CHAPTER 1: WAVE MECHANICS (WM)

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CLASSICAL MECHANICS (CM)

Physics in the Late 19th Century (prior to quantum mechanics (QM)) thought that

- Atoms are basic constituents of matter
- Newton's Laws apply universally
- The world is deterministic (Everything determined precisely)

According to CM

Given initial positions $\vec{r}_0$ and velocities $\vec{V}_0$, and given all forces $\vec{F}(t) \Longrightarrow$ all the future can be predicted!!

$$\vec{v}(t) = \int_{\vec{v}_0}^{\vec{v}} d\vec{v}' = \int_{t_0}^{t} \frac{\vec{F}}{m} dt' \qquad \left(\vec{F} = m\vec{a} = m\frac{d\vec{v}}{dt}\right)$$

$$\vec{r}(t) = \int_{\vec{r}_0}^{\vec{r}} d\vec{r}' = \int_{t_0}^{t} \vec{v} dt' \qquad \left(\frac{d\vec{r}}{dt} = \vec{v}\right)$$

CLASSICAL MECHANICS – SUCCESSES!!

Physics was complete except for a few decimal places !

- Newtonian mechanics explained macroscopic behavior of matter -- planetary motion, fluid flow, elasticity, etc.
- Thermodynamics had its first two laws and most of their consequences
- Basic statistical mechanics had been applied to chemical systems
- Light was explained as an electromagnetic wave

CLASSICAL MECHANICS – HOW MUCH??

There were several experiments that could not be explained by classical physics and the accepted dogma !

- Blackbody radiation
- Photoelectric effect
- Discrete atomic spectra
- The electron as a subatomic particle

❑ Some important conclusions would result from these problems

- Atoms are not the most microscopic objects
- Newton's laws do not apply to the microscopic world of the electron

OUTCOME ⇒ New Rules!!!

QUANTUM MECHANICS (QM) !

The failure of CM dawn the QM

- A new philosophy of nature
- Describes rules that apply to electrons in atoms and molecules
- Non-deterministic, probabilistic !
- Explains unsolved problems of late 19^{th} century physics
- Explains bonding, structure, and reactivity in chemistry

BLACK BODY RADIATION

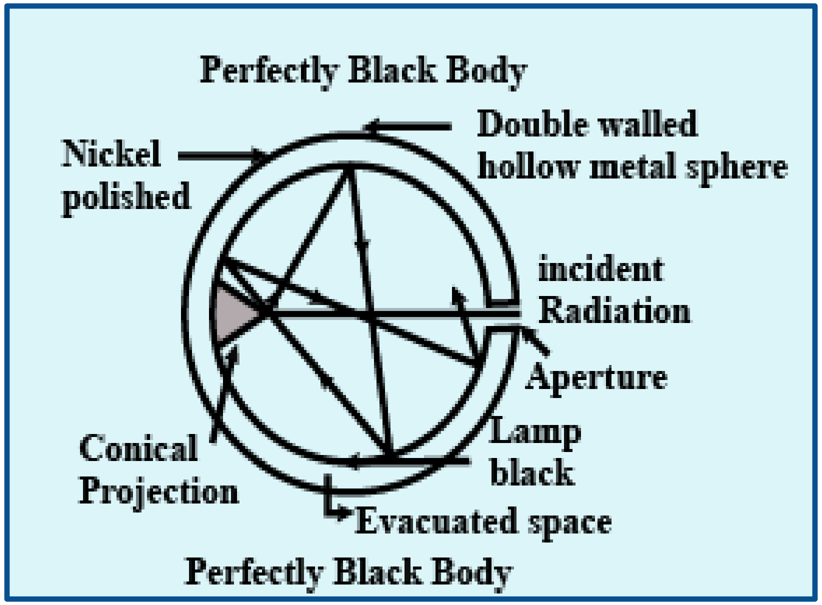
<u>Heating an object and glowing</u>

- An object is heated to 100◦C or to higher,
  - ✓ Glows visibly red, no matter what material it is made of.
  - ✓ Becomes orange, yellow, white, or even blue at enough high temperature.
- An object with a lower reflectivity glows more intensely.
- For theoretical modeling of this radiation requires object with zero reflectivity (absorbs all radiation).


BLACK BODY RADIATION

An ideal black body & its laboratory form

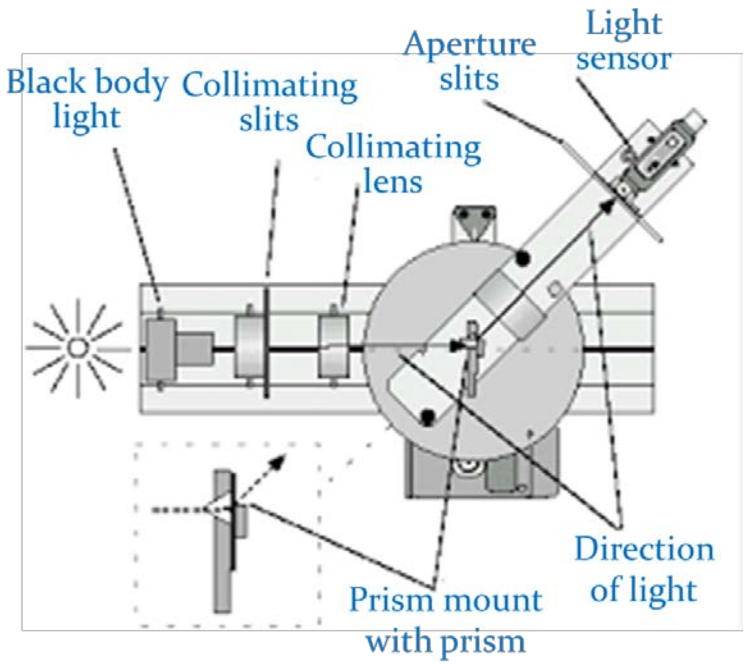
- A *black body, a model system* that reflects no radiation at any wavelength, has the maximum emissivity at every wavelength.
- The best laboratory approximation to a black body is not an object, but a small hole in the side of a hollow box.
- Any light falling on the hole from outside will be absorbed completely as it is reflected around in the box.



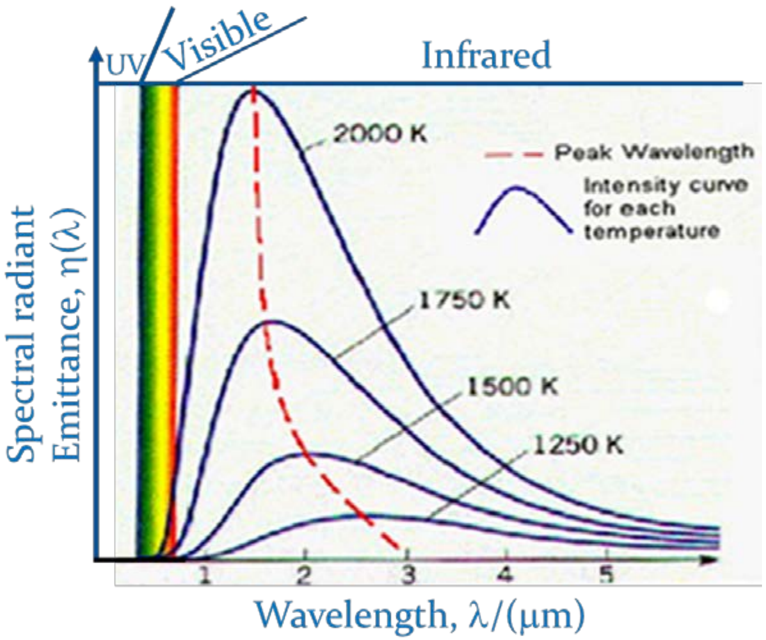
BLACK BODY RADIATION

Black body spectrum

- Measurements on the light emitted through the hole when the box is heated show that the amount of light emitted and its spectral distribution depend only on the temperature of the walls of the box.

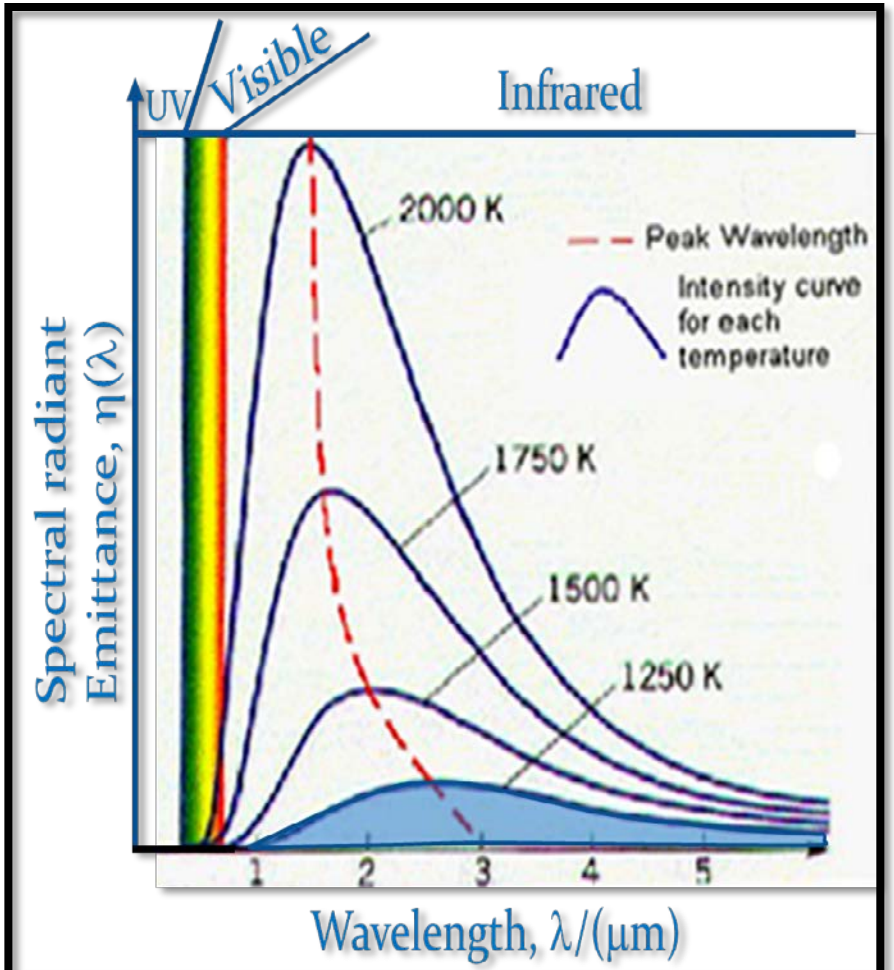


Experimental Setup



Spectral Distribution

BLACK BODY RADIATION

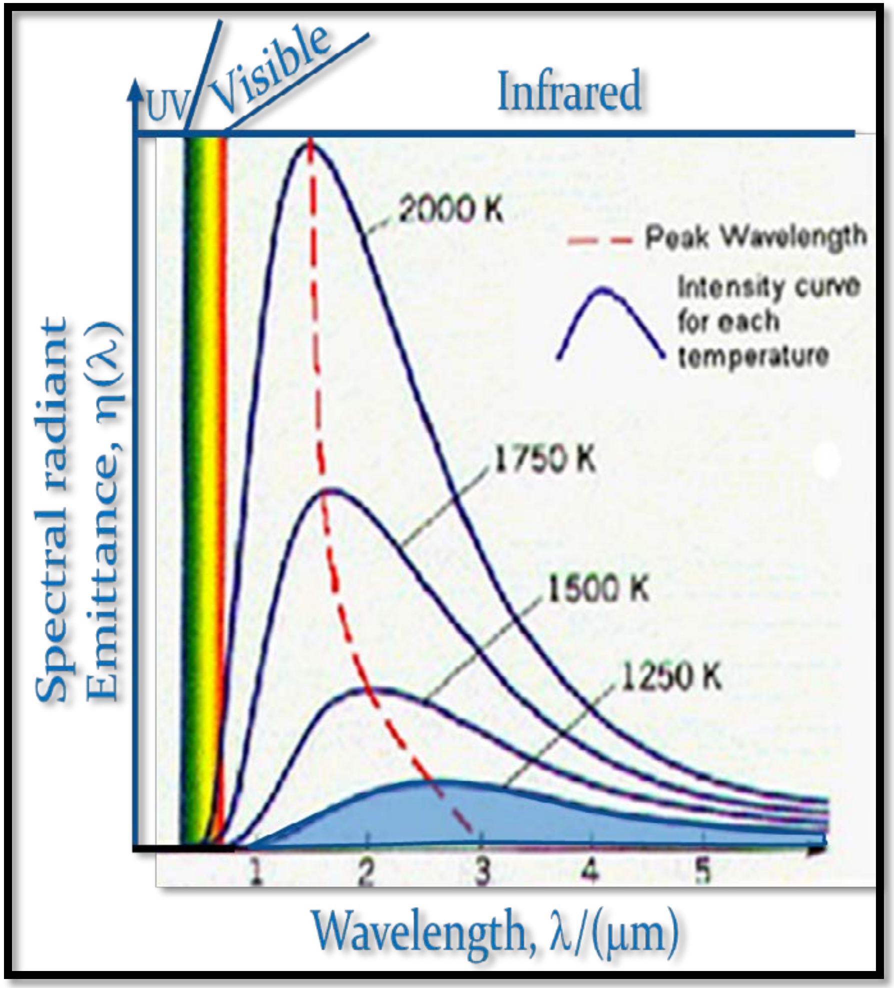


η(λ)dλ is the energy per unit time per unit area emitted in the wavelengths lying between *λ and λ + dλ.*

Characteristics of black body spectrum

- The total radiant emittance (area under the curve) increases as the temperature increases.
- η(λ) depends on λ. Only a small amount of the radiation is emitted at shorter wavelengths (λ)
- At a particular λ , η(λ) depends on temperature.
- At each temperature there is a wavelength, λ_{max} for which η(λ) has its maximum value.
- λ_{max} shifts to lower wavelengths as the temperature increases.

CLASSICAL THEORY OF BLACK BODY RADIATION



Stefan–Boltzmann law

Total radiant emittance = σT^4

σ = the Stefan–Boltzmann constant

The experimental value of

$\sigma = 5.67051 \times 10^{-8}\ \mathrm{Jm^{-2}\ s^{-1}\ K^{-4}}$

$= 5.67051 \times 10^{-8}\ \mathrm{Wm^{-2}\ K^{-4}}$

Limitation:

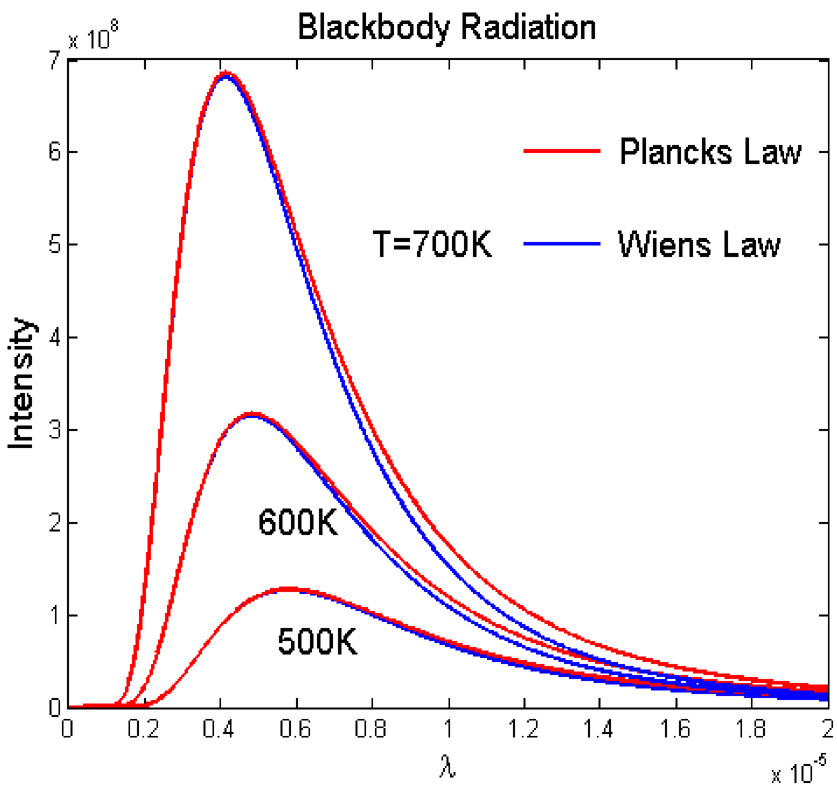
- Empirical
- No theoretical basis

Classical Theory of Black Body Radiation

Wien's law

✓ Proposed the following empirical law, $I(\lambda, T) = \frac{a}{\lambda^5} e^{-\frac{b}{\lambda T}}$

Where a and b are adjustable parameters



✓ This law fitted the experimental curve fairly well except at long wavelengths.

✓ However, it is not satisfactory in the sense that it is not derived from a model which would relate the emitted radiation to physical processes taking place within the enclosure.

CLASSICAL THEORY OF BLACK BODY RADIATION

Rayleigh and Jeans Law

- ✓ Based on classical electrodynamics and thermodynamics
- ✓ Assumptions:
  - ✓ The wall of cavity consists of a large number of charged atomic oscillator. Atomic oscillators can emit and absorb electromagnetic radiation. The superposition of incident and reflected waves of each frequency results in the formation of standing waves with nodes at the walls.
  - ✓ At thermal equilibrium, the average energy of standing waves of a given frequency equals the average energy of the wall oscillators of the same frequency. The number of oscillators per unit volume in the frequency range ν and $\nu + d\nu$ called Jean's number, is calculated as

$$n(\nu)d\nu = \frac{8\pi\nu^2}{c^3}d\nu$$

CLASSICAL THEORY OF BLACK BODY RADIATION

Rayleigh and Jeans Law

- ✓ According to the classical theory of equipartition of energy, the average energy of an oscillator at temperature *T* is kT, where *k* is the Boltzmann's constant.
- ✓ The energy density of the radiation of frequency, ν in the cavity at temperature, T is

$$U(\nu,T)d\nu = \frac{8\pi\nu^2}{c^3}kT\mathrm{d}\nu$$

This is the Rayleigh-Jean's law

- ✓ In terms of wavelength

$$U(\lambda,T)d\lambda = \frac{8\pi}{\lambda^4}kTd\lambda$$

$$\nu = c/\lambda$$

$$|d\nu| = \frac{c}{\lambda^2}d\lambda$$

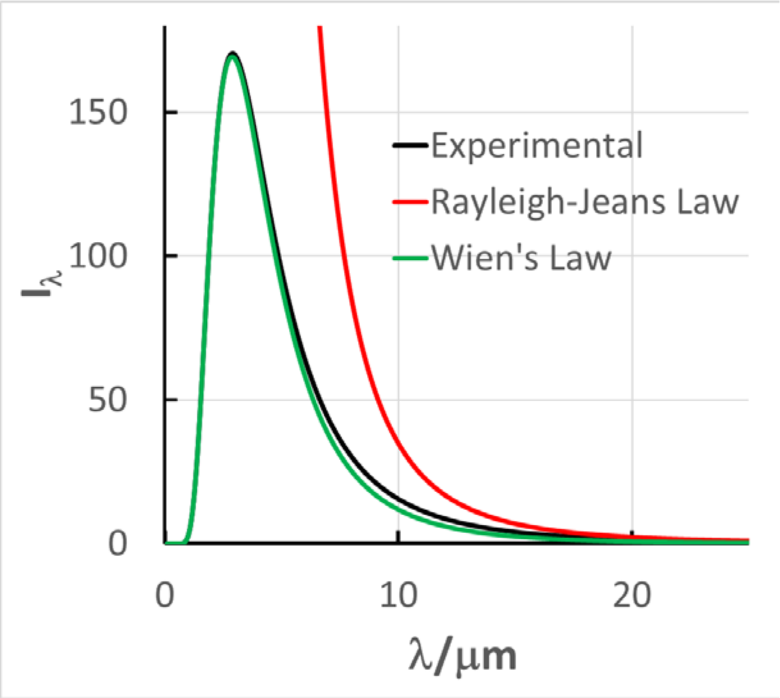
$$\therefore \frac{8\pi\nu^2}{c^3}kTd\nu$$

$$= \frac{8\pi\left(\frac{c}{\lambda}\right)^2}{c^3}kT\left(\frac{c}{\lambda^2}\right)d\lambda$$

$$= \frac{8\pi}{\lambda^4}kTd\lambda$$

CLASSICAL THEORY OF BLACK BODY RADIATION

Rayleigh and Jeans Law



- ✓ Rayleigh-Jeans law agrees with the experimental results in the long wavelength region.
- ✓ It disagrees as the wavelength tends to zero.
- ✓ The failure of Rayleigh-Jeans law is referred to as the "*ultraviolet catastrophe*".
- ✓ Moreover, the total energy emitted at all temperatures except absolute zero is given by

$$U(T) = \int_0^\infty U(\nu, T)d\nu = \frac{8\pi kT}{c^3}\int_0^\infty \nu^2 d\nu = \infty$$

- ✓ Which is obviously impossible.

QUANTUM THEORY OF BLACK BODY RADIATION

Advocacy of Max Planck (1900)

Assumptions:

- ✓ What assumptions made by Rayleigh-Jeans were also made by Max Plank except the energy distribution over the standing modes (or oscillators).
- ✓ He assumed that the emission and absorption of radiation by an oscillator take place in the form of discrete packet of energy called photons, and is given by

Quantized energy values

$E_n = nh\nu$, n = 0, 1, 2, ...

n is called quantum number and
h is plank constant

The energy of an oscillator can take on any of these fixed values, but cannot take on any value in-between them.

QUANTUM THEORY OF BLACK BODY RADIATION

Derivation of Max Planck Equation

- ✓ According to max Plank, an oscillator can absorb whole number of photons, the allowed values of energy of oscillators are

$$E_0 = 0, E_1 = h\nu, E_2 = 2h\nu, E_3 = 3h\nu, \text{and so on}$$

- ✓ Let N_0, N_1, N_2, ... , N_n be the number of oscillators with energy E_0, E_1, E_2, ... , E_n. The total number of oscillators, N and total energy E of the system is given by

$$N = N_0 + N_1 + N_2 + \ldots + N_n = \sum_{n=0}^{\infty} N_n$$

$$E = 0\, h\nu N_0 + 1\, h\nu N_1 + 2\, h\nu N_2 + \ldots + n\, h\nu N_n = h\nu \sum_{n=0}^{\infty} nN_n$$

QUANTUM THEORY OF BLACK BODY RADIATION

Derivation of Max Planck Equation

- ✓ According to Boltzmann Statistics, the number of oscillators with energy E_n = nhν is given by

$$N_n = Ae^{-\frac{E_n}{kT}} = Ae^{-\frac{nh\nu}{kT}}, \qquad \text{A is constant}$$

- ✓ Taking $x = e^{-\frac{h\nu}{kT}}$,

$$N = A\sum_{n=0}^{\infty} e^{-nh\nu/kT} = A\sum_{n=0}^{\infty} x^n$$

- ✓ Expanding summation,

$$N = A(1 + x + x^2 + x^3 + \ldots.) = \frac{A}{1-x}$$

QUANTUM THEORY OF BLACK BODY RADIATION

Derivation of Max Planck Equation

- ✓ Similarly,

$$E = h\nu A\sum_{n=0}^{\infty} ne^{-nh\nu/kT} = h\nu A\sum_{n=0}^{\infty} nx^n$$

$$E = h\nu A(0 + x + 2x^2 + 3x^3 + \ldots\ldots)$$

$$E = h\nu xA(1 + 2x + 3x^2 + \ldots\ldots) = \frac{h\nu xA}{(1-x)^2}$$

- ✓ The average energy of oscillator, $\bar{E}$ is

$$\bar{E} = \frac{E}{N} = \frac{h\nu xA}{(1-x)^2}\left(\frac{1-x}{A}\right)$$

$$= \frac{h\nu x}{1-x} = h\nu\frac{e^{-\frac{h\nu}{kT}}}{1-e^{-\frac{h\nu}{kT}}} = h\nu\frac{e^{-\frac{h\nu}{kT}}}{e^{-\frac{h\nu}{kT}}\left(e^{\frac{h\nu}{kT}}-1\right)} = \frac{h\nu}{e^{\frac{h\nu}{kT}}-1}$$

QUANTUM THEORY OF BLACK BODY RADIATION

Derivation of Max Planck Equation

- ✓ Multiplying average energy by the Jean's number gives the energy density within the frequency range between ν and $\nu + d\nu$ at temperature T

$$U(\nu, T)d\nu = \frac{8\pi\nu^2}{c^3}\frac{h\nu}{e^{h\nu/kT} - 1}d\nu$$

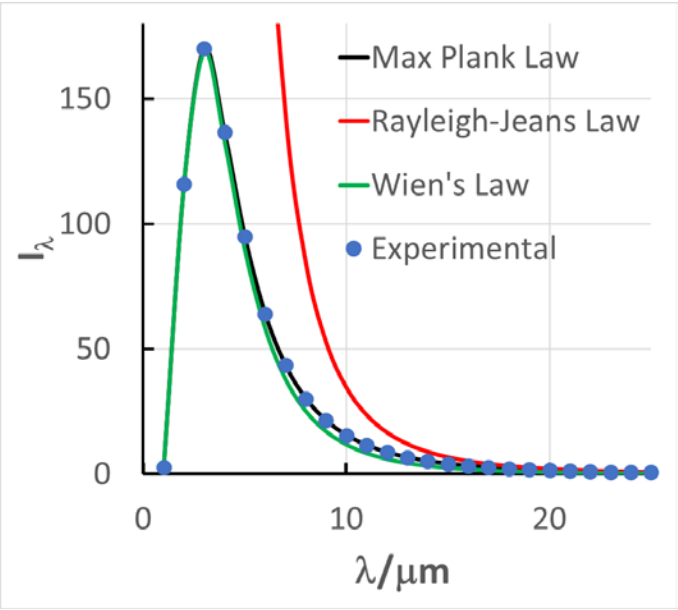
This is **Planck's radiation law.**

- ✓ In terms of wavelength,

$$U(\lambda, T)d\lambda = \frac{8\pi hc}{\lambda^5}\frac{1}{e^{hc/\lambda kT} - 1}d\lambda$$

QUANTUM THEORY OF BLACK BODY RADIATION

Validity of Max Planck Equation



- ✓ Planck's law agrees very close with the experimental spectral distribution curves for all values of λ and T.
- ✓ It reduces to Wien's law as $\lambda \to 0$. and Rayleigh-Jean's law as $\lambda \to \infty$.
- ✓ It is found to be consistent with Wien's displacement law, $\lambda_m T =$ constant and Stefan-Boltzmann law, $U \propto T^4$.
- ✓ Thus, it incorporates all that is valid from the classical theory and yet, makes a fundamental departure, which ultimately shook the foundation of classical mechanics.
- ✓ Planck was awarded the 1918 Nobel prize for the discovery of energy quanta.

QUANTUM THEORY OF BLACK BODY RADIATION

Validity of Max Planck Equation

PROBLEM Show that Wien's law and Rayleigh-Jeans' law are special case of Plank's law corresponding to short and long wavelength, respectively.

Solution: When λ is small, then $e^{hc/\lambda kT} \gg 1$. Therefore,

$$U(\lambda, T) \sim \frac{8\pi hc}{\lambda^5} e^{-\frac{hc}{\lambda kT}} = \frac{a}{\lambda^5} e^{-\frac{b}{\lambda T}}, \quad a = 8\pi hc\,, \quad b = \frac{hc}{k}$$

which is Wien's law.

When λ is large, then $e^{\frac{hc}{\lambda kT}} = 1 + \frac{hc}{\lambda kT} + \frac{1}{2}\left(\frac{hc}{\lambda kT}\right)^2 + \cdots$

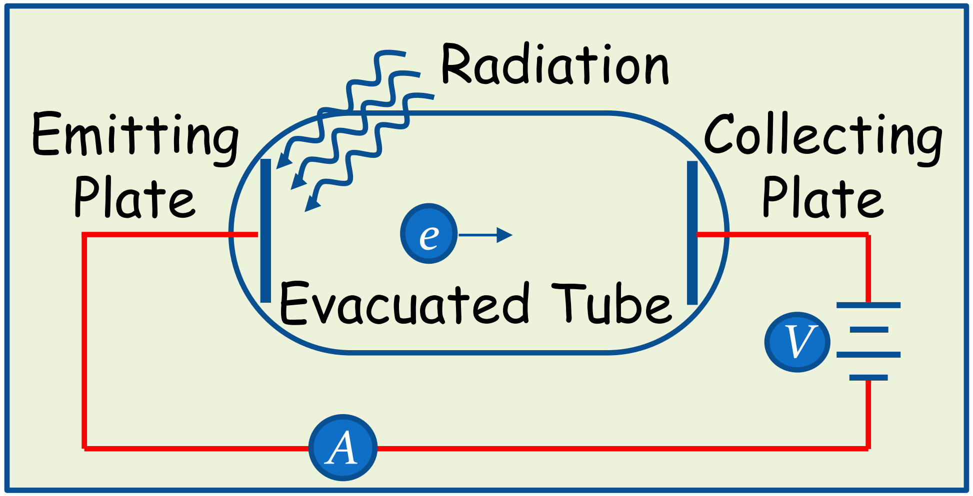
Neglecting higher power terms, $e^{\frac{hc}{\lambda kT}} = 1 + \frac{hc}{\lambda kT}$

Therefor, $U(\lambda, T) \sim \frac{8\pi hc}{\lambda^5} \frac{\lambda kT}{hc} = \frac{8\pi kT}{\lambda^4}$

Which is Rayleigh-Jeans' law

PHOTO-ELECTRIC EFFECT

- ✓ When electromagnetic radiation of high frequency is incident on a metal surface, electrons are emitted from the surface.
- ✓ This phenomena is called *photoelectric effect*.
- ✓ The emitted electrons are generally called *photoelectrons*.
- ✓ This effect was discovered by Heinrich Hertz in 1887.
- ✓ The apparatus used to study the photoelectric effect is shown in right figure.



Schematic arrangement of the apparatus used for the study of photoelectric effect

Photo-electric Effect

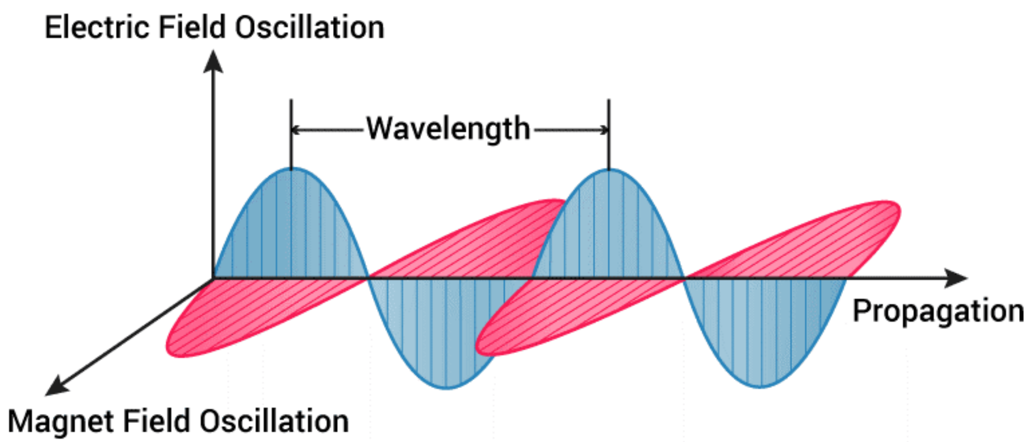
Results from the study of photoelectric effect

- ✓ The number of photoelectrons emitted per second, or the photoelectric current, is proportional to the intensity of radiation but is independent of the frequency.
- ✓ No electrons are emitted if the incident radiation has a frequency less than a *threshold* value ν_0. The value of ν_0 varies from metal to metal.
- ✓ The kinetic energy of the emitted electrons varies from zero to a maximum value. The maximum value of energy depends on the frequency and not on the intensity of radiation. It varies linearly with the frequency.
- ✓ The photoelectric emission is an instantaneous process, *i.e.*, there is negligible time lag between the incidence of radiation and the emission of electrons, regardless of how low the intensity of radiation is.

PHOTO-ELECTRIC EFFECT

Classical failure of photoelectric effect

✓ According to classical theory (CT)



- Intensity, I

$$I \propto E^2$$

- Force exerted on electron by incident radiation

$$F = eE$$

✓ Hence, K.E. of photoelectron should depend on I, but experimental results are contrary to prediction.

✓ According to CT, incident radiations collide with electron, so electrons should eject by radiation of any frequency, but classical theory is blind about the threshold frequency.

✓ Further, ejection of electron should take long time, but results are against to prediction.

PHOTO-ELECTRIC EFFECT

Einstein's explanation of photoelectric effect (1905)

- ✓ With analogy to Planck's quantum hypothesis, Einstein assumed that EMR itself consists of quanta of energy $h\nu$ called photon, where h is Planck's constant.
- ✓ Some part of photon of energy, $h\nu$ is spent in making electron free, rest appears as kinetic energy of electron.
- ✓ The minimum energy required to liberate loosely bound electrons is called *work function, ϕ* of material.
- ✓ The maximum kinetic of photoelectrons is given by

$$T_{Max} = h\nu - \phi$$

- ✓ If frequency, ν_0 of radiation is sufficient to eject electron with zero kinetic energy, then ϕ is given by

$$\phi = h\nu_0$$

the frequency, ν_0 is the threshold of cut-off frequency.

PHOTO-ELECTRIC EFFECT

Einstein's explanation of photoelectric effect (1905)

✓ Einstein's photoelectric equation can be written as

$$T_{Max} = h\nu - h\nu_0$$

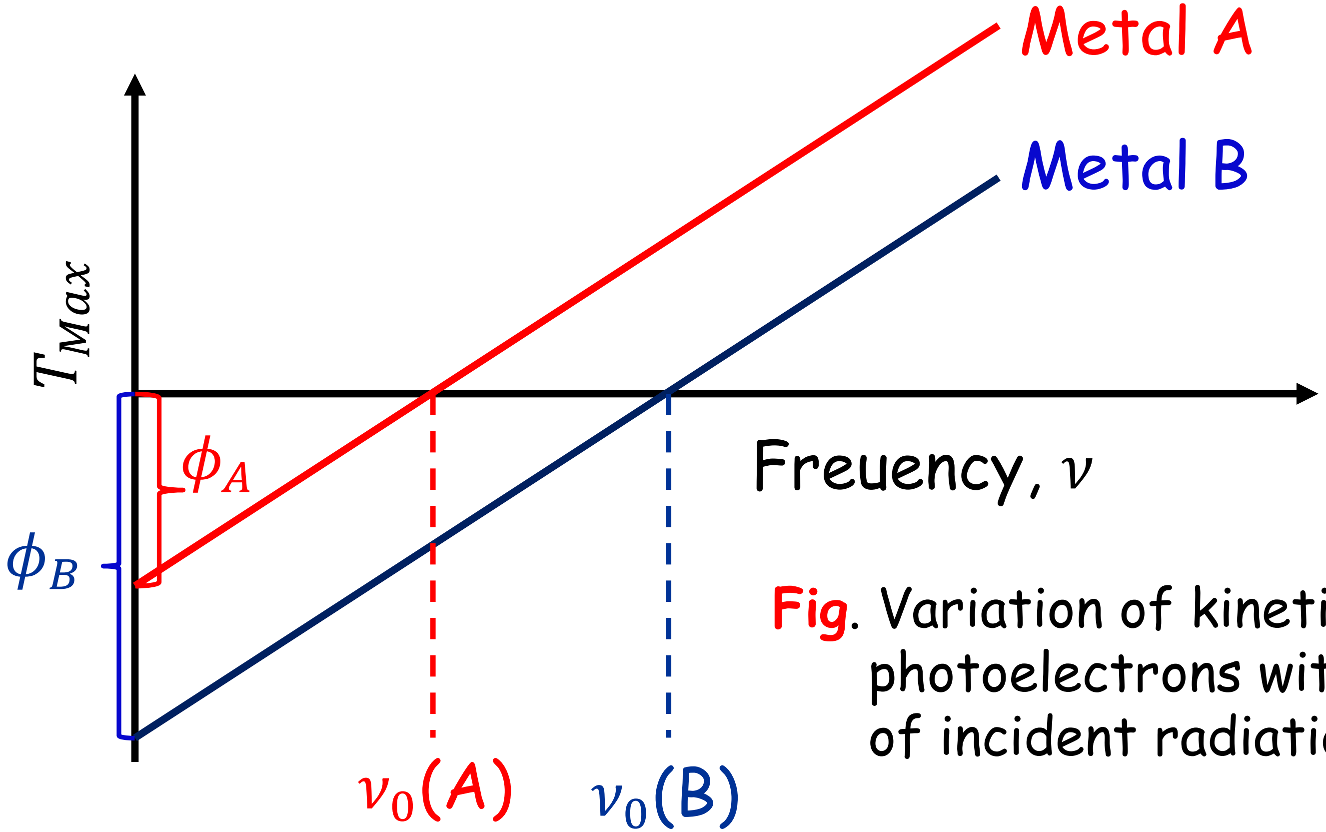


Fig. Variation of kinetic energy of photoelectrons with frequency of incident radiation

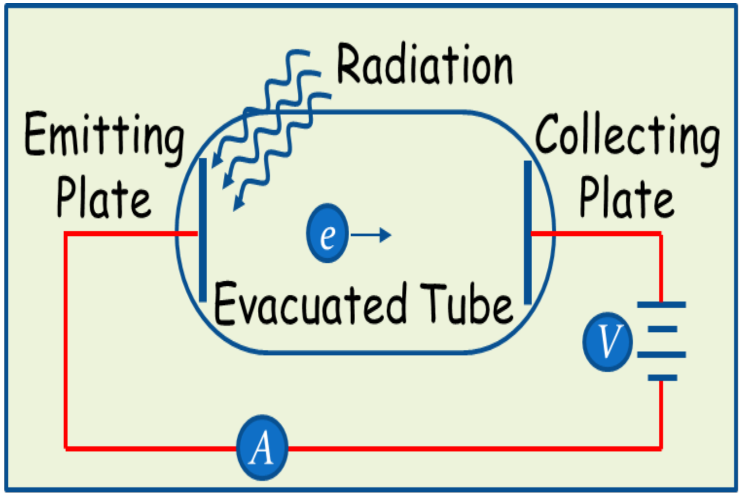
PHOTO-ELECTRIC EFFECT

Einstein's explanation of photoelectric effect (1905)

- ✓ Increase in the intensity of radiation increases the number of photon but not the energy of photon.
  - ➢ Hence increase in intensity increase the probability of collision, thereby the number of photoelectrons.
- ✓ Since the energy of photon is concentrated in a small region and photon is moving at very high speed (*c*),
  - ➢ the energy of photon is instantaneously transferred to electron and consequently there is no appreciable time lag between the incidence of light and the emission of electron.

PHOTO-ELECTRIC EFFECT

Experimental verification of Einstein's Equation



✓ If the potential, V_0 of collector plate is made negative, the electrons are repelled back. For a certain value V_0, the most energetic electrons are just turned back and photoelectric current becomes zero. This V_0 is called the *stopping or cut-off potential*.

✓ It is clear that at V_0, $T_{Max} = eV_0$

✓ Einstein's equation becomes,

$$eV_0 = h\nu - h\nu_0$$

$$V_0 = \frac{h}{e}\nu - \frac{h}{e}\nu_0$$

✓ The plot of V_0 vs. ν would be a straight line with slope, $\frac{h}{e}$ and intercept, $-\frac{h}{e}\nu_0$.

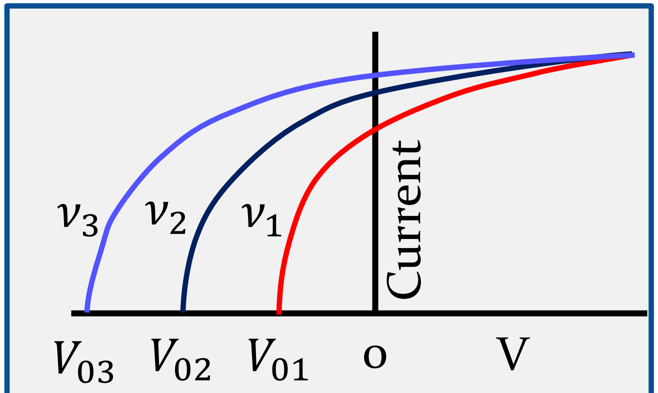


Fig. Variation of photocurrent with acceleration potential

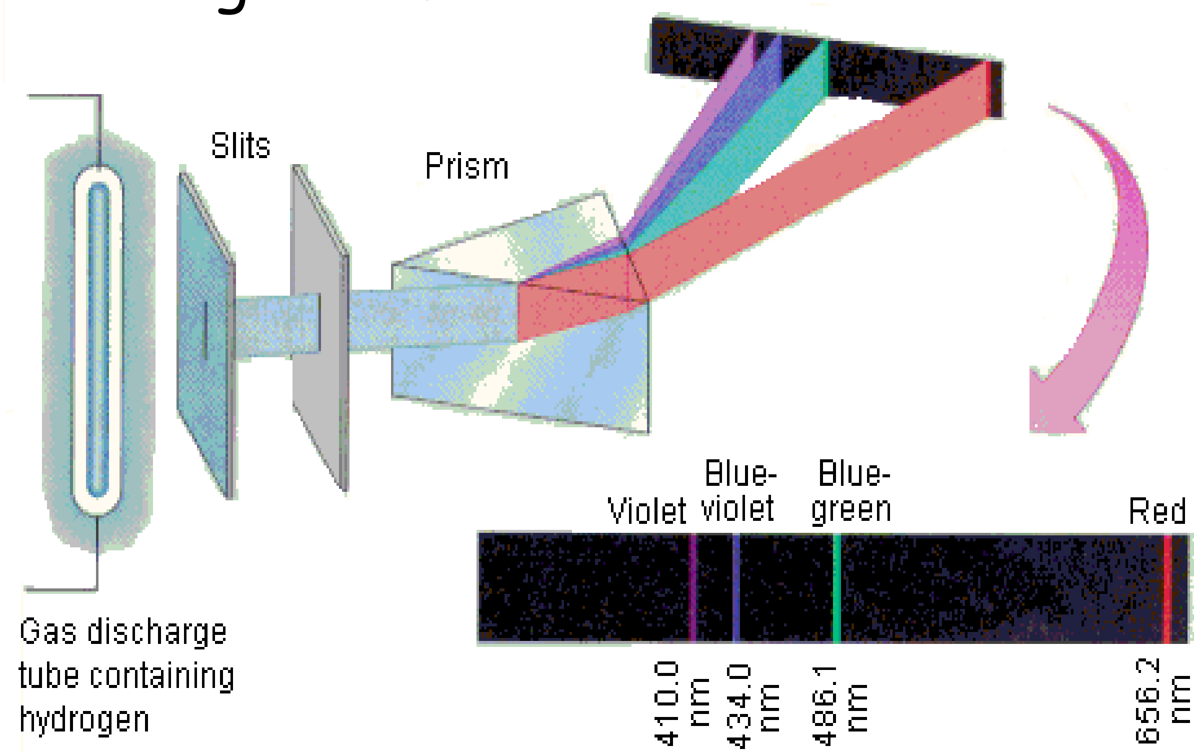
PHOTO-ELECTRIC EFFECT

Experimental verification of Einstein's Equation

- ✓ In order to verify this equation, R. A. Millikan measured V_0 for different metal targets by illuminating light of different frequencies.
- ✓ From the slope of V_0 vs. ν plot, he obtained h, which was the same as that obtained by Planck from the black body radiation experiment.
- ✓ This great achievement established the correctness of the quantum concept and Einstein's theory.
- ✓ Einstein awarded the 1921 Nobel prize.
- ✓ Millikan awarded the 1923 Nobel prize.

FINE SPECTRA OF HYDROGEN ATOM

- ✓ When an electric current is passed through a glass tube that contains hydrogen gas at low pressure the tube gives off blue light.
- ✓ When this light is passed through a prism, four narrow bands of bright light are observed against a black background.



Wavelength	Color
656.2	red
486.1	blue-green
434.0	blue-violet
410.1	violet

Table: **Characteristic wavelengths and colors**

FINE SPECTRA OF HYDROGEN ATOM

During the period 1885-1908, many spectroscopists (Ritz. Rhydberg, Balmer. etc.) had shown that spectra of hydrogen atoms consisted of lines whose frequency could be expressed as a difference of two terms,

$$\bar{\nu} = \frac{\nu}{c} = \frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \qquad (1)$$

Where, $n_1 = 1, 2, \cdots$, $n_2 = 2, 3, \cdots$, and R_H = Rhydberg constant

Lyman series	$\mathbf{n_1 = 1}$	$\mathbf{n_2 = 2, 3, 4, ..}$	UV region
Balmer series	$\mathbf{n_1 = 2}$	$\mathbf{n_2 = 3, 4, 5, ..}$	Vis region
Paschen series	$\mathbf{n_1 = 3}$	$\mathbf{n_2 = 4, 5, 6, ..}$	Vis region
Brackett series	$\mathbf{n_1 = 4}$	$\mathbf{n_2 = 5, 6, 7, ..}$	Vis region
Pfund series	$\mathbf{n_1 = 5}$	$\mathbf{n_2 = 6, 7, 8, ..}$	Vis region

FINE SPECTRA OF HYDROGEN ATOM

Failure of Classical Mechanics:

- ✓ The formulae (1) was obtained empirically. Although this formulae well-explained the line spectra of hydrogen atoms, it was lacked of theoretical support.
- ✓ The classical (Rutherford) picture of atomic structure predicted continuous band spectra and not spectral lines, as according to the electromagnetic theory, an electron rotating around the nucleus could emit radiation whose frequency changed continuously.

FINE SPECTRA OF HYDROGEN ATOM

QM explanation of line spectra of Hydrogen atoms:

- ✓ Neils Bohr (1913) first interpreted line spectra of hydrogen atom using Quantum Theory. He assumed that
  - ➢ Electrons revolve round the nucleus. In "stationary state",

    Coulombic attraction to nucleus = Centrifugal force

$$\frac{e^2}{4\pi\varepsilon_0 r^2} = \frac{m_e v^2}{r} \qquad (1)$$

  - ➢ Angular momentum,

$$mvr = \frac{nh}{2\pi} \qquad (2)$$

Combining (1) & (2)

$$r = \frac{(4\pi\varepsilon_0)h^2 n^2}{4\pi^2 m_e e^2} \qquad (3)$$

FINE SPECTRA OF HYDROGEN ATOM

QM explanation of line spectra of Hydrogen atoms:

- Energy of stationary state of H atom,

$$\text{Energy} = \text{Kinetic Energy} + \text{Potential energy}$$

$$E_n = \frac{1}{2} m_e v^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

Eliminating v and r from (2) & (3)

$$E_n = -\frac{m_e e^4}{8\varepsilon_0^2 h^2 n^2} \qquad (4)$$

- Energy change between two stationary states

$$\Delta E = E_{n_2} - E_{n_1} = h\nu = h\bar{\nu}c$$

$$\Rightarrow h\bar{\nu}c = \frac{m_e e^4}{8\varepsilon_0^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

FINE SPECTRA OF HYDROGEN ATOM

QM explanation of line spectra of Hydrogen atoms:

$$\Rightarrow \bar{\nu} = \frac{m_e e^4}{8\varepsilon_0^2 h^3 c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad (5)$$

Where, $R = \frac{m_e e^4}{8\varepsilon_0^2 h^3 c}$

$$\Rightarrow R = \frac{(9.1 \times 10^{-31} kg) \times (4.8 \times 10^{-19} C)^4}{8 \times (8.85 \times 10^{-12} C^2 N^{-1} m^{-2})^2 \times (6.62 \times 10^{-34} J)^3 \times 3 \times 10^8 m s^{-1}}$$

$$R = 1.09737 \times 10^7 m^{-1}$$

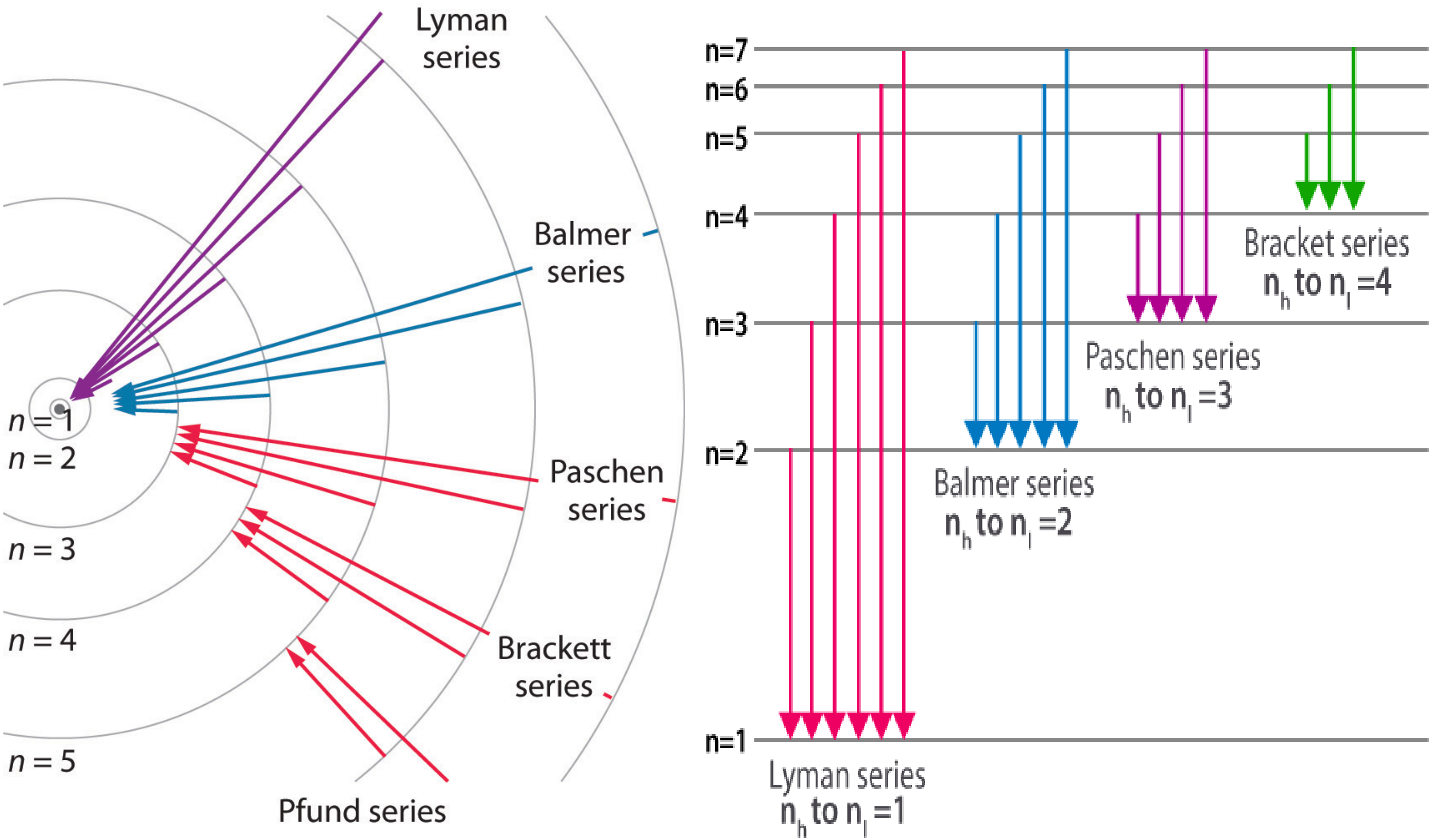
Rhydberg constant

$$R_H = 1.09678 \times 10^7 m^{-1}$$

✓ Excellent agreement between R & R_H

FINE SPECTRA OF HYDROGEN ATOM

QM explanation of line spectra of Hydrogen atoms:



WAVE NATURE OF PARTICLES

De Broglie Concept:

- In 1924, Louis de Broglie was guided by the intuitive feeling that nature loves symmetry. Nature has two entities—matter and radiation.
- Therefore, if radiation has particle-like properties, then material particles (electron, proton, neutron etc.) should possess wave-like properties.
- A photon of frequency ν has energy

$$E = h\nu$$

- and momentum

$$p = \frac{E}{c} = \frac{h\nu}{c} = \frac{h}{\lambda} \qquad Or, \qquad \lambda = \frac{h}{p}$$

WAVE NATURE OF PARTICLES

De Broglie Concept:

- De Broglie proposed that this relation can be applied to material particles as well as photons. Thus, de Broglie postulated that a wave having wavelength, λ is associated with every material particle,

$$\lambda = \frac{h}{p} \text{ (de Broglie wavelength)}$$

- For a particle of mass m, moving with a speed v, this becomes

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

- For relativistic particle, *m* is given by

$$m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}} \quad [\text{ } m_0 \text{ is the rest mass}]$$

WAVE NATURE OF PARTICLES

De Broglie Concept:

- de Broglie's hypothesis, when proposed, had no supporting experimental evidence. Such evidence came three years later in 1927.

- de Broglie equation can be written in different forms
  - In terms kinetic energy

$$K = \frac{p^2}{2m} \quad \Rightarrow p = \sqrt{2mK} \quad \Rightarrow \lambda = \frac{h}{\sqrt{2mK}}$$

  - In terms of acceleration potential

$$K = qV \qquad [q \text{ is charge of particle of mass } m]$$

$$\lambda = \frac{h}{\sqrt{2mqV}} = \frac{6.625 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 1.6 \times 10^{-19}}} \frac{1}{\sqrt{V}}$$

$$\lambda = \frac{1.23 \times 10^{-10}}{\sqrt{V}} m = \frac{1.23}{\sqrt{V}} \mathring{A}$$

WAVE NATURE OF PARTICLES

De Broglie Concept & Bohr's quantized hypothesis of angular momentum :

- For the orbit to be stable, it is reasonable to assume that the wave must "match," or be in phase, as the electron makes one complete revolution (as shown Figure). .
- Otherwise, there will be cancellation of some amplitude upon each revolution, and the wave will disappear.

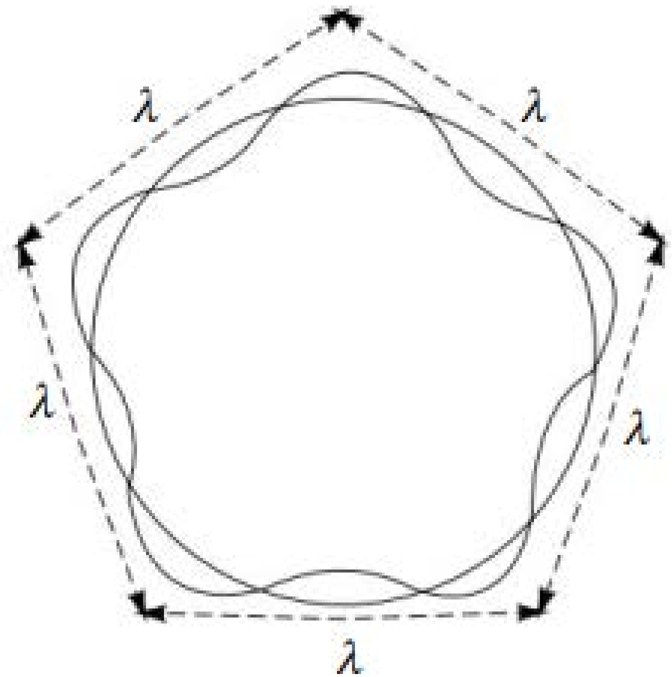


Fig. A standing electron wave in the Bohr's orbit

WAVE NATURE OF PARTICLES

De Broglie Concept & Bohr's quantized hypothesis of angular momentum :

- For the wave pattern around an orbit to be stable, we are led to the condition that an integral number of complete wavelengths must fit around the circumference of the orbit. Because the circumference of a circle is $2\pi r$, we have the *quantum condition*

$$2\pi r = n\lambda$$

- If we substitute de Broglie's relation into above equation, we obtain the Bohr quantization condition

$$2\pi r = \frac{nh}{mv} \quad \Longrightarrow mvr = \frac{nh}{2\pi}$$

WAVE NATURE OF PARTICLES

Experimental evidence of De Broglie Concept:

- A narrow beam of electrons accelerated through a potential difference, V was directed normally towards the surface of nickel crystal.
- The electrons were scattered in all directions by the atoms in crystal. The intensity of the scattered electrons was measured as a function of the latitude angle ϕ measured from the axis of the incident beam for different accelerating potential.

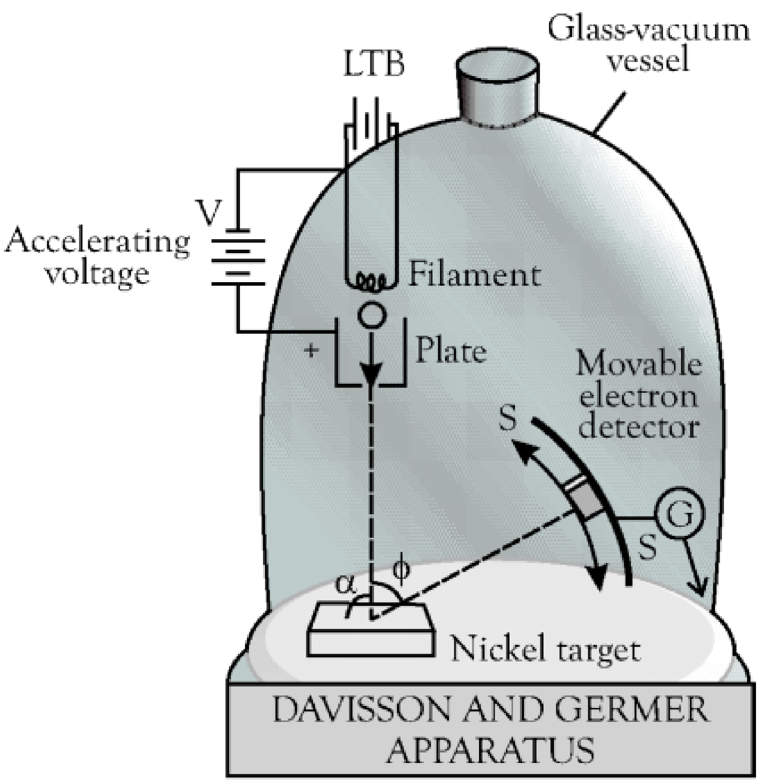


Fig 1. Schematic diagram of the Davisson-Germer Experiment

WAVE NATURE OF PARTICLES

Experimental evidence of De Broglie Concept:

- Fig. 2 shows the polar graph of the variation of the intensity with ϕ for V = 54 volts.
- At each angle, the intensity is given by the distance of the point from the origin. It is seen that as ϕ increase from zero, the intensity first decreases , passes through a minimum at 35^0 and then rises to a peak values at 50^0.

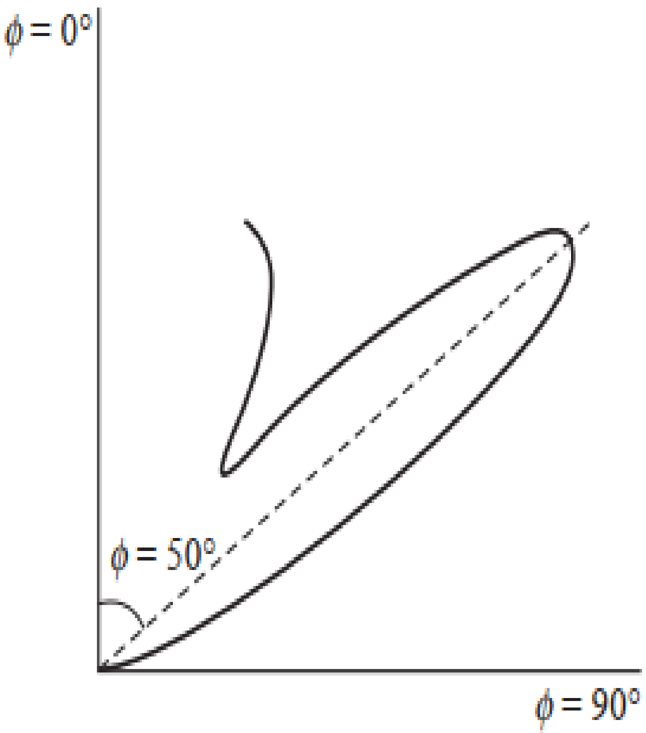


Fig 2. Polar plot of the intensity as a function of the scattering angle for 54 eV electrons.

WAVE NATURE OF PARTICLES

Experimental evidence of De Broglie Concept:

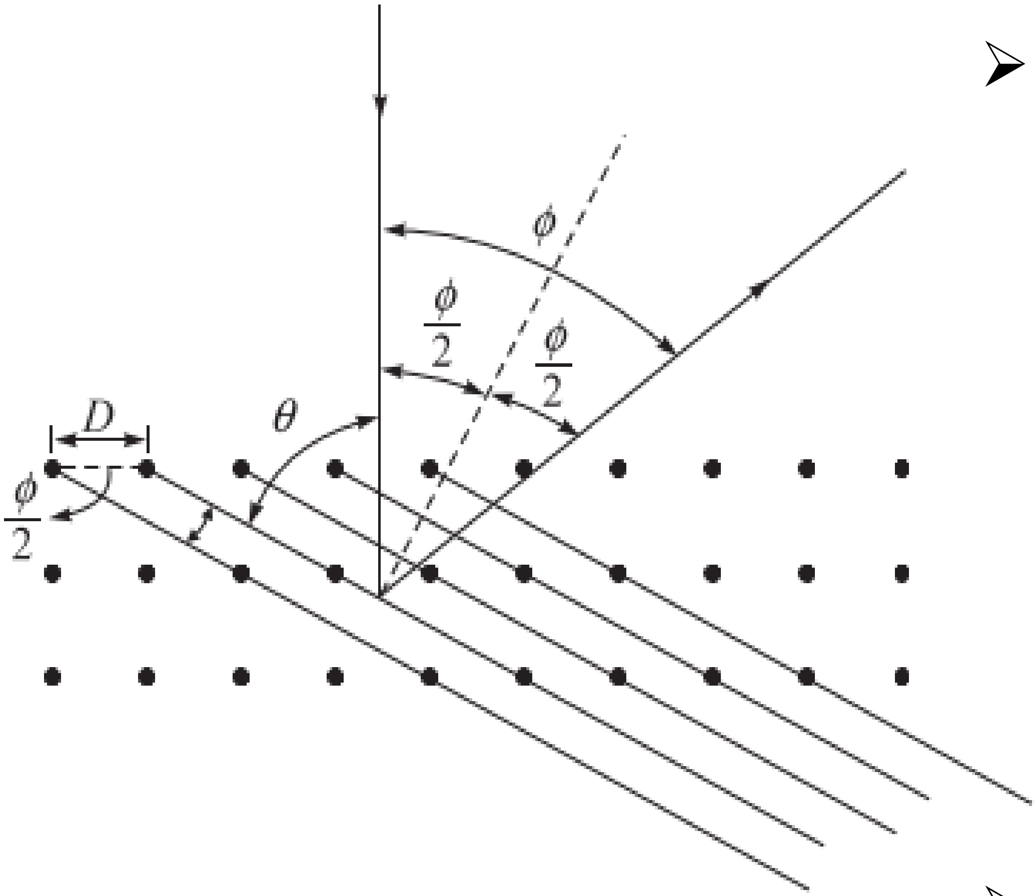


Fig 3. Diffraction of electron waves by the crystal

- The occurrence of this peak can be explained as being due to constructive interference of the electron wave reflected from some particular set of Bragg planes in the crystal lattice as in the case of X rays cases.
- This shown in the figure 3.

WAVE NATURE OF PARTICLES

Experimental evidence of De Broglie Concept:

The Bragg condition for constructive interference is

$$n\lambda = 2d\sin\theta$$

Where d is the spacing between the adjacent Bragg planes and n is an integer.

The angle θ is shown in the figure, We have

$$\theta + \phi + \theta = 180^0$$

$$\theta = \frac{180^0 - \phi}{2} = 90^0 - \frac{\phi}{2}$$

From geometry,

$$d = D\sin\frac{\phi}{2}$$

Where D is the interatomic distance.

WAVE NATURE OF PARTICLES

Experimental evidence of De Broglie Concept:

Therefore, $n\lambda = 2D\sin\frac{\phi}{2}\sin\left(90^0 - \frac{\phi}{2}\right)$

$$n\lambda = 2D\sin\frac{\phi}{2}\cos\frac{\phi}{2} = D\sin\phi$$

For Nickel D = 2.15 Å . Assuming that the peak at $\phi = 50^0$ for the first order diffraction, we take n = 1. Therefore,

$$\lambda = 2.15 \times \sin 50^0 = 1.65\ \text{Å}$$

Now according to de Broglie's hypothesis, we have for electron accelerated through a potential difference, V

$$\lambda = \frac{1.23}{\sqrt{V}}\ \text{Å} = \frac{1.23}{\sqrt{54}}\ \text{Å} = 1.66\ \text{Å}$$

The agreement between the two values is remarkably close.

WAVE NATURE OF PARTICLES

Human perception of de Broglie wave:

Example 1: An electron of mass, $m_e = 9.1 \times 10^{-31} kg$ having velocity $v = 10^6\ ms^{-1}$ would have a wavelength,

$$\lambda = \frac{h}{m_e v}$$

$$= \frac{6.62 \times 10^{-34} js}{9.1 \times 10^{-31} kg \times 10^6\ ms^{-1}}$$

$$= 70 \times 10^{-10}\ m$$

$$= 70\ nm$$

WAVE NATURE OF PARTICLES

Human perception of de Broglie wave:

Example 2: A large object of mass, $m = 1\,kg$ having velocity $v = 33.10\,ms^{-1}$ would have a wavelength,

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

$$= \frac{6.62 \times 10^{-34} js}{1\,kg \times 33.10\,ms^{-1}}$$

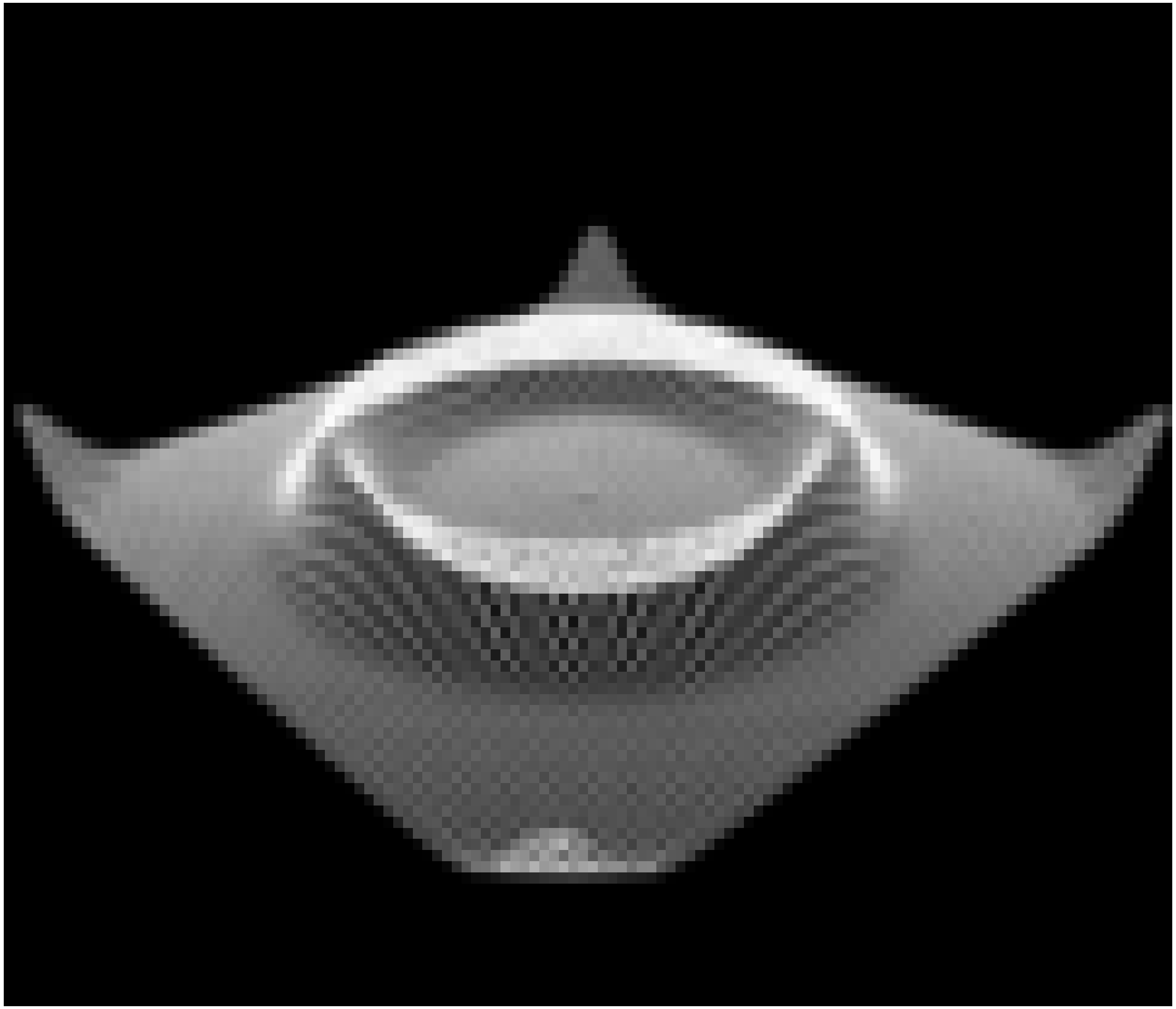
$$= 2.0 \times 10^{-35}\,m$$

The wavelength is too small, indeed human unbales to percept the wave effect of large object.

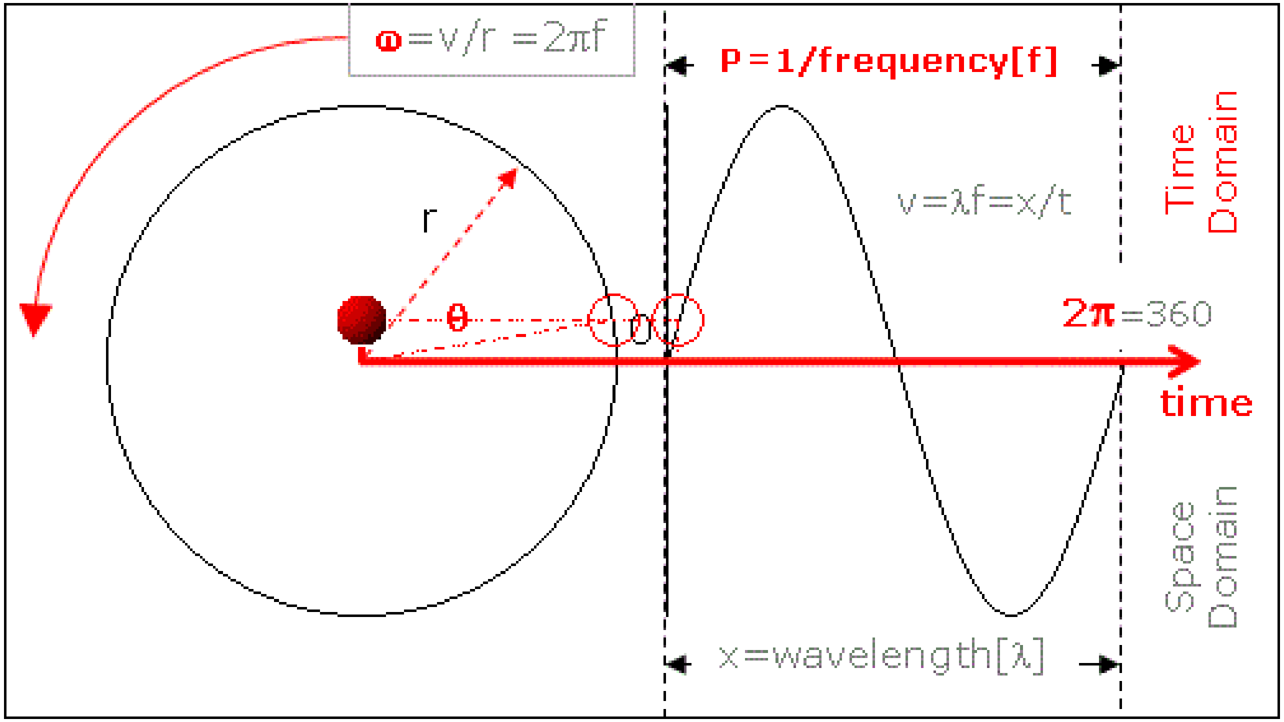
WAVES VS PARTICLES

Sl.	Waves	Particles
1.	A wave is described by frequency ν, wavelength	

Classical Waves



HARMONIC STATIONARY WAVES



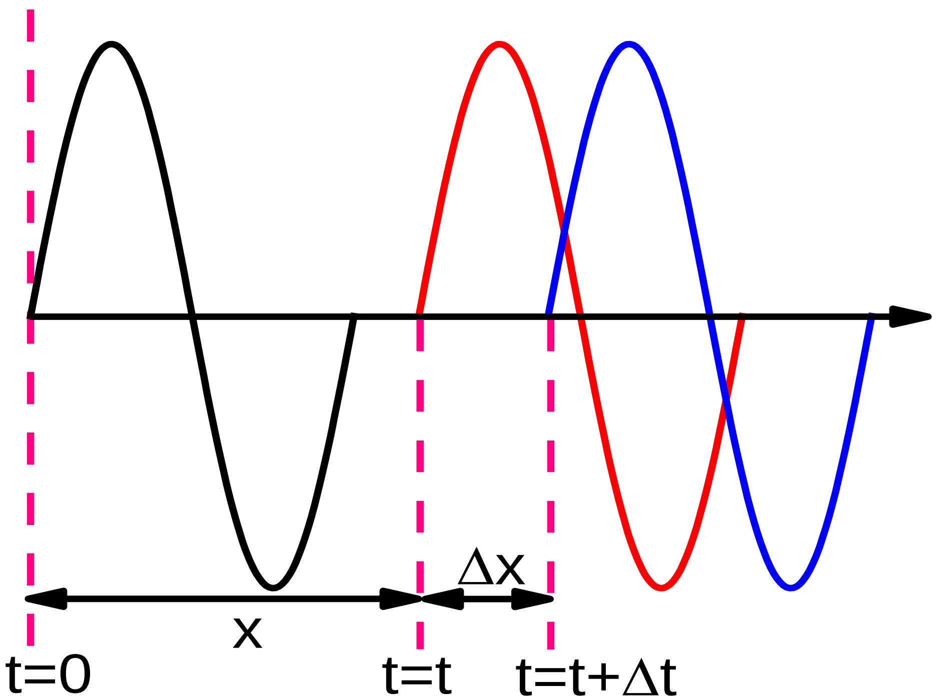
The displacement of particles (along Y- axis) from the equilibrium position (along x-axis

$$y(x=0,t=0)=A\sin\omega t$$

$$y(x=0,t=0)=A\cos\omega t$$

Note: two waves are the same except phase difference by $\pi/2$

TRAVELLING WAVES

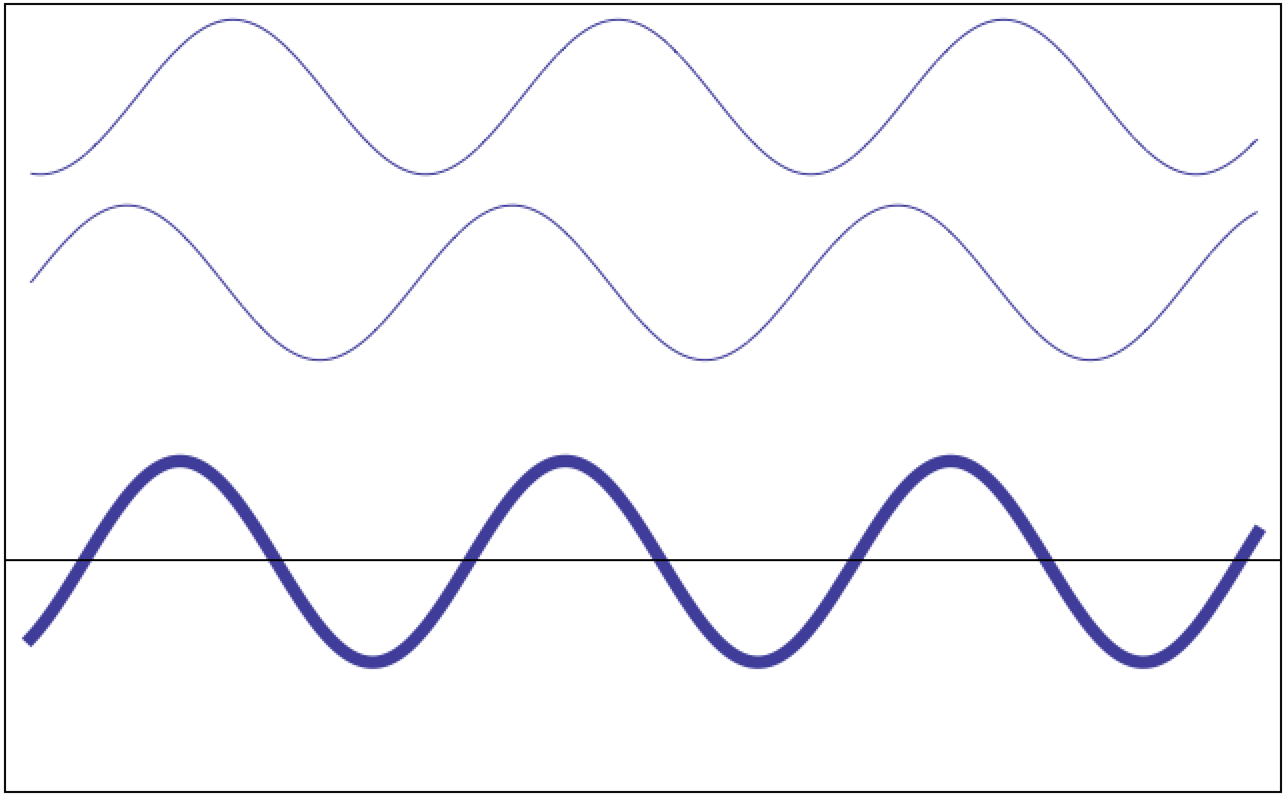


$$y(x,t) = A\sin\left(\frac{2\pi}{\lambda}x + \phi\right)$$

$$y(x,t) = A\sin\left[\frac{2\pi}{\lambda}(x - vt) + \phi\right]$$

$$x = x_0 + vt, \qquad \Delta x = x - x_0 = vt$$

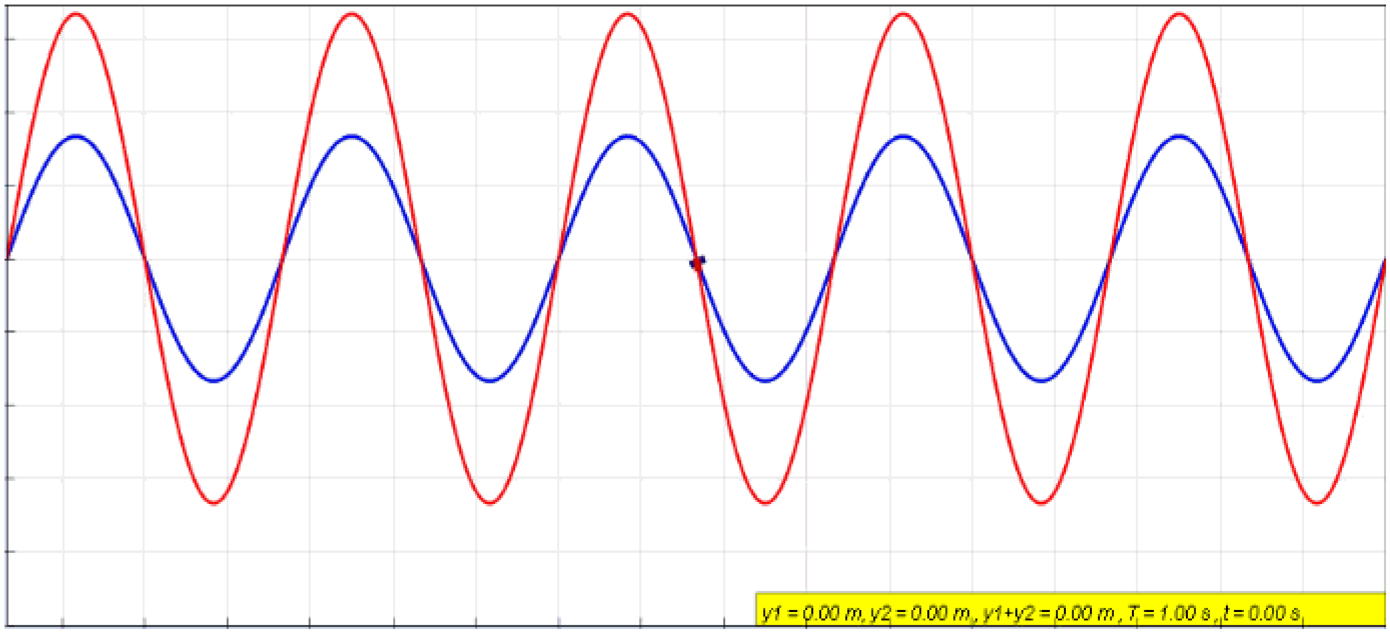
Principle of Superposition

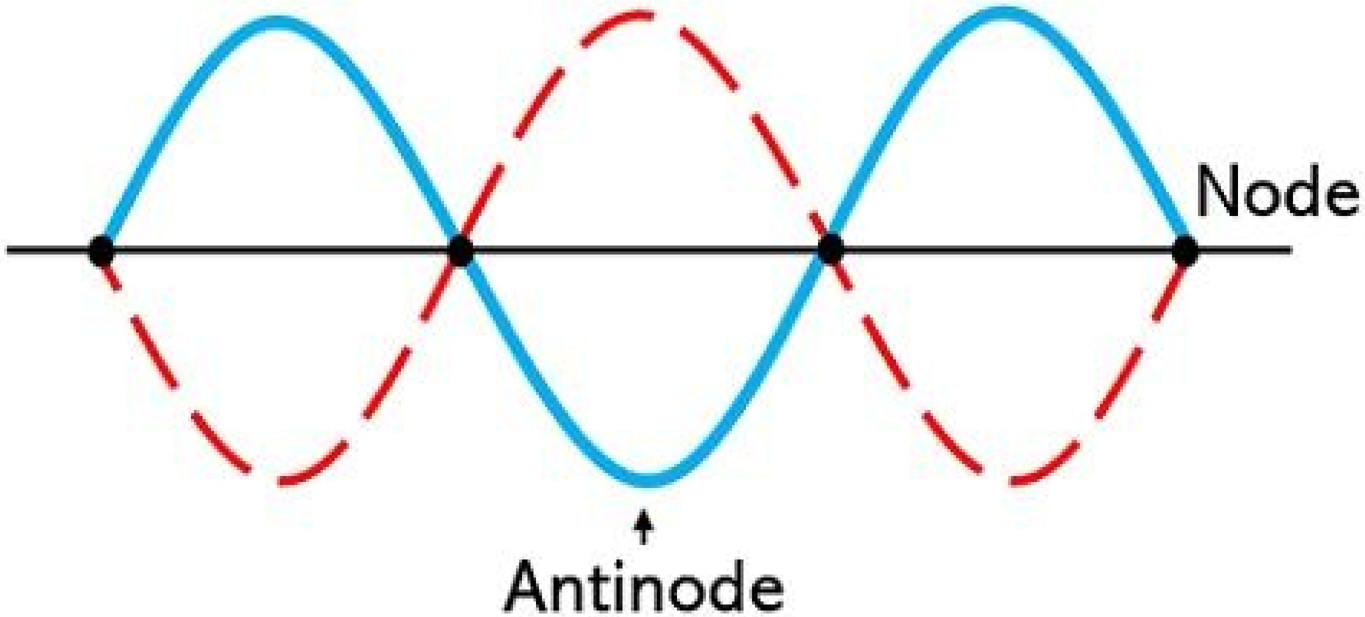


$$y(x,t) = y_1 + y_2$$

$$y(x,t) = 2Acos\left(\frac{\phi}{2}\right)\sin\left[\frac{2\pi}{\lambda}(x - vt) + \frac{\phi}{2}\right]$$

Standing waves





CLASSICAL WAVE EQUATION

- The displacement of a wave is

$$y(x,t) = A\sin\left[\frac{2\pi}{\lambda}(x-ct)+\phi\right]$$

- Partial differential with respect to t, x gives

$$\frac{\partial y}{\partial t} = -\frac{2A\pi c}{\lambda}\cos\left[\frac{2\pi}{\lambda}(x-ct)+\phi\right]$$

$$\frac{\partial^2 y}{\partial t^2} = -\frac{4\pi^2 c^2}{\lambda^2}\mathrm{A}\sin\left[\frac{2\pi}{\lambda}(x-ct)+\phi\right]$$

$$\frac{\partial y}{\partial x} = \frac{2A\pi}{\lambda}\cos\left[\frac{2\pi}{\lambda}(x-ct)+\phi\right]$$

$$\frac{\partial^2 y}{\partial x^2} = -\frac{4\pi^2}{\lambda^2}\mathrm{A}\sin\left[\frac{2\pi}{\lambda}(x-ct)+\phi\right]$$

$$y(x,t) = A\cos\left[\frac{2\pi}{\lambda}(x-ct)+\phi\right]$$

$$y(x,t) = Ae^{i\left\{\frac{2\pi}{\lambda}(x-ct)+\phi\right\}}$$

$$\frac{\partial^2 y}{\partial t^2} = -\frac{4\pi^2 c^2}{\lambda^2}\left(-\frac{\lambda^2}{4\pi^2}\frac{\partial^2 y}{\partial x^2}\right) \Longrightarrow \boxed{\frac{\partial^2 y}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 y}{\partial t^2}}$$

WAVE PACKETS AND MATTER WAVES

- Do the classical waves represent matter waves?
  - NO, why??

The velocity of waves called phase velocity, v_{ph} can be obtained from phase.

$$y(x,t) = A\sin\left[\overbrace{\frac{2\pi}{\lambda}(x-ct)+\phi}^{\text{Total Phase}}\right]$$

Total phase, $\Phi = kx - \omega t + \phi \quad \left[k = \frac{2\pi}{\lambda},\ \ k \rightarrow \text{Wave vector}\right]$

$$\frac{d\Phi}{dt} = k\frac{dx}{dt} - \omega = 0 \quad [\text{since } \Phi \text{ is constant with time}]$$

$$v_{ph} = \frac{dx}{dt} = \frac{\omega}{k}$$

WAVE PACKETS AND MATTER WAVES

1. The phase velocity of de Broglie waves

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

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

$$E = h\nu = \frac{h}{2\pi} \cdot 2\pi\nu = \hbar\omega$$

Since, particle velocity $v \ll$ light velocity c.

$$v_{ph} \gg c^2$$

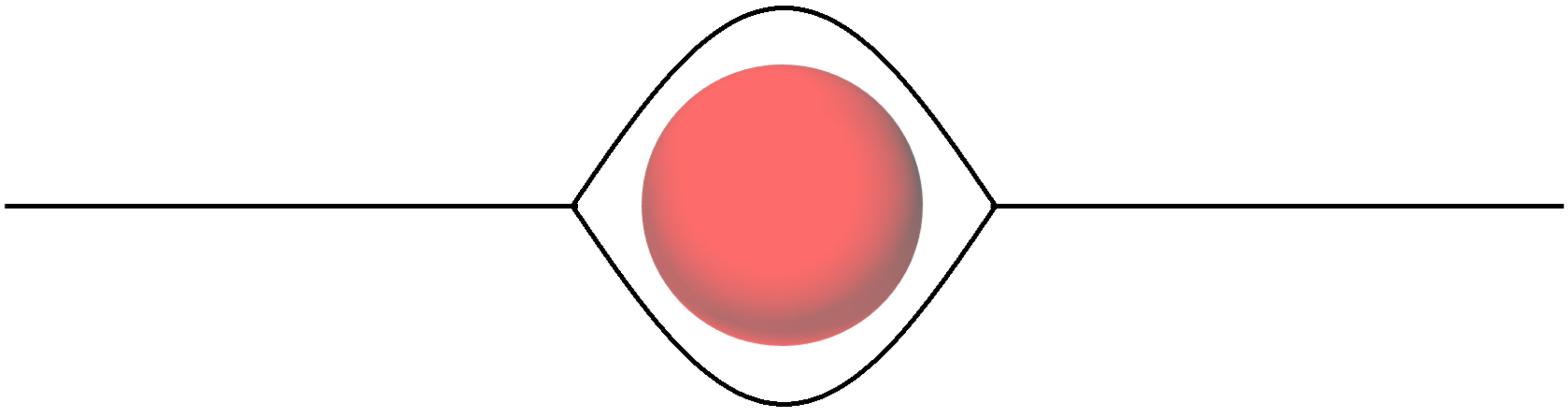
This is totally absurd.

2. The classical waves, $\psi(x,t) = Ae^{i(kx-\omega t+\phi)}$

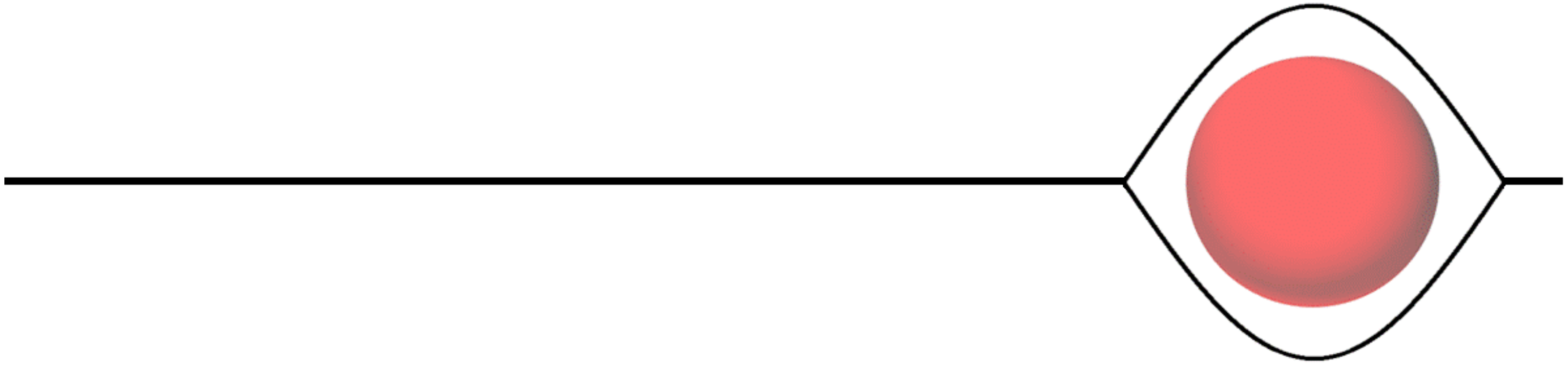
Probability density, $|\psi(x,t)|^2 = A^2$ is independent of position. This is also physically inconsistent.

PROPERTIES OF MATTER WAVES

1. Stationary particle



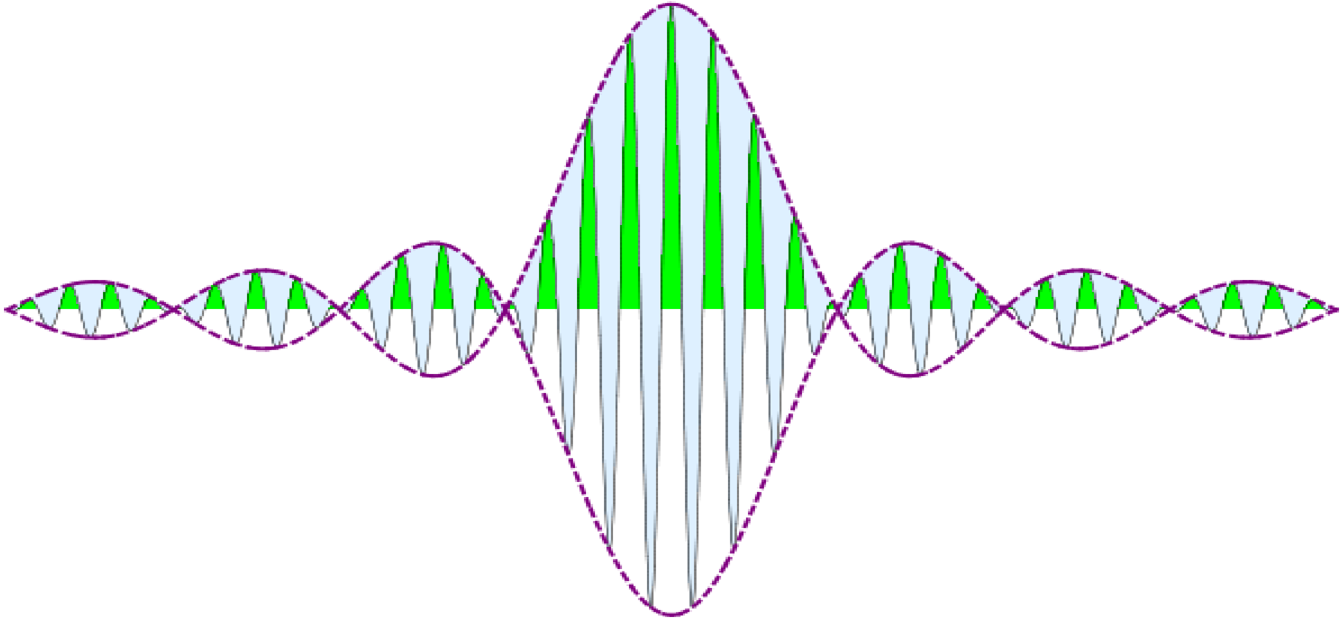
2. Dynamic particle



Wave packets and Matter waves

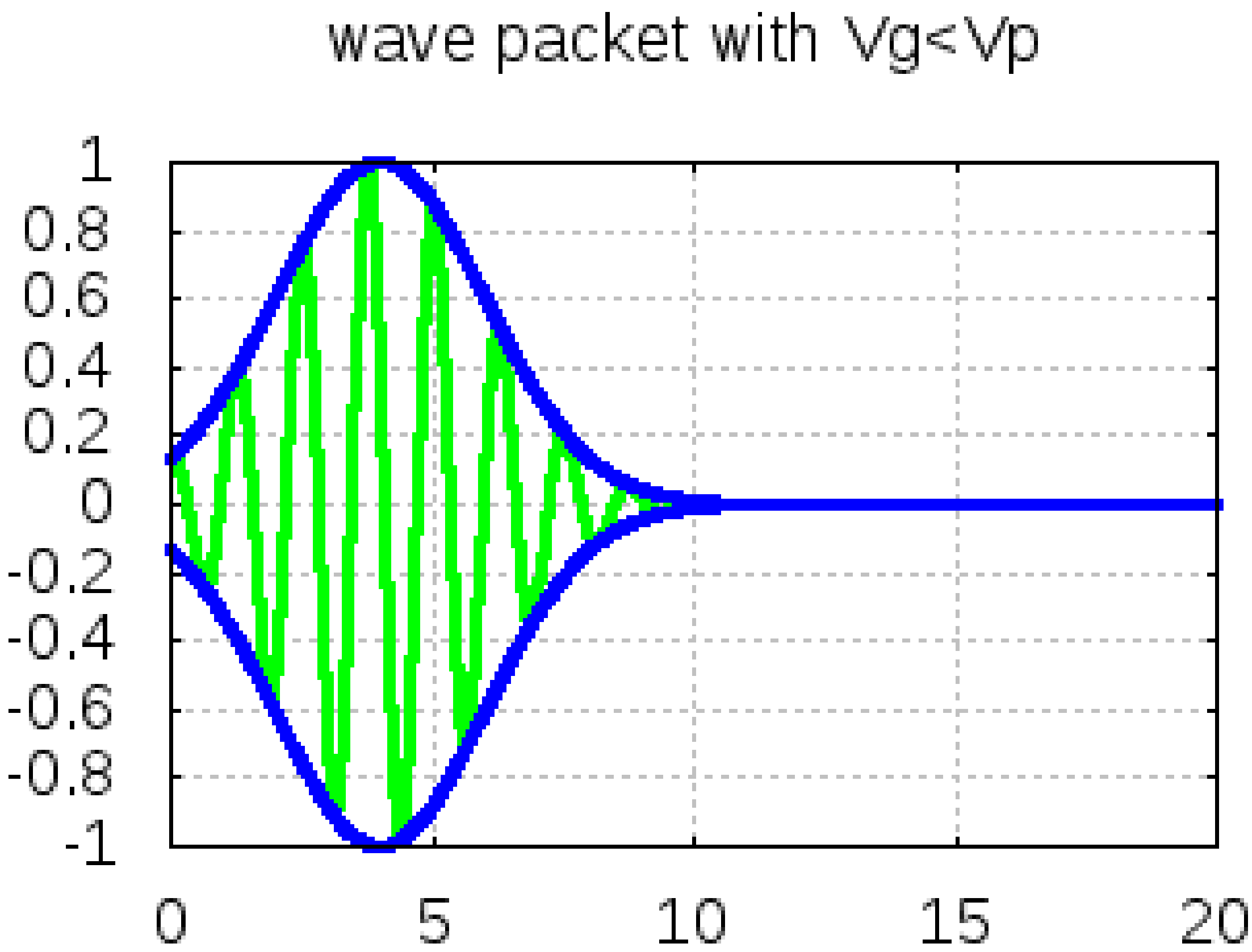
What is wave packet?

Superposition of infinite number of waves with slightly different k and ω that dk and $d\omega$ are small shows



Wave packets and Matter waves

Formation of wave packet



WAVE PACKETS AND MATTER WAVES

Formation of wave packet

$$\psi_1 = A\sin(k_1 x - \omega_1 t) \qquad v = \frac{\omega}{k}$$

$$\psi_2 = A\sin(k_2 x - \omega_2 t) \qquad \sin\alpha + \sin\beta = 2\sin\left(\frac{\alpha+\beta}{2}\right)\cos\left(\frac{\alpha-\beta}{2}\right)$$

$$\psi = \psi_1 + \psi_2$$

$$\psi = A\sin(k_1 x - \omega_1 t) + A\sin(k_2 x - \omega_2 t)$$

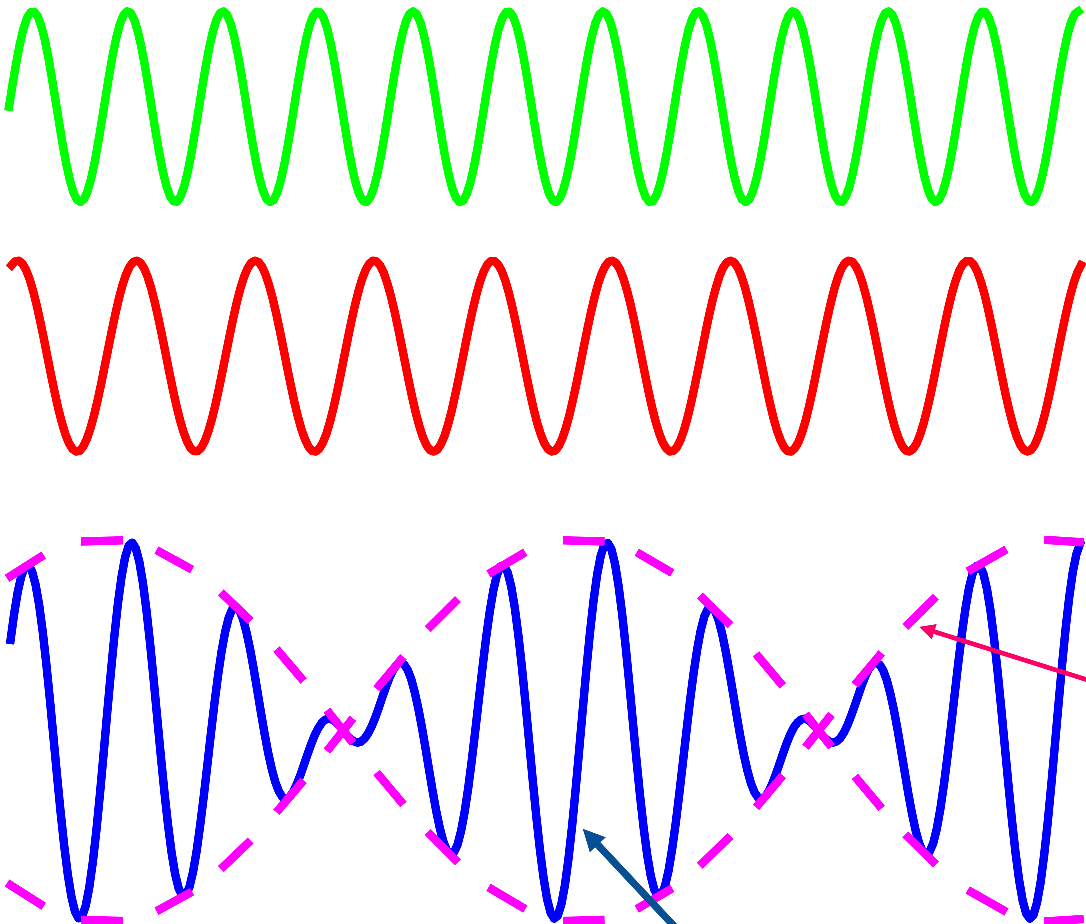
$$\psi = 2A\cos\left\{\left(\frac{k_1 - k_2}{2}\right)x - \left(\frac{\omega_1 - \omega_2}{2}\right)t\right\}\sin\left\{\left(\frac{k_1 + k_2}{2}\right)x - \left(\frac{\omega_1 + \omega_2}{2}\right)t\right\}$$

$$\psi = 2A\cos\left\{\left(\frac{\Delta k}{2}\right)x - \left(\frac{\Delta\omega}{2}\right)t\right\}\sin\left(\bar{k}x - \bar{\omega}t\right)$$

$$\Delta k = k_1 - k_1, \qquad \Delta\omega = \omega_1 - \omega_2, \qquad \bar{k} = \frac{k_1 + k_2}{2}, \qquad \bar{\omega} = \frac{\omega_1 + \omega_2}{2}$$

WAVE PACKETS AND MATTER WAVES

Formation of wave packet



$$\psi_1 = A\sin(k_1 x - \omega_1 t)$$

$$\psi_2 = A\sin(k_2 x - \omega_2 t)$$

Group velocity, $v_g = \dfrac{\Delta w}{\Delta k}$

$$\psi = 2A\cos\left\{\left(\frac{\Delta k}{2}\right)x - \left(\frac{\Delta \omega}{2}\right)t\right\}$$

$$\psi = 2A\cos\left\{\left(\frac{\Delta k}{2}\right)x - \left(\frac{\Delta \omega}{2}\right)t\right\}\sin(\bar{k}x - \bar{\omega}t)$$

WAVE PACKETS AND MATTER WAVES

Formation of wave packet

Summation of an infinite number of waves having infinitesimally different frequencies, ω and wave vector, k may form a single group.

$$y(x,t) = \sum_{n} A_n e^{i(kx-\omega t)}$$

Furrier Series

If the component waves have continuous distribution of frequencies and wave vectors, the above sum becomes an integral.

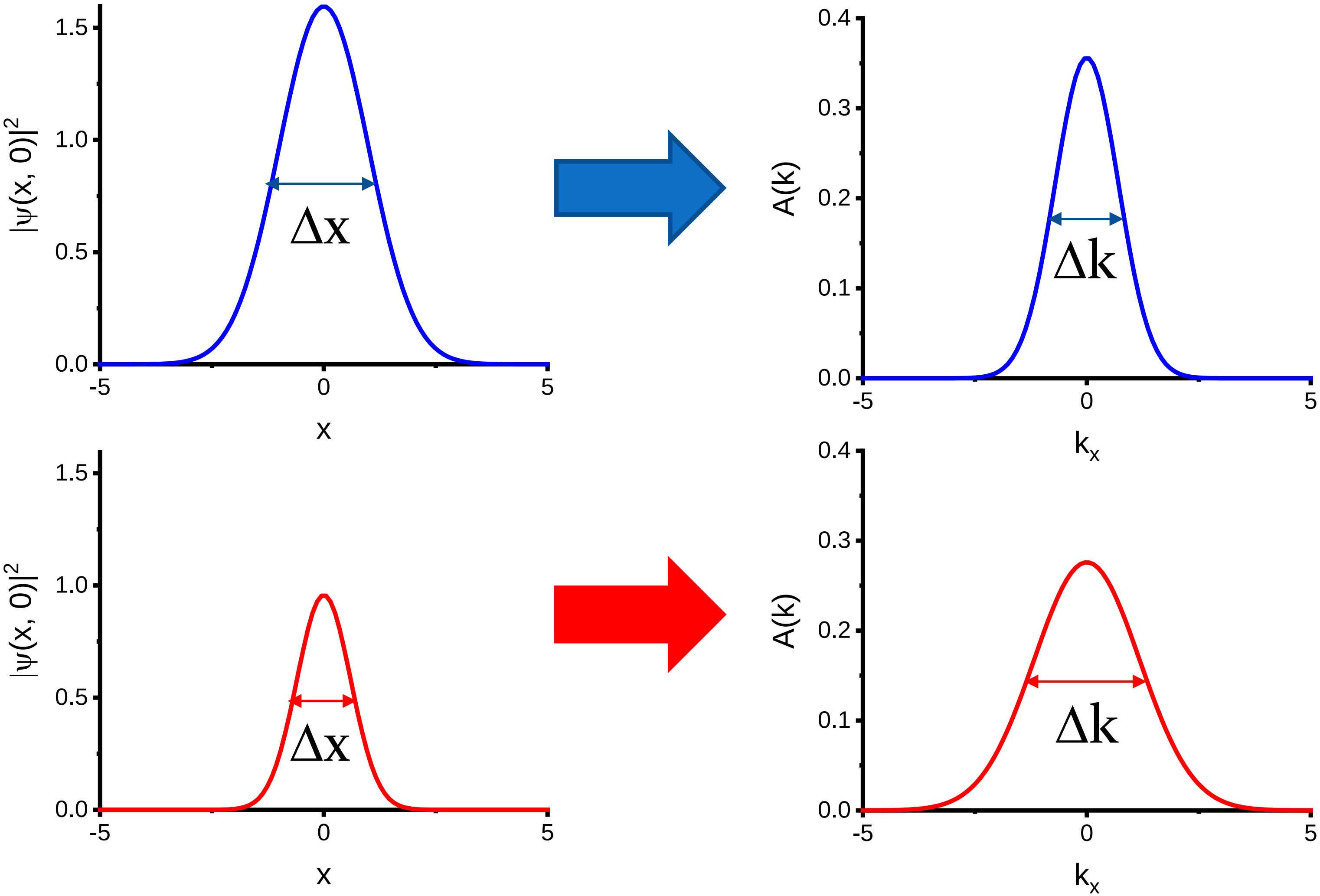
$$y(x,t) = \int A(k)\, e^{i(kx-\omega t)}\, dk$$

Furrier Integral

$$A(k) = \int y(x,t)\, e^{-i(kx-\omega t)}\, dx$$

Furrier Transform

Wave packets and Matter waves



$$\Delta x \cdot \Delta k = Constant$$

WAVE PACKETS AND MATTER WAVES

Group velocity, $v_g = \frac{\Delta w}{\Delta k}$

If the frequencies and wave vectors of component waves forming a single group differ infinitesimally, then

$$v_g = \frac{dw}{dk}$$

Now,

$$\omega = \frac{E}{\hbar} = \frac{p^2}{2m\hbar} = \frac{\hbar^2 k^2}{2m\hbar} = \frac{\hbar k^2}{2m}$$

$$v_g = \frac{dw}{dk} = \frac{2\hbar k}{2m} = \frac{p}{m} = v_p \rightarrow \text{Particle velocity}$$

Thus, the representation of a particle by wave packet gets logical support.

WAVE PACKETS AND UNCERTAINTY PRINCIPLE

- ✓ For a Gaussian shaped wave packet, the product $\Delta x \cdot \Delta k$ is minimum and is equal to unity .

$$\Delta x \cdot \Delta k = 1$$

- ✓ For other types of wave packets, such as square, triangle or rectangular,

$$\Delta x \cdot \Delta k > 1$$

- ✓ In generally,

$$\Delta x \cdot \Delta k \geq 1$$

$$\Delta x \cdot \Delta \left(\frac{p}{\hbar}\right) \geq 1$$

$$\Delta x \cdot \Delta p \geq \hbar$$

$$\boxed{\Delta x \cdot \Delta p \geq \frac{h}{2\pi}}$$

Heisenberg Uncertainty relation

Wave packets and Uncertainty Principle

Energy -Time Uncertainty Relation

$$E = \frac{p^2}{2m}$$

$$\Delta E = \frac{2p\Delta p}{2m}$$

$$\Delta E = \frac{mv\Delta p}{m}$$

$$\Delta E = v\Delta p$$

$$\Delta p = \frac{\Delta E}{v}$$

$$x = x_0 + vt$$

$$\Delta x = v\Delta t$$

Now,

$$\Delta \mathrm{x} \cdot \Delta p = \hbar$$

$$v\Delta t \cdot \frac{\Delta E}{v} = \hbar$$

$$\boxed{\Delta E \cdot \Delta t = \hbar}$$

Heisenberg Uncertainty relation

Derivation of Matter Waves

The classical wave equation:

$$\frac{\partial^2\psi}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2} \qquad (1)$$

It's a 2nd order partial differential equation of degree 1. ψ is a function of x and t. If x and t don't interfere each other then ψ can be written as the product of two functions whose are function of single variable, i.e.,

$$\psi(x,t) = X(x)\cdot T(t)$$

The solution of equation (1) was shown as

$$\psi(x,t) = Ae^{i\left\{\frac{2\pi}{\lambda}(x-ct)+\phi\right\}}$$

$$\psi(x,t) = Ae^{i\phi}\, e^{i\left(\frac{2\pi}{\lambda}\right)x}\cdot e^{-i\left(\frac{2\pi c}{\lambda}\right)t}$$

$$\psi(x,t) = X(x)\cdot e^{-i\left(\frac{2\pi c}{\lambda}\right)t} \qquad (2)$$

Derivation of Matter Waves

Now differentiating equation (2) wrt x and t,

$$\frac{\partial^2\psi}{\partial x^2} = \frac{d^2X}{dx^2} \cdot e^{-i\left(\frac{2\pi c}{\lambda}\right)t}$$

and $$\frac{\partial^2\psi}{\partial t^2} = -\frac{4\pi^2c^2}{\lambda^2}X(x) \cdot Ae^{-i\left(\frac{2\pi c}{\lambda}\right)t}$$

Putting these partial derivatives in equation (1),

$$\frac{d^2X}{dx^2} \cdot e^{-i\left(\frac{2\pi c}{\lambda}\right)t} = \frac{1}{c^2}\left(-\frac{4\pi^2c^2}{\lambda^2}\right)X(x) \cdot e^{-i\left(\frac{2\pi c}{\lambda}\right)t}$$

$$\frac{d^2X}{dx^2} = -\frac{4\pi^2}{\lambda^2}X(x) \qquad (3)$$

The equation(3) is time-independent classical wave equation.

Derivation of Matter Waves

According to de Broglie equation,

$$\lambda = \frac{h}{p} \Longrightarrow \lambda^2 = \frac{h^2}{p^2}$$

Substituting λ in equation (3)

$$\frac{d^2X}{dx^2} = -\frac{4\pi^2 p^2}{h^2} X(x) \qquad (4)$$

Total Energy , E = Kinetic Energy, KE + Potential Energy, V

Or, KE = E – V

Or, $\frac{p^2}{2m} = E - V \quad \Longrightarrow \quad p^2 = 2m(E - V)$

Substituting p in equation (4)

One dimensional Schrodinger equation

$$\frac{d^2X}{dx^2} = -\frac{8\pi^2 m(E - V)}{h^2} X(x) \qquad (5)$$

Derivation of Matter Waves

Considering the motion of micro-particle in three dimension, this equation (5) has been modified as

$$\frac{d^2\Psi}{dx^2}+\frac{d^2\Psi}{dy^2}+\frac{d^2\Psi}{dz^2}=-\frac{8\pi^2m(E-V)}{h^2}\Psi \qquad (6)$$

$$\nabla^2\Psi=-\frac{8\pi^2m(E-V)}{h^2}\Psi \qquad (7)$$

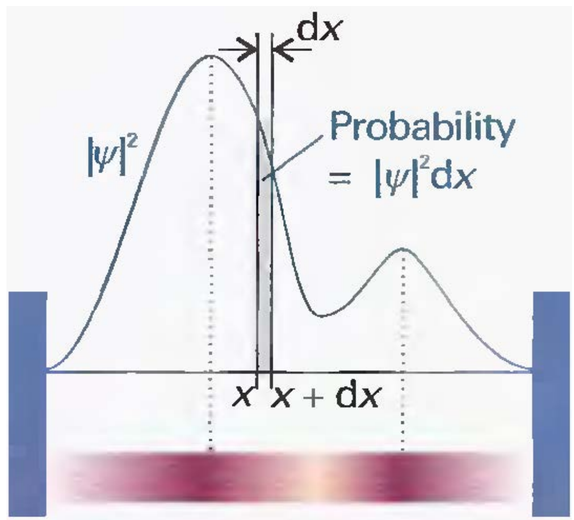
Where Laplacian Operator, $\nabla^2=\frac{d^2}{dx^2}+\frac{d^2}{dy^2}+\frac{d^2}{dz^2}$

Equation (6) and (7) are three-dimensional time-independent Schrodinger equation.

$$|\Psi|^2$$

Probability density is always positive

The probability of experimentally finding the body described by the wave function Ψ at the point x, y, z, at the time t is proportional to the value of $|\Psi|^2$ there at t.



In a one-dimensional case, the probability that the particle will be found in the interval dx around some point x_1 is -

$$|\Psi(\quad)|$$

A large value of $|\Psi|^2$ means the strong possibility of the body's presence, while a small value of $|\Psi|^2$ means the slight possibility of its presence. As long as $|\Psi|^2$ is not actually 0 somewhere, however, there is a definite chance, however small, of detecting it there. This interpretation was first made by Max Born in 1926.

Ψ

Wave functions are usually complex with both real and imaginary parts. A probability, however, must be a positive real quantity. The probability density $|\Psi|^2$ for a complex Ψ is therefore taken as the product $\Psi^*\Psi$ of Ψ and its **complex conjugate** Ψ^*.

Wave function $\Psi = A + iB$

Complex conjugate $\Psi^* = A - iB$

and so probability density $|\Psi|^2 = \Psi^*\Psi = A^2 - i^2B^2 = A^2 + B^2$

Always real and positive

Ψ must be finite

Since $|\Psi|$ is proportional to the probability density of finding the particle described by Ψ,

$$\int_{-\infty}^{\infty} |\Psi|^2 \quad =$$

$$\int_{-\infty}^{\infty} |\Psi|^2 \quad \neq \infty$$

Maximum probability can be which means certainty of the particles presence

$$\int_{-\infty}^{\infty} |\Psi|^2 \quad =$$

Means the particle does not exist

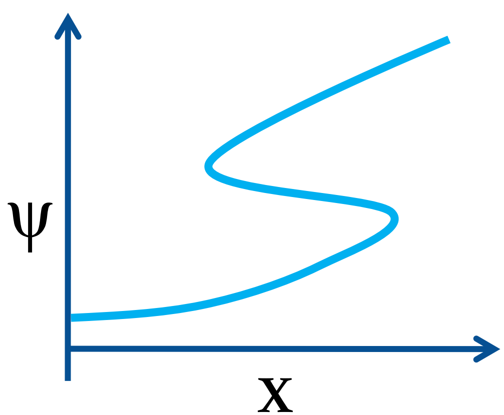
Ψ

The probability of finding the particle in a given region (say, between x_1 and x_2 along x-direction) is given by :

$$\text{Probability} = \int |\Psi|$$

ψ

This is obvious because there can not be more than one probability for an event at the same place and time.

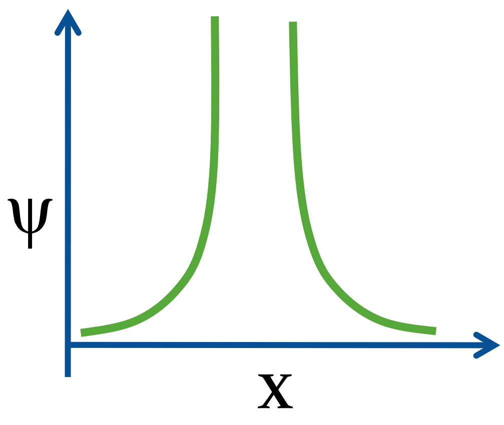


Unacceptable for not being single-valued

The born interpretation immediately imposes some restrictions on acceptable values of ψ:

ψ

An infinite value of ψ at any point would mean an infinite probability of finding the particle at that point, which is absurd, as the maximum probability (i.e., certainty) equals 1.

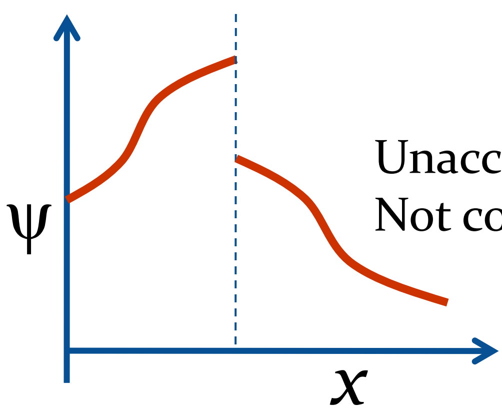


Unacceptable:
Infinite over a finite region

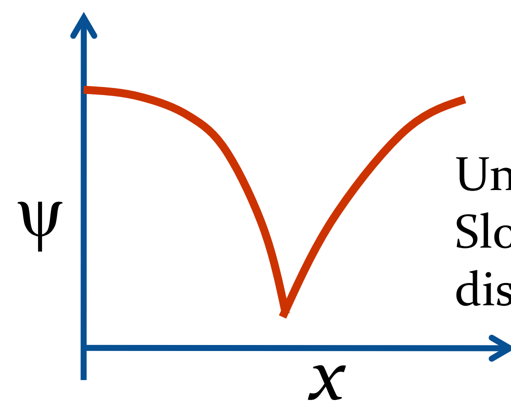
$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \mathcal{V}(x)\psi = E\psi$$

$\frac{^{2}\psi}{^{2}}$ must be well defined

We can take the 2nd derivative of ψ only if it is continuous and also its first derivative (sloe of ψ) is continuous (there must not be any infection point on the plot of the function)



Unacceptable:
Not continuous



Unacceptable:
Slope (1st derivative) discontinuous

ψ

$$\int |\psi|^2 \quad \tau = C \qquad\qquad \int \psi^* \psi \quad \tau = C$$

This also means that ψ must go to zero as x ⟶ ±∞; y ⟶ ±∞; z ⟶ ±∞ (otherwise ψ would become infinite)

A wave function that satisfies the conditions 1 – 4 is said to be a well-behaved function. Only a well-behaved wave function can yield physically meaningful results when used in calculation.

A consequence of the probabilistic interpretation of the wave-function is that it must be normalized:

$$\int_{-\infty}^{+\infty} |\psi|^2 \qquad = 1 \qquad\qquad \int_{-\infty}^{+\infty} \psi^* \psi \qquad = 1 \qquad\qquad \int |\psi|^2 \qquad = 1 \qquad \text{for} \quad \leq \quad \leq$$

Since the particle is to be found somewhere in space, the total probability of its finding over all space must be unity.

If ψ happens to be complex, * would be always real.

$$\int |\psi|^2 \quad \tau = 1 \qquad\qquad \int \psi^* \psi \quad \tau = 1 \qquad\qquad \tau = \quad . \quad .$$

(in 3-dimensions)

If we find that the wave-function for a particular system (obtained by solving the corresponding Schrödinger equation) does not satisfy the above characteristics, we have to make it so behave. This is known as normalization of the wave-function.