Unit-IV

Quantum Mechanics

Quantum theory of black body radiation

Assumptions

- A black body radiator contains electrons or simple harmonic oscillators, which are capable of vibrating with all possible frequencies.
- The frequency of radiation and emission are equal.
- The radiated energy is in the discrete manner.
- The exchange of energy is in the form of absorption or emission, in terms of quanta of magnitude '$h\gamma$'

ie $E = nh\gamma$ where n is an integer

Planck's Radiation Law

Let us consider N is the no. of oscillators with their total energy as E_T Then the average energy of an oscillator is

$$\bar{E} = \frac{E_T}{N} \qquad ---1$$

If $N_0, N_1, N_2, N_3, \ldots N_r$ are the oscillators of energy 0, E, 2E……rE

The total no. of oscillators $N = N_0 + N1 + N2 + \ldots\ldots + N_r$ ------- 2

The total energy of the oscillators $E_T = 0\,N_0 + E\,N_1 + 2EN_2 + \ldots\ldots + rE\,N_r$ -------- 3

According to Maxwell's distribution formula, the no. of oscillator having an energy rE is

$$N_r = N_0 e^{-rE/K_BT} \text{ ----------- } 4$$

For various values of r , $N_r = N_0 e^{-rE/K_BT}$

$$N = N_0 e^0 + N_0 e^{-E/K_BT} + \ldots\ldots + N_0 e^{-rE/K_BT}$$

$$N = N_0\left[1 + e^{-E/K_BT} + \ldots\ldots + e^{-rE/K_BT}\right] \text{ ----------- } 5$$

The total no. of oscillators $N = N_0\left[\frac{1}{1 - e^{-E/K_BT}}\right]$ ----------- 6

$$E_T = N_0 E e^{-E/K_BT}\left[\frac{1}{\left(1 - e^{-E/K_BT}\right)^2}\right] \text{ ----------- } 7$$

$$\bar{E} = \frac{E_T}{N} = \frac{N_0 E e^{-E/K_BT}}{N_0\left[\frac{1}{1-\ e^{-E/K_BT}}\right]}\left[\frac{1}{(1-\ e^{-E/K_BT})^2}\right]$$

$$\bar{E}\ = \frac{E}{e^{-E/K_BT} - 1} \quad \text{-----------} \ 8$$

After Substituting the value of E = hγ $\bar{E} = \frac{h\gamma}{e^{-E/K_BT} - 1}$ ----------- 9

Eqn 9 represents the average energy of the oscillator

The no. of oscillators per unit volume within the range of frequency $\gamma +\ d\gamma$ is

$$N = \frac{8\pi\gamma^2}{C^3} d\gamma \quad \text{-----------} \ 10$$

Therefore Total energy per unit volume = No. of oscillators per unit volume x Average energy of the oscillator

$$E_\gamma = \frac{8\pi h\gamma^3}{C^3\left(e^{h\gamma/K_BT} - 1\right)} \quad \text{-----------} \ 11$$

Eqn 11 represents Planck's radiation law in terms of frequency.

In terms of wavelength

$$E_\lambda = \frac{8\pi hC}{\lambda^5\left(e^{hc/\lambda K_BT} - 1\right)} \quad \text{-----------} \ 12$$

Wein's displacement law – Shorter wavelength

If λ is less 1/ λ will be greater so $e^{hc/\lambda K_BT} \gg 1$

$$E_\lambda = \frac{8\pi hC}{\lambda^5\left(e^{hc/\lambda K_BT}\right)} \quad \text{-----------} \ 13$$

Rayleigh Jean's displacement law - Longer wavelength

If λ is greater 1/ λ will be lesser

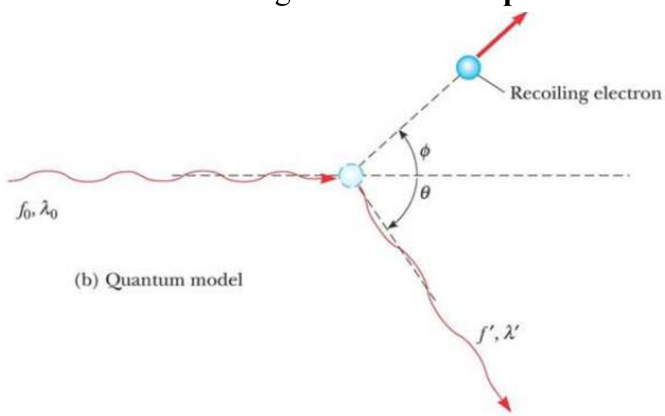
$$e^{hc/\lambda K_BT} = 1 + \frac{hc}{\lambda K_BT}$$

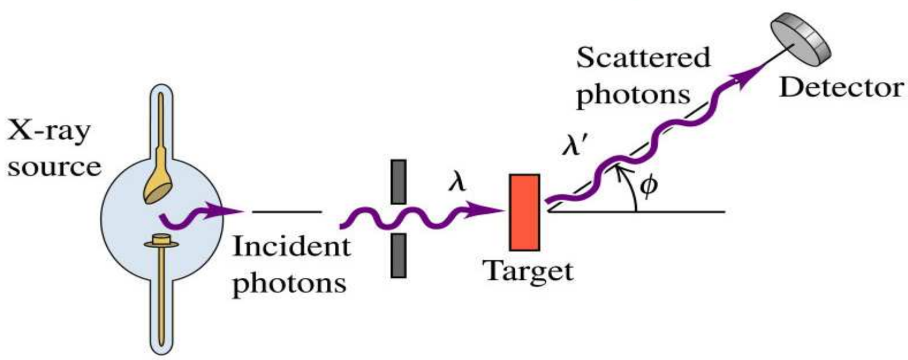
$$E_\lambda = \frac{8\pi K_B T}{\lambda^4} \text{ ----------- } 14$$

Compton Effect

When a photon of energy h ν collides with a scattering element , the scattered beam has two components, one of the same frequency as that of the incident radiation and the other has lower frequency compared to incident frequency. This effect is called Compton Effect.

The shift in wavelength is called **Compton shift.**





- **x-rays scattered from target containing very loosely bound electrons**
- **Wavelength of scattered x-rays found to be different from that of incident X-rays AND to depend on detection angle ϕ:**

Total energy before and after collision $h\gamma + m_0c^2 = h\gamma' + mc^2$ --- 1

Total momentum before and after collision along X component

$$\frac{h\gamma}{c} = \frac{h\gamma'}{c}\cos\theta + mv\cos\varphi \quad --- 2$$

Total momentum before and after collision along Y component

$$0 = \frac{h\gamma'}{c}\sin\theta - mv\sin\varphi \quad --- 3$$

From eqn 2

$$mvc\cos\varphi = h(\gamma - \gamma'\cos\varphi) \quad --- 4$$

From eqn 3

$$mv\sin\varphi = h\gamma'\sin\theta \quad --- 5$$

Squaring and adding eqn 5

$$m^2c^2v^2 = h^2[\gamma^2 - 2\gamma\gamma'\cos\theta + (\gamma')^2] \quad --- 6$$

From eqn 3

$$mc^2 = m_0c^2 + h(\gamma - \gamma') \quad --- 7$$

Squaring on both sides

$$m^2c^4 = m_0^2c^4 + 2hm_0c^2(\gamma - \gamma') + h^2[\gamma^2 - 2\gamma\gamma' + (\gamma')^2] \quad --- 8$$

Subtracting eqn 6 from 8

$$m^2c^2(c^2 - v^2) = m_0^2c^4 + 2hm_0c^2(\gamma - \gamma') - 2h^2\gamma\gamma'(1 - \cos\theta) \quad --- 9$$

We know $m = \frac{m_0^2}{\sqrt{1-\frac{v^2}{c^2}}}$ --- 10

Squaring on both sides and rearranging eqn 10

$$m^2(c^2 - v^2) = m_0^2c^2 \quad --- 11$$

Multiplying c^2 on both sides

$$m^2c^2(c^2 - v^2) = m_0^2c^4 \quad --- 12$$

Equating eqn 12 and 9 we get

$$m_0^2c^4 = m_0^2c^4 + 2hm_0c^2(\gamma - \gamma') - 2h^2\gamma\gamma'(1 - \cos\theta) \quad --- 13$$

Since $\lambda = c/v$ finally we get

$$\Delta\lambda = \lambda' - \lambda = \frac{h}{m_0 c}(1 - cos\theta)$$

We know Compton shift $\Delta\lambda = h / m_o c$ (1- cos θ)

Case i) when $\theta = 0$, $\Delta\lambda = 0$

Case ii) when $\theta = 45^o$, $\Delta\lambda = 0.0071$

Case iii) when $\theta = 90^o$, $\Delta\lambda = 0.02424$

Case iv) when $\theta = 180^o$, $\Delta\lambda = 0.0472$

Time independent Schrödinger equation

Schrödinger wave equation time independent. Consider a system of stationary waves associated with a particle. Let x,y,z be the coordinate of the particle and ψ wave displacement for de-Broglie's waves at any time 't'.

The classical differential eqn of a wave motion is given by

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = \frac{1}{v^2}\frac{\partial^2\psi}{\partial t^2} \quad ---------- 1$$

$$\nabla^2\psi = \frac{1}{v^2}\frac{\partial^2\psi}{\partial t^2} \quad ------------- 2$$

∇ is a Laplacian's operator.

The solution of the eqn 2 is

$$\psi(x, y, z, t) = \psi_0(x, y, z)e^{-i\omega t}$$

$$\psi = \psi_0 e^{-i\omega t} \qquad -----3$$

$\psi_0(x, y, z)$ *is a function of of x, y, z only and it gives the amplitude at the point considered.*

Differentiating the eqn 3 with respect to t , we get

$$\frac{\partial\psi}{\partial t} = -i\omega\psi_0 e^{-i\omega t}$$

Again Differentiating with respect to t ,

$$\frac{\partial^2\psi}{\partial t^2} = -\omega^2\psi ----4$$

$$\nabla^2\psi + \frac{\omega^2}{v^2}\psi = 0 ----5$$

We know $\omega = 2\ \pi\nu = 2\pi\left(\frac{v}{\lambda}\right)$

$$\frac{\omega^2}{v^2} = \frac{4\pi^2}{\lambda^2} ----6$$

Substitute equation 6 in 5

$$\nabla^2\psi + \frac{4\pi^2}{\lambda^2}\psi = 0 ----7$$

Substitute $\lambda = \frac{h}{mv}$ in equation 7

$$\nabla^2\psi + \frac{4\pi^2 m^2 v^2}{h^2}\psi = 0 ----8$$

If E is the total energy, V is the potential energy and $\frac{1}{2}mv^2$ is the kinetic energy then,

$$E = V + \frac{1}{2}mv^2$$

Rearranging the above equation and multiplying by m on both sides we get

$$m^2 v^2 = 2m(E - V) - - - -9$$

Subs eqn 9 in 8 we get

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 - - - -10$$

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

This is Schroedinger's time independent equation.

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

Time dependent wave equation

Schrödinger time dependent wave equation is derived from time independent wave equation.The solution of classical differential equation is given by eqn 1

$$\psi(x, y, z, t) = \psi_0(x, y, z)e^{-i\omega t} - - - -1$$

Differentiating equation 1we get

$$\frac{\partial \psi}{\partial t} = -i\omega\psi_0 e^{-i\omega t} - - - -2$$

$$\frac{\partial \psi}{\partial t} = -i2\pi \nu \psi_0 e^{-i\omega t}$$

$$\omega = 2\pi\nu$$

$$E = h\nu$$

$$\frac{\partial \psi}{\partial t} = -i\frac{E}{\hbar}\psi - - - -3$$

Multiplying i on both sides

$$E\psi = i\hbar\frac{\partial \psi}{\partial t} - - - -4$$

We know

$$\nabla^2 \psi + \frac{2m}{\hbar^2}(E - V)\psi = 0 - - - -5$$

On substituting the value of $E\psi$ in eqn 5

$$\nabla^2\psi + \frac{2m}{\hbar^2}\left(i\hbar\frac{\partial\psi}{\partial t} - V\psi\right) = 0$$

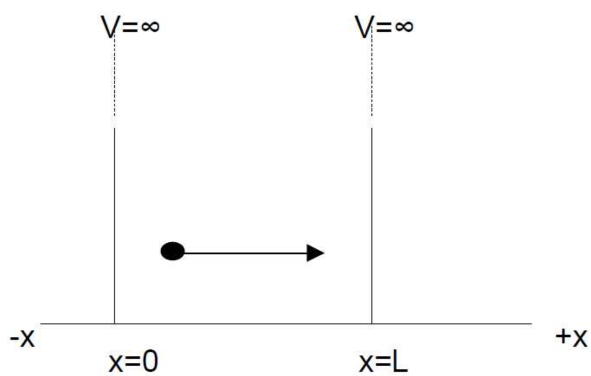
$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = i\hbar\frac{\partial\psi}{\partial t} - - - - -6$$

$$\mathbf{H}\psi = \mathbf{E}\psi$$

Where H – Hamiltonian operator and E – Energy operator

One dimensional potential box

Consider a particle of mass m moving between two rigid walls of a box at x = 0 and x = a along x- axis. This particle is moving back and forth between the walls of the box. The potential energy (V) of a particle inside the box is constant. And it is taken as zero. The walls are infinitely high. The potential energy V of the particle is infinite outside the walls.



$$V(x) = 0 \; for \; 0 < x < a$$

$$V(x) = \infty \; for \; 0 \geq x \geq a$$

Schrödinger's wave eqn. one dimension box is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0 \qquad \text{----------} \; 1$$

Since V = 0 between the walls, eqn. 1 reduces to

$\frac{\partial^2\psi}{\partial x^2} + k^2\psi = 0$ ---------- 2

The general eqn of eqn 2 is given by

$\psi(x) = A \sin kx + B \cos kx$ ---------- 3

here A and B are constants. This can be obtained by applying the boundary conditions .

Boundary condition (i) $\psi = 0 \; at \; x = 0$

Applying the condition to eqn (3)

0 = Asin0 + B cos 0 [since sin 0 = 0, cos 0 = 1]

0 = 0 + B, B = 0

Boundary condition (i) $\psi = 0 \; at \; x = a$

Applying the condition to eqn (3)

0 = A sin ka + 0

Asin ka = 0

It is found that either A = 0 or sin ka = 0

A cannot be 0 since already one of the constants B = 0. If A is also zero. Hence A should not be zero.

Sin ka = 0

Sin ka = 0 when ka takes the valus of nπ

$k = \frac{n\pi}{a}$ ------------ (4)

$k^2 = \frac{8\pi^2 mE}{h^2}$ ------------ (5)

$\frac{n^2\pi^2}{a^2} = \frac{8\pi^2 mE}{h^2}$

$E_n = \frac{n^2h^2}{8ma^2}$ ----------------------- (6)

$\psi_n(x) = A \sin\frac{n\pi x}{a}$

Normalization of wave function

The constant A is determined by normalization of wave function as follows:

Probability density given by $\psi^*\psi$

$$\psi^*\psi = A^2 \sin^2\left[\frac{n\pi x}{a}\right]$$

It is certain that the particle is somewhere inside the box. Thus the probability of finding the particle inside the box of length a is given by

$$\int_0^a \psi^*\psi \, dx = 1$$

$$\int_0^a A^2 \sin^2\left[\frac{n\pi x}{a}\right] dx = 1$$

$$A = \sqrt{\frac{2}{a}}$$

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a}$$

This expression is known as normalized eigen function.

<u>Extension to three Dimensions:</u>

For cubical box a= b= c

$$E_{n_x n_y n_z} = \frac{h^2\left[n_x^2 + n_y^2 + n_z^2\right]}{8ma^2}$$

$$\psi_{n_x n_y n_z} = \sqrt{\frac{8}{a^3}} \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{a} \sin\frac{n_z \pi z}{a}$$

It is noted that several combinations of the three quantum numbers lead to different energy eigen values and eigen functions.

Similarly for a combinations $n_x = 1$, $n_y = 1$, $n_z = 1$ we have

$$E_{112} = E_{121} = E_{211} = \frac{6h^2}{8ma^2}$$

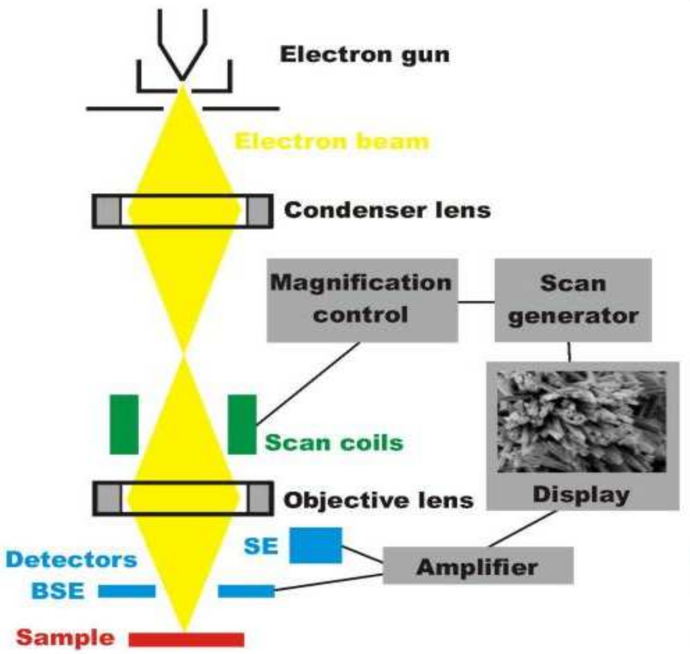
$$\psi_{112} = \sqrt{\frac{8}{a^3}} \sin\frac{\pi x}{a} \sin\frac{\pi y}{a} \sin\frac{2\pi z}{a}$$

$$\psi_{121} = \sqrt{\frac{8}{a^3}} \sin\frac{\pi x}{a} \sin\frac{2\pi y}{a} \sin\frac{\pi z}{a}$$

$$\psi_{211} = \sqrt{\frac{8}{a^3}} \sin\frac{2\pi x}{a} \sin\frac{\pi y}{a} \sin\frac{\pi z}{a}$$

$$E_{222} = \frac{12h^2}{8ma^2}$$

Scanning electron Microscope



A **scanning electron microscope** (**SEM**) is a type of electron microscope that images a sample by scanning it with a beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity.

The types of signals produced by a SEM include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence), specimen current and transmitted electrons. Secondary electron detectors are common in all SEMs, but it is rare that a single machine would have detectors for all possible signals.

The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details less than 1 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample.

This is exemplified by the micrograph of pollen shown above. A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful hand-lens) to more than 500,000 times, about 250 times the magnification limit of the best light microscopes.

The electron beam, which typically has an energy ranging from 0.2 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface.

When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 µm into the surface. The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density.

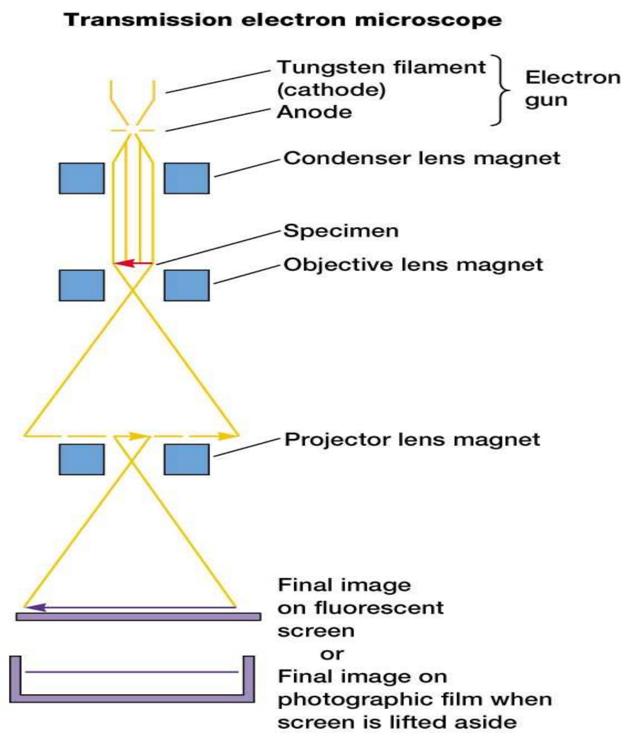
The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals, which are displayed as variations in brightness on a computer monitor (or, for vintage models, on a cathode ray tube).

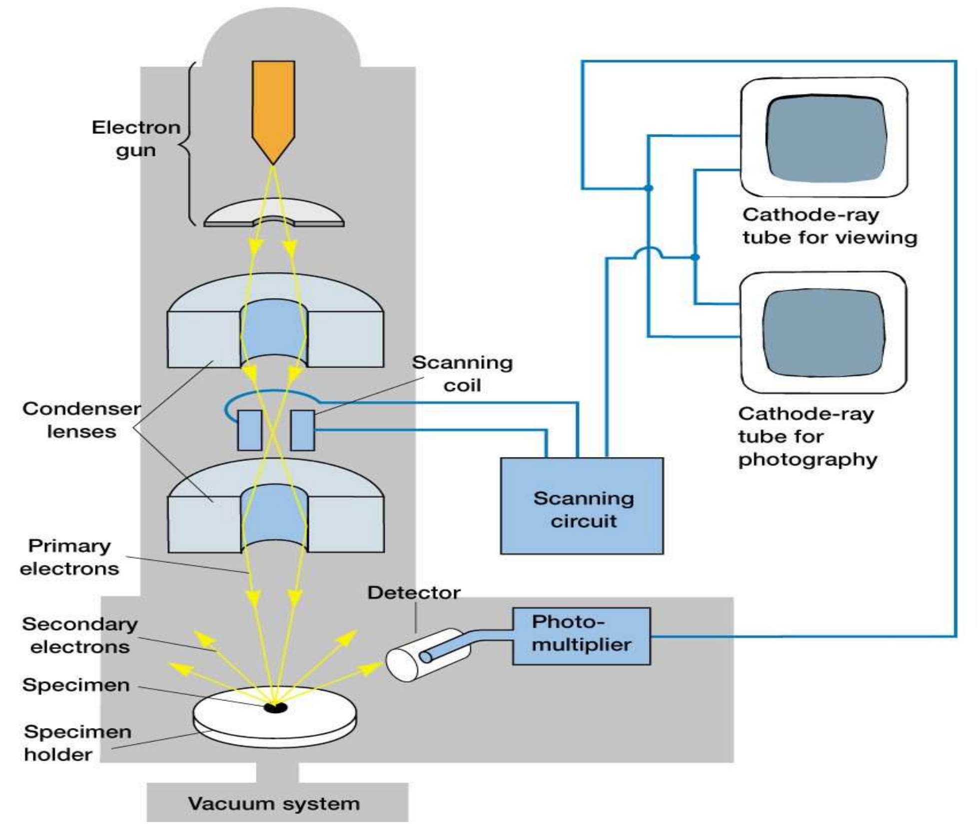
Each pixel of computer video memory is synchronized with the position of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. In older microscopes image may be captured by photography from a high-resolution cathode ray tube, but in modern machines image is saved to a computer data storage.

In a typical SEM, an electron beam is thermionic ally emitted from an electron gun fitted with a tungsten filament cathode. Tungsten is normally used in thermionic electron guns because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission, and because of its low cost.

Other types of electron emitters include lanthanum hexaboride (LaB_6) cathodes, which can be used in a standard tungsten filament SEM if the vacuum system is upgraded and field emission guns (FEG), which may be of the cold-cathode type using tungsten single crystal emitters

Transmission electron Microscope.





Transmission electron microscopy (**TEM**) is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera.

TEMs are capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument's user to examine fine detail—even as small as a single column of atoms, which is tens of thousands times smaller than the smallest resolvable object in a light microscope. TEM forms a major analysis method in a range of scientific fields, in both physical and biological sciences. TEMs find application in cancer research, virology, materials science as well as pollution, nanotechnology, and semiconductor research.

At smaller magnifications TEM image contrast is due to absorption of electrons in the material, due to the thickness and composition of the material. At higher magnifications complex wave interactions modulate the intensity of the image, requiring expert analysis of observed images. Alternate modes of use allow for the TEM to observe modulations in chemical identity, crystal orientation, electronic structure and sample induced electron phase shift as well as the regular absorption based imaging.