in fig.

The value of transmission coefficient T depends on the mass of the particle (m), thickness of the barrier (l) and the energy difference i.e., ($V-E$)

Examples :

1. The tunneling effect is observed in Josephson junction, in which electron pairs in the superconductors tunnel through the barrier layer, giving rise to Josephson current.
2. This effect is also observed in the case of emission of alpha particles by radioactive nuclei. Though the α -particle has very less kinetic energy they are able to escape from the nucleus whose potential wall is around 25 MeV high.
3. Tunnelling also occurs in certain semiconductor diodes called tunnel diodes.
4. Electron tunnels through insulating layer and act as a switch by tunneling effect.

SCANNING TUNNELING MICROSCOPE

Introduction :

A microscope is a device which is used to view the magnified image of a smaller object, which cannot be clearly seen through our naked eye.

In 1980, Gerd Binnig and Heinrich Rohrer invented a new type of microscope called Scanning Tunnelling Microscope (STM). In this microscope, we can obtain the images of electrically conducting surfaces in atomic scale, ie., STM is used to observe the surfaces in terms of atom by atom.

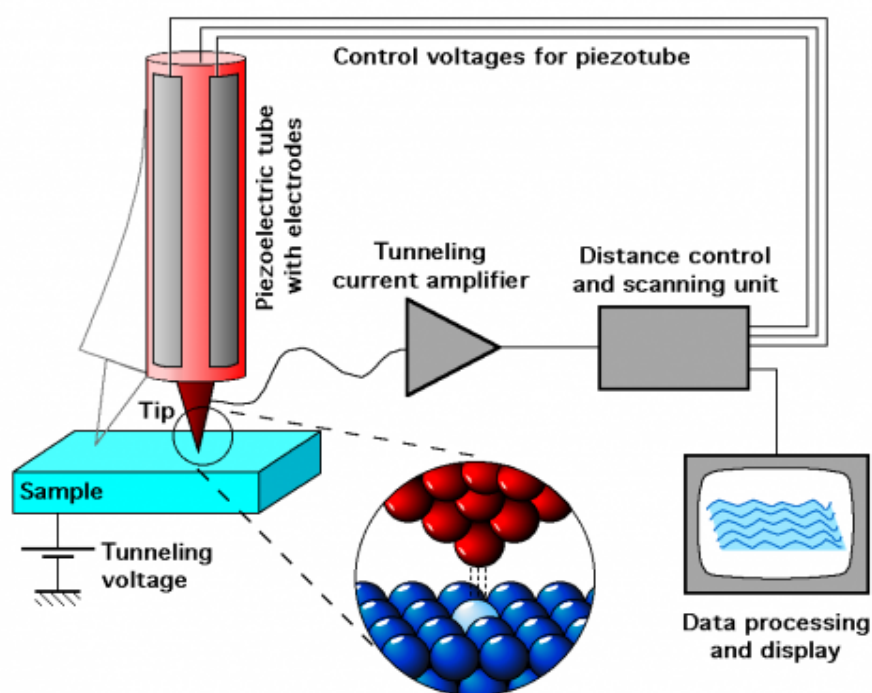
Principle:

The basic principle used in scanning tunnelling microscope (STM) is the tunnelling of electron between the sharp metallic tip of the probe and the surface of a sample.

Here, constant tunnelling current is maintained by adjusting the distance between the tip and the sample, with an air gap for electron to tunnel. In a similar way the tip is used to scan atom by atom and line by line of the sample and the topography of the sample is recorded in the computer.

Construction :

1. The experimental setup consists of a probe in which a small thin metal wire is etched in such a way that the tip of the probe will have only one atom as shown in the figure below.



Scanning Tunnelling Microscope (STM)

2. The tip is tapered down to a single atom, so that it can follow even a small change in the contours of the sample.

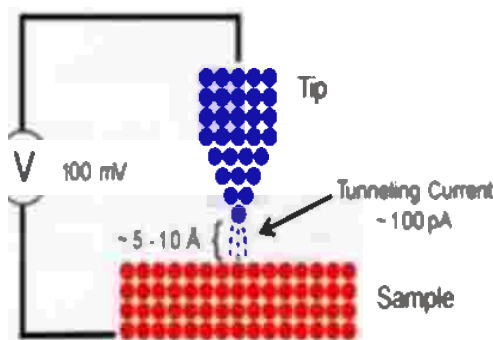
3. The tip is connected to the scanner and it can be positioned to X,Y,Z co-ordinates using a computer as shown in the figure.
4. The sample for which the image has to be recorded is kept below the tip of the probe at a particular distance of at least 2 atom spacing so that the tip is not touching the sample.
5. The computer is also used to record the path of the probe and the topography of the sample in a grey scale or colour.
6. Necessary circuit connections along with an amplifier are provided to measure the tunnelling current in the circuit.

Components of STM

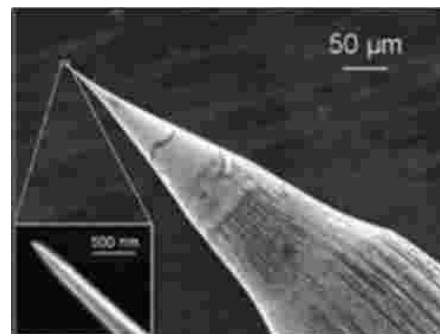
The main components of STM include scanning tip, Piezoelectric scanner, Distance control and scanning unit, Vibration isolation system and Data processing unit (Computer).

1. Scanning Tip:

STM tips are usually made from tungsten metal or a platinum-iridium alloy where at the very end of the tip (called apex) there is one atom of the material. Scanning tip is the most important aspect of the STM as tunneling current is carried by that particular atom.



Sample and Tip at atomic level

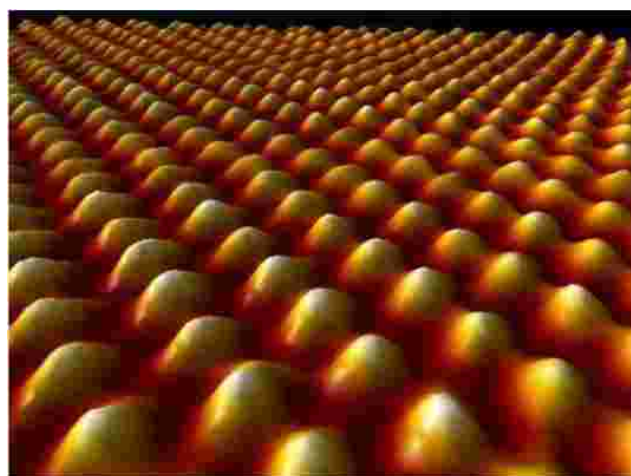
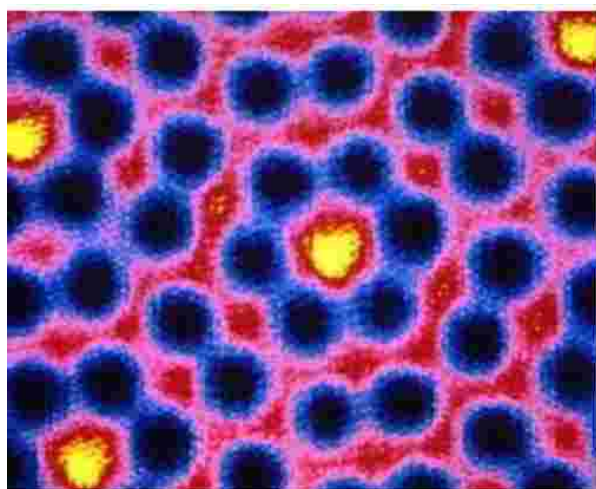
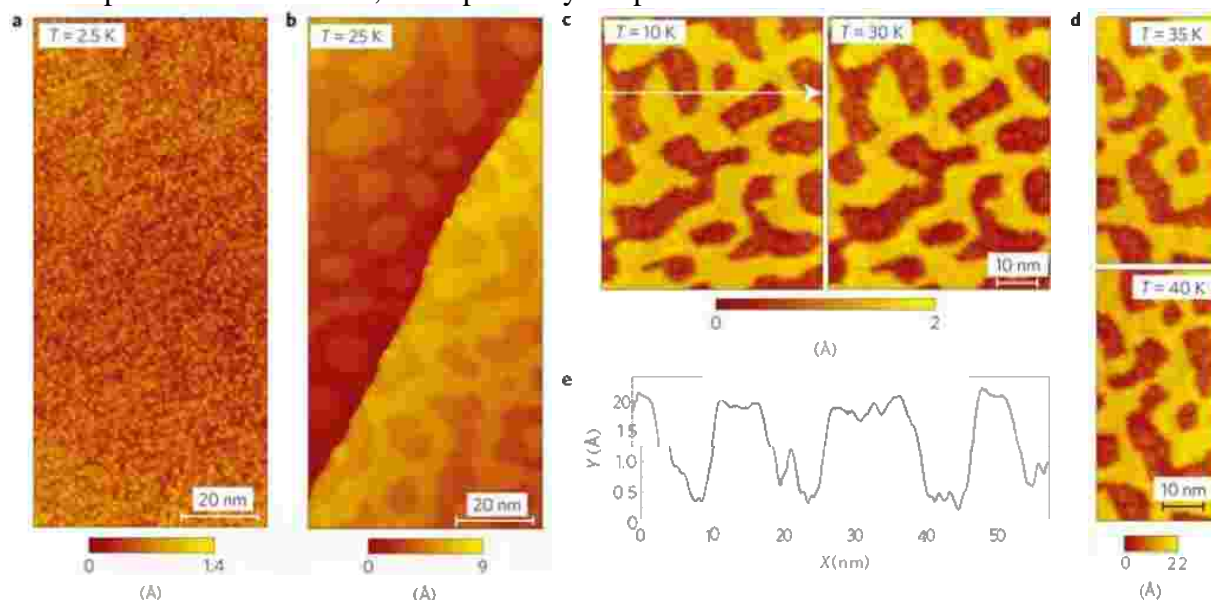


STM tip under $10^3\times$ and $10^5\times$ magnification

Working :

1. Circuit is switched ON and necessary biasing voltage is given to the probe.
2. Due to biasing the electrons will tunnel or jump between the tip of the probe and sample and therefore produces a small electric current called tunnelling current.
3. The tunnelling current flows through the circuit only if the tip is in contact with the sample through the small air gap at a distance d between them.
4. The current produced is amplified and measured in the computer.
5. It is found that the current increases or decreases based on the distance between the tip of the probe and the sample.
6. The current in the circuit should be monitored in such a way that it should be maintained constant.
7. Therefore, for maintaining the constant current, the distance d between the tip and the sample should be continuously adjusted whenever the tip moves over the surface of the sample.

8. The height of fluctuations (d) between the tip and the sample is accurately recorded and as a result, a map of 'bumps' is obtained in the computer as shown in the figure.
9. In a similar way the tip is scanned atom by atom and line by line of the sample and the topography of the sample is recorded in the computer.
10. The STM does not show the picture of the atom, rather it records only the exact position of the atoms, more precisely the position of electrons.



Advantages :

1. It can scan the positions and topography atom by atom or even electrons.
2. It is the latest technique used in research laboratories for scanning the materials.
3. Very accurate measurement shall be obtained.
4. Magnification is upto nanoscale.

Disadvantages :

1. Even a very small sound or vibrations will disturb the measurement setup.
2. It should be kept in vacuum, as even a single dust particle may damage the tip of the probe.
3. Cost is high.
4. More complexity.

Applications :

1. It is used to produce Integrated circuits.
2. Scanning tunneling microscopy has recently been introduced as a promising tool for analyzing surface atomic structure. It allows the analysis of surface structure with sizes that range down to one ångström (0.1 nm).
3. It has the capability to readily store the data digitally for further processing.
4. STM has made it possible to modify the surfaces at nanometer scale and to manipulate even single atom with the help of its tip.
5. STM can manipulate atoms, fabricate nanostructures and characterize their novel properties.