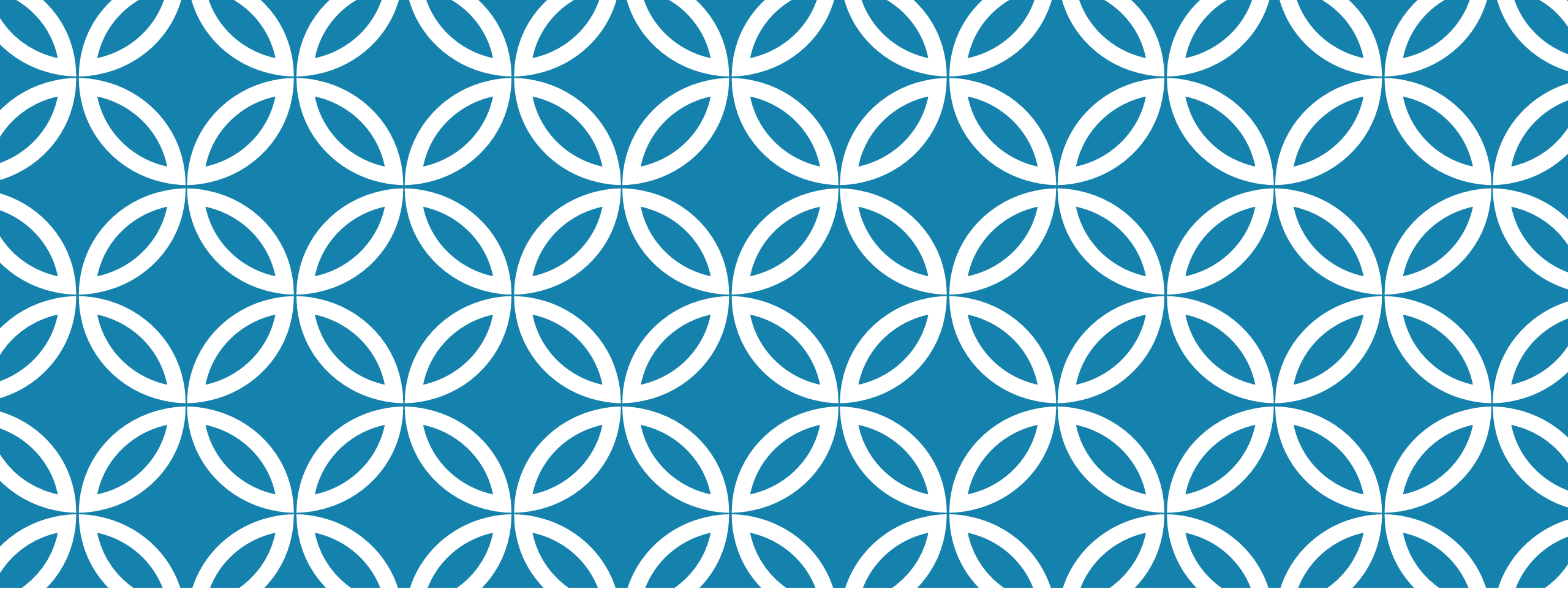




ELEMENTS OF QUANTUM MECHANICS

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Assistant Professor
Department of Physics
VIT Vellore

SYLLABUS AND REFERENCE BOOKS

Syllabus:

Need for Quantum Mechanics: Idea of Quantization (Planck and Einstein) - Compton effect (Qualitative)– de Broglie hypothesis - justification of Bohr postulate-Davisson-Germer experiment - Wave function and probability interpretation - Heisenberg uncertainty principle - Gedanken experiment (Heisenberg's microscope) - Schrödinger wave equation (time-dependent and time-independent)

Reference Books:

1. H. D. Young and R. A. Freedman, University Physics with Modern Physics, 2020, 15th Edition, Pearson, USA.(Section 40.1 to 40.6, Page No: 1321-1350)
2. Arthur Beiser, Concepts of Modern Physics; Sixth Edition (2020), McGraw Hill Publication.
3. Raymond A. Serway, Clement J. Moses, Curt A. Moyer Modern Physics, 2010, 3rd Indian Edition Cengage learning.

NEED OF QUANTUM MECHANICS: BACKGROUND

Classical Mechanics (16th- 19th Century)

- How does an object move?
- What kind of forces are acting upon it and how are they acting?



Collision of Billiard Balls

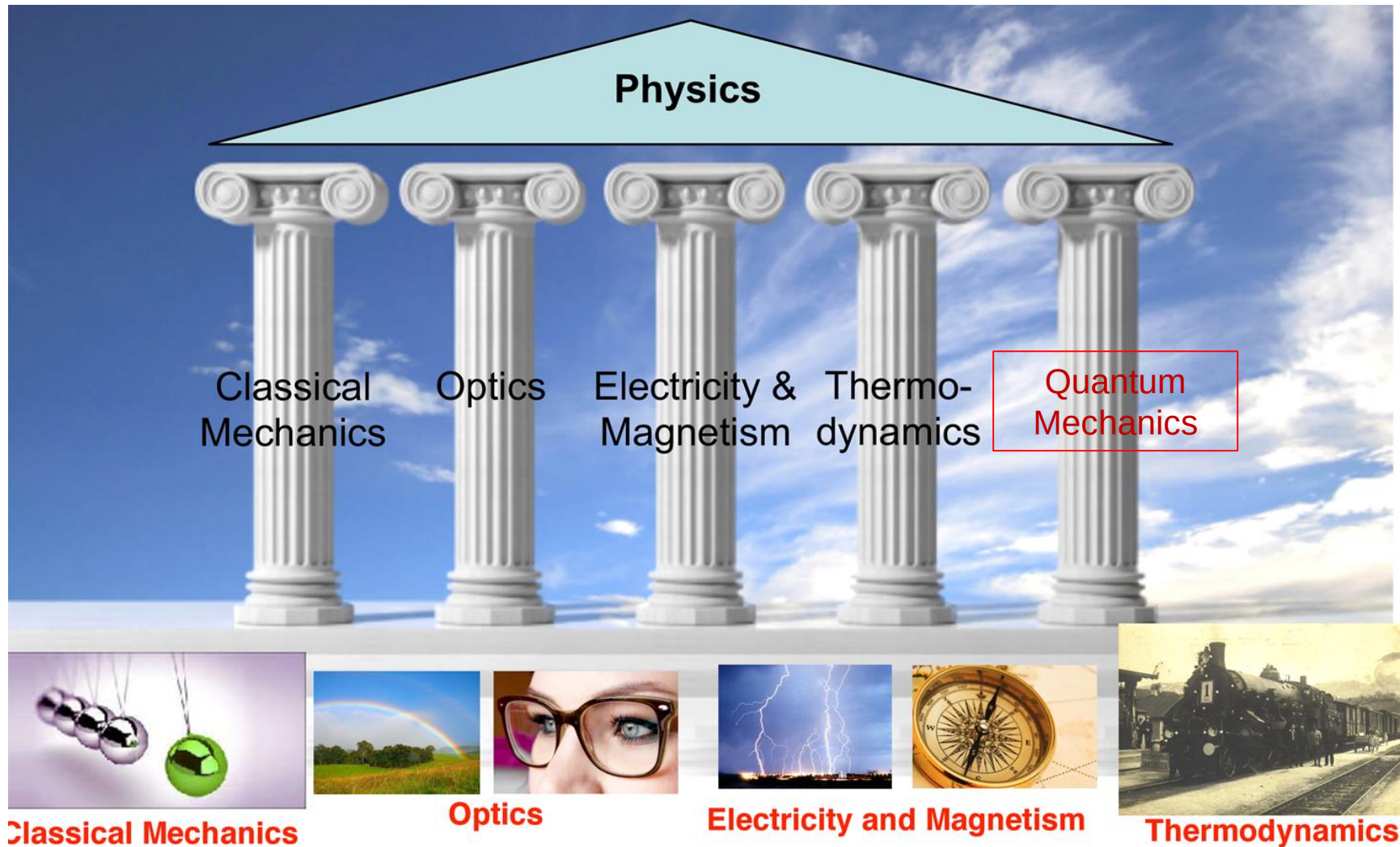


How does an airplane fly?

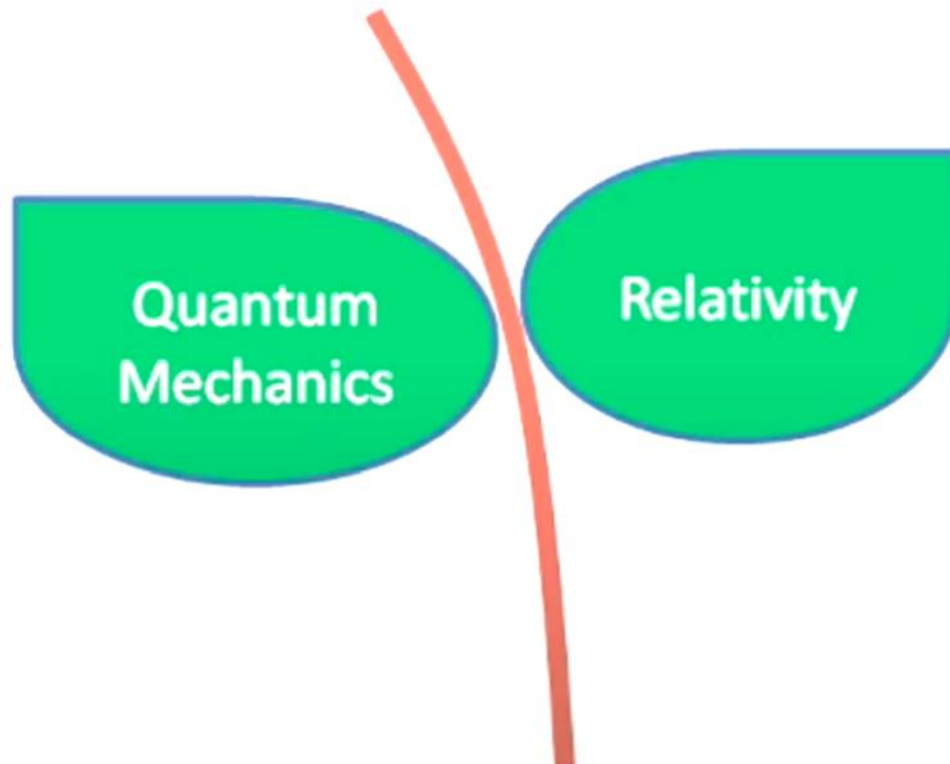


Planetary motion

CONT'D....



CONT'D.: BIRTH OF QUANTUM MECHANICS



Relativity works when speed of object is almost equal to speed of light

Quantum mechanics works well when size of objects is very small ,nearly size of atom, electron & proton



Molecules



Atom

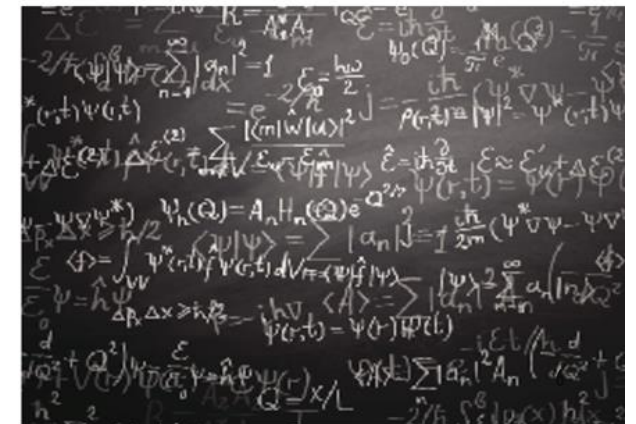
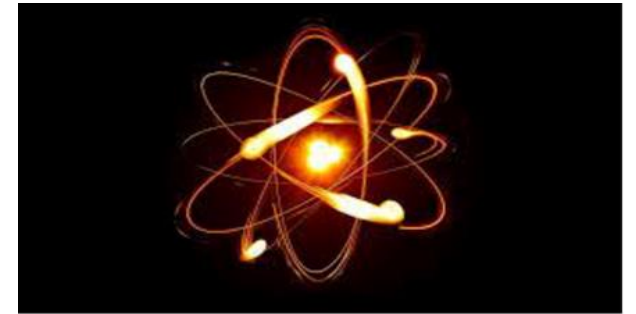


Electron, proton, neutron, α -particle,

CONT'D...: WHAT IS QUANTUM MECHANICS?

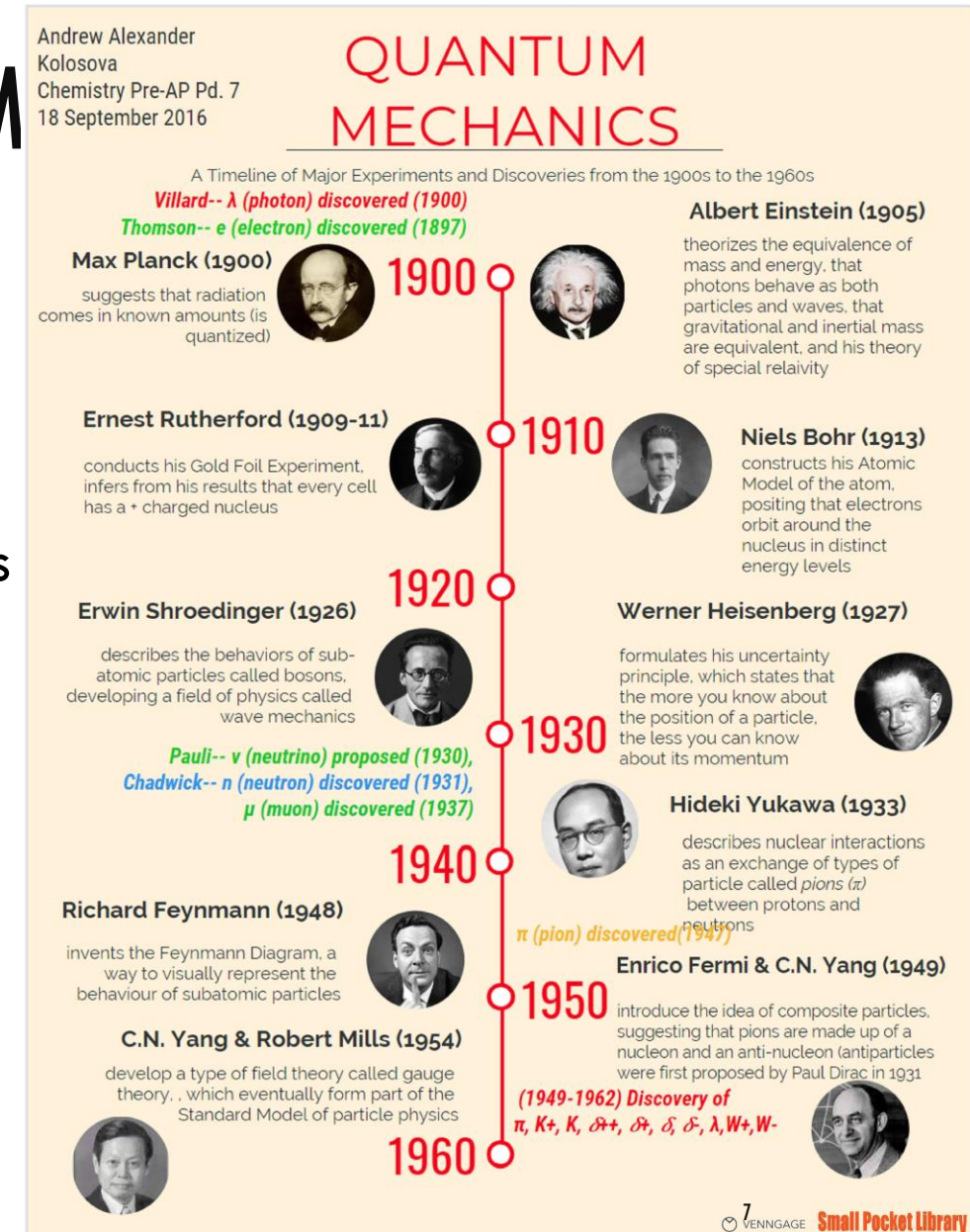
Quantum mechanics is branch of physics that provides a description of the physical properties of nature at the scale of atoms and subatomic particles. It is the foundation of all quantum physics including quantum chemistry, quantum field theory, quantum technology, and quantum information science.

The branch of mechanics that deals with the mathematical description of the motion and interaction of subatomic particles, incorporating the concepts of quantization of energy, wave-particle duality, the uncertainty principle, and the correspondence principle.



CONT'D...:DEVELOPMENT OF QM

- No one had an aim to build quantum mechanics It built by itself
- Historical period of 1897 to 1940 where the ideas of quantum mechanics evolved and settled
- Max Planck, Niels Bohr, de Broglie, Werner Heisenberg, Erwin Schrödinger, Max Born, Wolfgang Pauli, Paul Dirac
- Quantum mechanics plays a decisive role when technology becomes delicate



CONT'D....



SOLVAY CONFERENCE 1927

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A. PICARD	E. HENRIOT	P. EHRENFEST	Ed. HERSEN	Th. DE DONDER	E. SCHRÖDINGER	E. VERSCHAFFELT	W. PAULI	W. HEISENBERG	R.H FOWLER	L. BRILLOUIN
P. DEBYE	M. KNUDSEN	W.L. BRAGG	H.A. KRAMERS	P.A.M. DIRAC	A.H. COMPTON	L. de BROGLIE	M. BORN	N. BOHR		
I. LANGMUIR	M. PLANCK	Mme CURIE	H.A. LORENTZ	A. EINSTEIN	P. LANGEVIN	Ch.E. GUYE	C.T.R. WILSON	O.W. RICHARDSON		

Absents : Sir W.H. BRAGG, H. DESLANDRES et E. VAN AUBEL

CONT'D....

Quantum mechanics plays a decisive role when technology becomes delicate, i.e. devices become extremely small

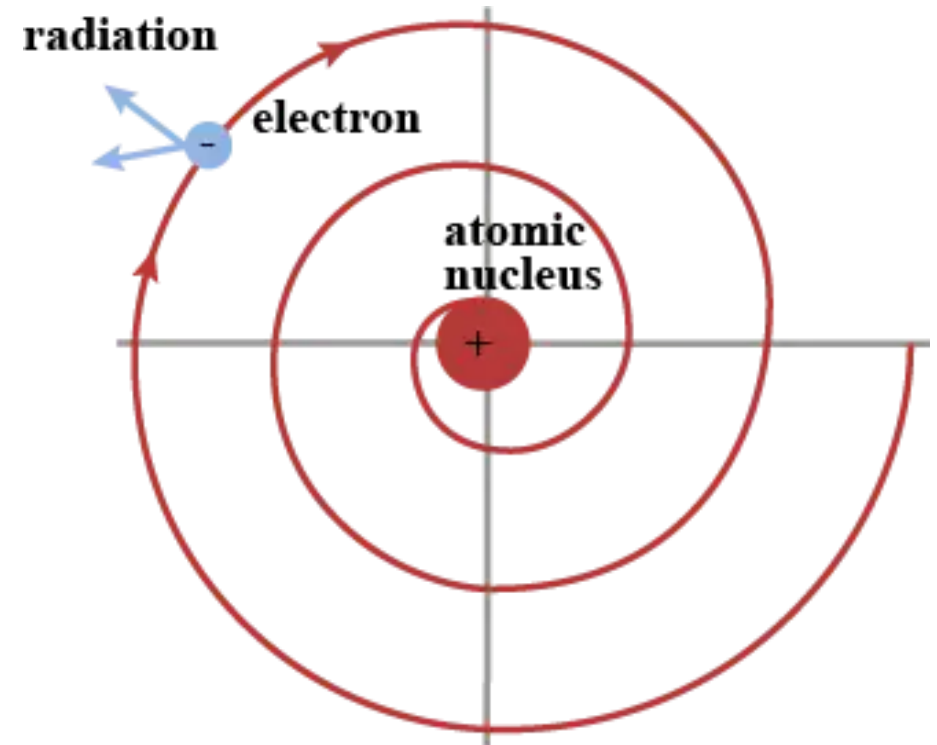
- Invention of Transistor – Reduced size, cost, and power consumption of an electronic gadget
- High precession microscopes -SEM, TEM, STEM, AFM
- LASER
- SQUID
- Single electron transistor
- Photonics- Photon based electronics
- Spintronics-electron spin based electronics (Quantum Computers)
- Nanotechnology
- Molecular electronics



FAILURES OF CLASSICAL MECHANICS

Newtonian laws failed to explain behavior of atoms, molecules, or an object moving with a very high speed.

- In an atom, negatively charged electrons revolve around positively charged nucleus.
- According to classical picture, there should be an electrostatic force of attraction between them, thus they should come close to each other and collapse.



CONT'D....

Development of QM to explain three important Experiments:

(Classical, Newtonian mechanics failed to explain)

- ❖ Black Body Radiation
- ❖ Photoelectric Effect
- ❖ Compton Effect

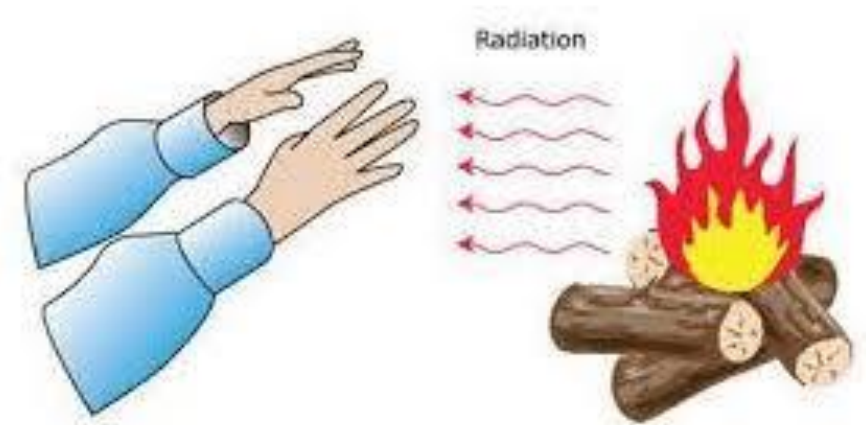
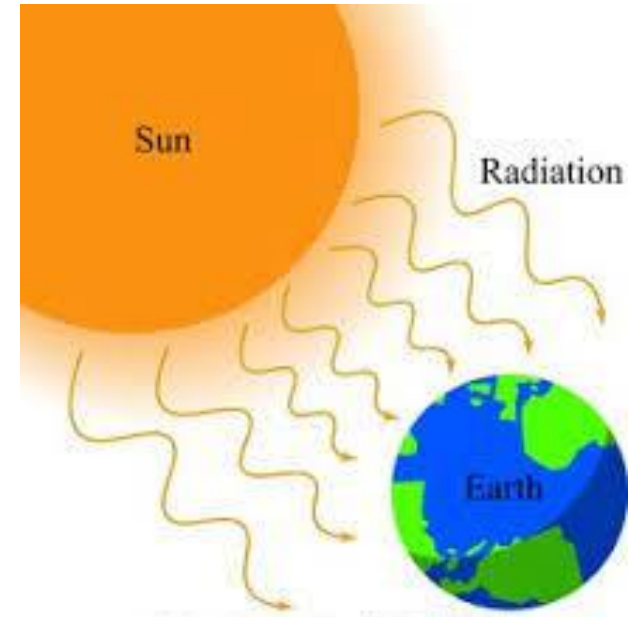
There are many more phenomena like specific heat of solids which could not be explained using classical physics.

RADIATION

In physics, **radiation** is the emission or transmission of energy in the form of waves or particles through space or through a material medium.

For example:

Electromagnetic radiation such as radio waves, microwaves, infrared, visible light, ultraviolet, X-rays, and gamma radiation.

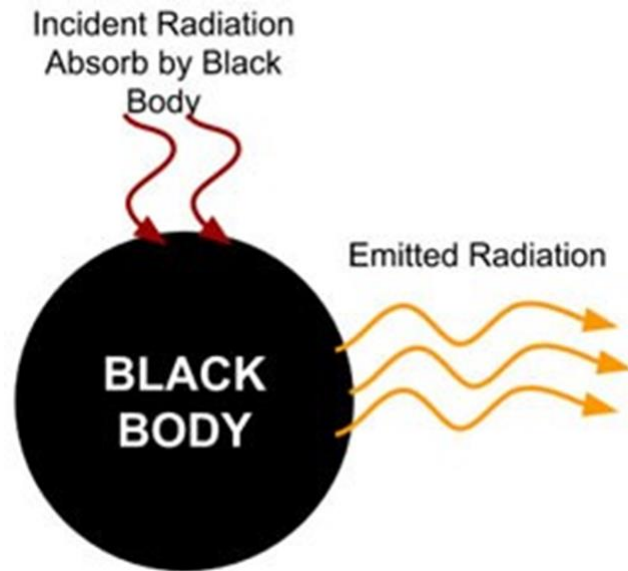


EXPERIMENTAL OBSERVATIONS ABOUT RADIATION

- ❖ All objects emit and absorb electromagnetic radiation (thermal/optical) over various wavelengths.
- ❖ All objects with a temperature above absolute zero ($0\text{ K} = -273.15\text{ °C}$) emit energy in the form of electromagnetic radiation.
- ❖ As the temperature of the object rises, the object glows with the colors corresponding to the frequency (or wavelength) of the electromagnetic spectrum.
- ❖ All objects emit all kind of wavelengths.



BLACK BODY RADIATION

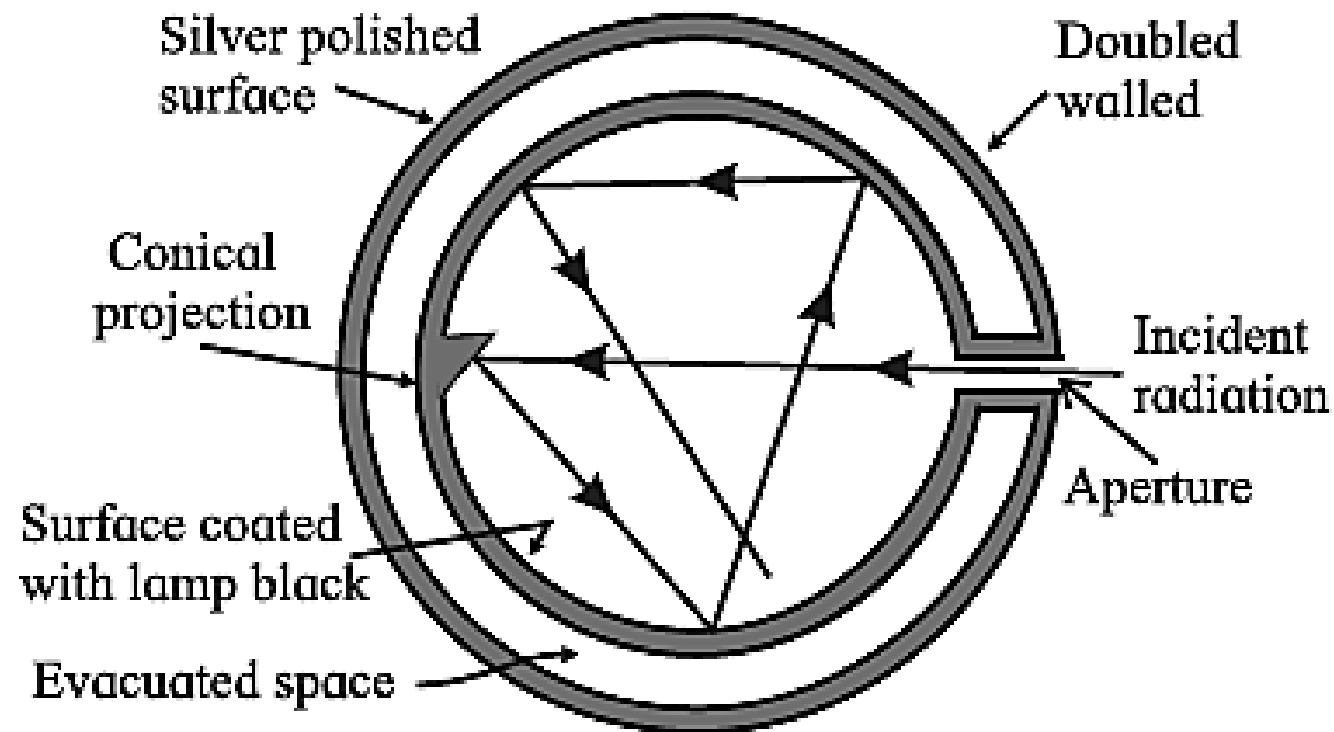


What is a Blackbody?

- A blackbody is a theoretical or model body which absorbs all radiation falling on it, reflecting or transmitting none.
- It is a hypothetical object which is a “perfect” absorber and a “perfect” emitter of radiation over all wavelengths.
- At room temperature, it appears black as no visible light is emitted
- At a particular temperature the black body would emit the maximum amount of energy possible for that temperature

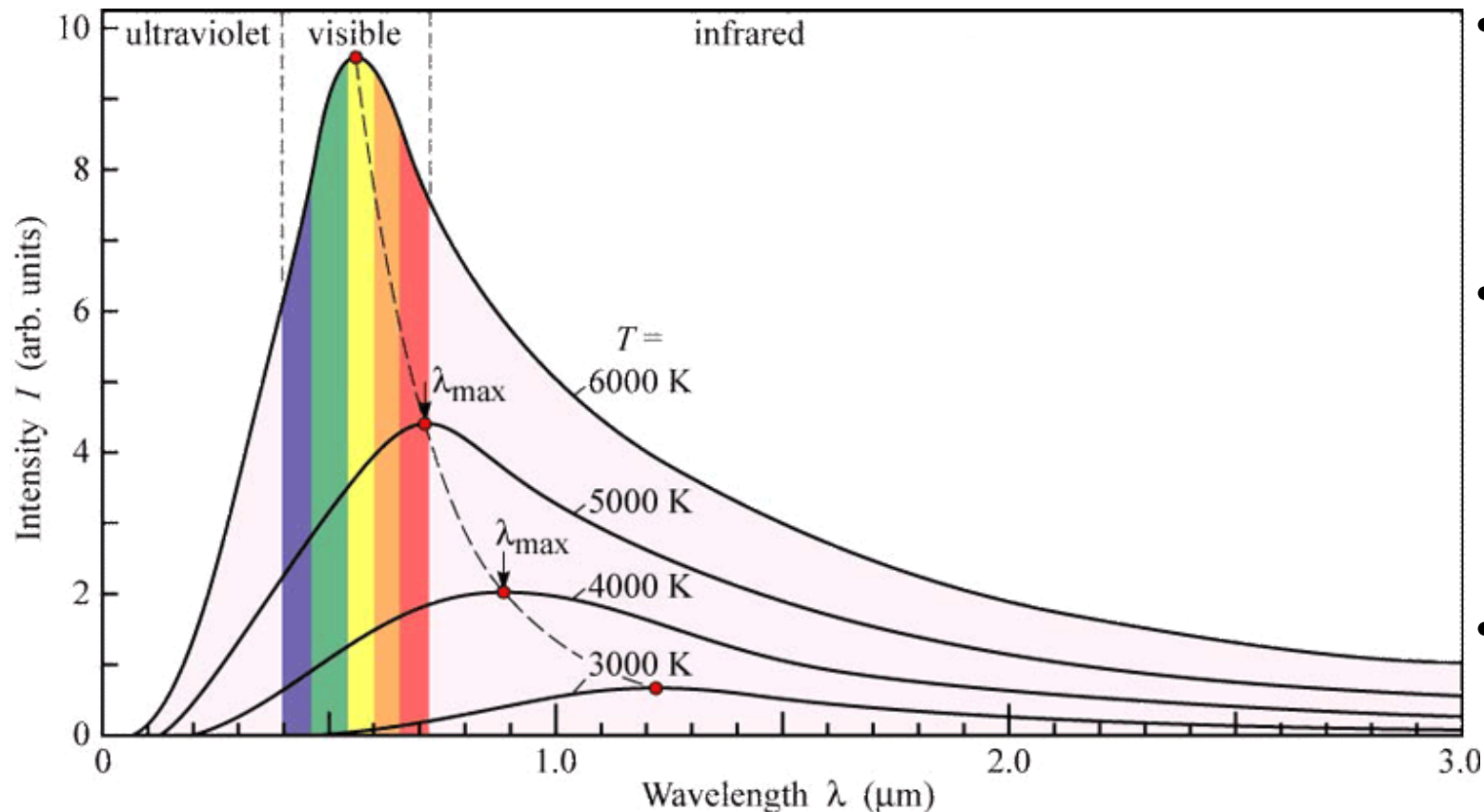
Blackbody radiation: When a black body is at a uniform temperature, its emission has a characteristic wavelength/frequency distribution that depends on its temperature. Its emission is called black-body radiation. The wavelength (i.e. color) of radiant energy emitted by such a body depends only on its temperature, not its surface or composition

REALIZATION OF A BLACKBODY



Ferry's blackbody.

BLACKBODY RADIATION SPECTRUM



- The Intensity distribution curve is continuous that means all the wavelengths of EMW are emitted
- At a specific wavelength, the intensity is maximum and inversely proportional to the temperature of the blackbody (Wien's Displacement law)
- Total Intensity is directly proportional to the fourth power of the temperature of the blackbody (Stefan's Law)

WIEN'S DISPLACEMENT LAW

- ❖ All objects emit radiant energy.
- ❖ Hotter objects emit more energy than colder objects (per unit area).
- ❖ The amount of energy radiated is proportional to the temperature of the object.
- ❖ The hotter the object, the shorter the wavelength (λ) of emitted energy.

This is Wien's displacement law:

Mathematically, The wavelength (in m) corresponding to a temperature, T (in K) can be calculated as:

$$\lambda_{max} = \frac{2.898 \times 10^{-3}}{T}$$

STEFAN'S LAW

The power radiated per unit surface area of the radiator is given by the Stefan-Boltzmann law.

The Stefan-Boltzmann Law

* The amount of energy radiated is proportional to the temperature of the object raised to the fourth power.

$$E = \sigma T^4$$

E = flux of energy (W/m^2), T = temperature (K)

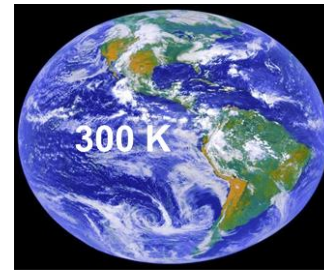
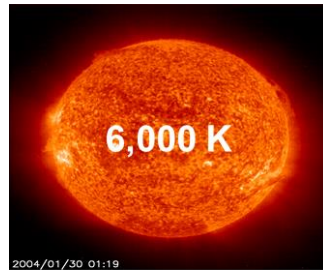
$\sigma = 5.67 \times 10^{-8} \text{ W}/\text{m}^2\text{K}^4$ (Stefan-Boltzmann constant)

This law gives the total energy being emitted at all wavelengths by the blackbody (which is the area under the Planck Law curve).

* Explains the growth in the height of the curve as the temperature increases. Notice that this growth is very abrupt.

CONT'D....

We can use these two laws to calculate properties of energy radiating from the Sun and the Earth.



	T (K)	λ_{max} (μm)	Region in spectrum	E (W/m²)
Sun	6000	0.5	Visible	7×10^7
Earth	300	10	Infrared	460

WIEN'S RADIATION LAW

To find a relation between the intensity of black body radiation versus wavelengths for several temperatures as given in the following figure, Many theoretical physicists tried to derive an expression but they were all unsuccessful.

One expression that is derived according to the laws of nineteenth century is *Wien's radiation law or Wien's fifth power law*:

$$u(\lambda)d\lambda = \frac{C_1}{\lambda^5} e^{-C_2/\lambda T} d\lambda$$

where $C_1 = 8\pi hc$,
and $C_2 = hc/k$

In terms of frequency,

$$u(\nu)d\nu = \frac{8\pi h\nu^3}{c^3} e^{-h\nu/kT} d\nu$$

And it was found that for small wavelengths (high frequencies), the previous equation fitted the experimental data but it deviates at larger wavelengths i.e. in IR region.

THE RAYLEIGH-JEANS LAW: ASSUMPTIONS

- They started by considering the radiation inside a cavity of absolute temperature T whose walls are perfect reflectors to be a series of standing em waves (Fig.).
- This is a three dimensional generalization of standing waves in a stretched string.
- The condition for standing waves in such a cavity is that the path length from wall to wall, whatever the direction, must be a whole number of half-wavelengths, so that a node occurs at each reflecting surface.
- The number of independent standing waves $G(\nu)d\nu$ in the frequency interval between ν and $d\nu$ per unit volume in the cavity turned out to be

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

- This formula is independent of the shape of the cavity. As we would expect, the higher the frequency, the shorter the wavelength and the greater the number of possible standing waves.



Figure 2.7 Em radiation in a cavity whose walls are perfect reflectors consists of standing waves that have nodes at the walls, which restricts their possible wavelengths. Shown are three possible wavelengths when the distance between opposite walls is L .

CONT'D....

- The next step was to find the average energy per standing wave.
- According to the **theorem of equipartition of energy**, a mainstay of classical physics, the average energy per degree of freedom of an entity (such as a molecule of an ideal gas) that is a member of a system of such entities in thermal equilibrium at the temperature T is $1/2kT$, Here k is **Boltzmann's constant** ($k = 1.38 \times 10^{-23} \text{JK}^{-1}$)
- A degree of freedom is a mode of energy possession.
- Thus a monatomic ideal gas molecule has three degrees of freedom, corresponding to kinetic energy of motion in three independent directions, for an average total energy of $3/2kT$.
- A one-dimensional harmonic oscillator has two degrees of freedom, one that corresponds to its kinetic energy and one that corresponds to its potential energy.
- Because each standing wave in a cavity originates in an oscillating electric charge in the cavity wall, two degrees of freedom are associated with the wave and it should have an average energy of $2(1/2)kT$.

CONT'D....

Classical average energy per standing wave

$$\bar{\epsilon} = kT$$

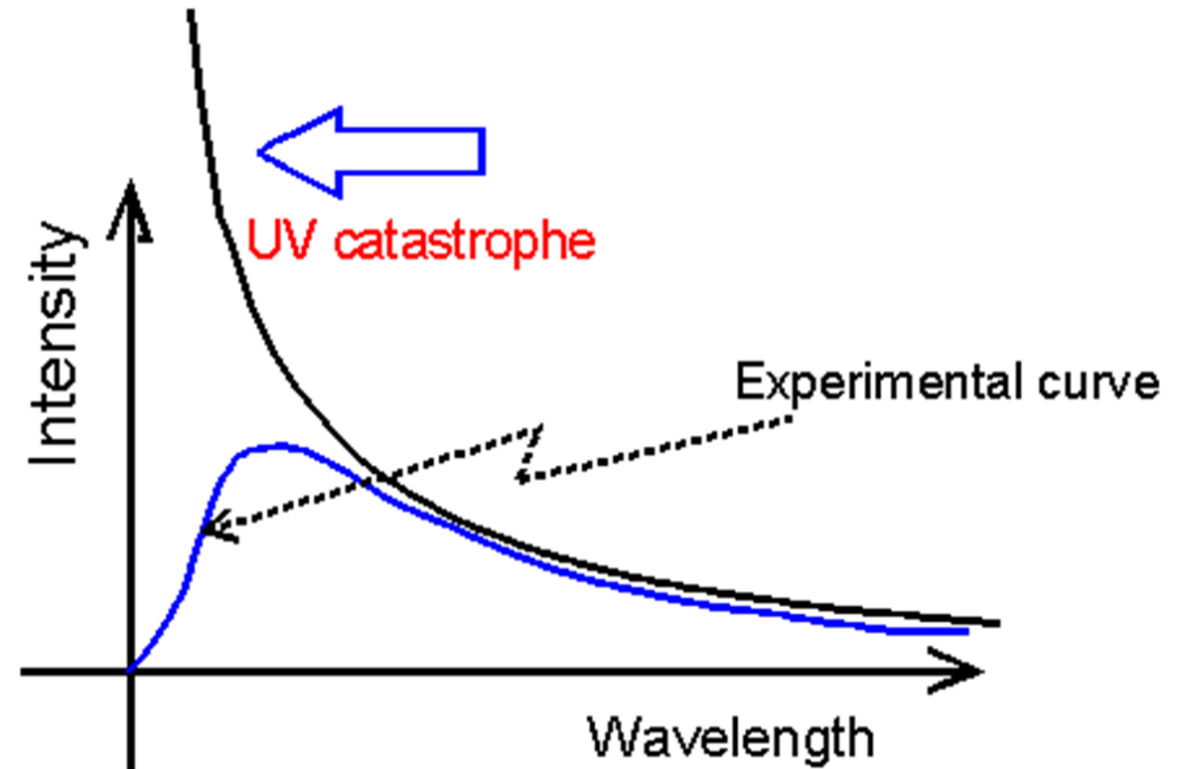
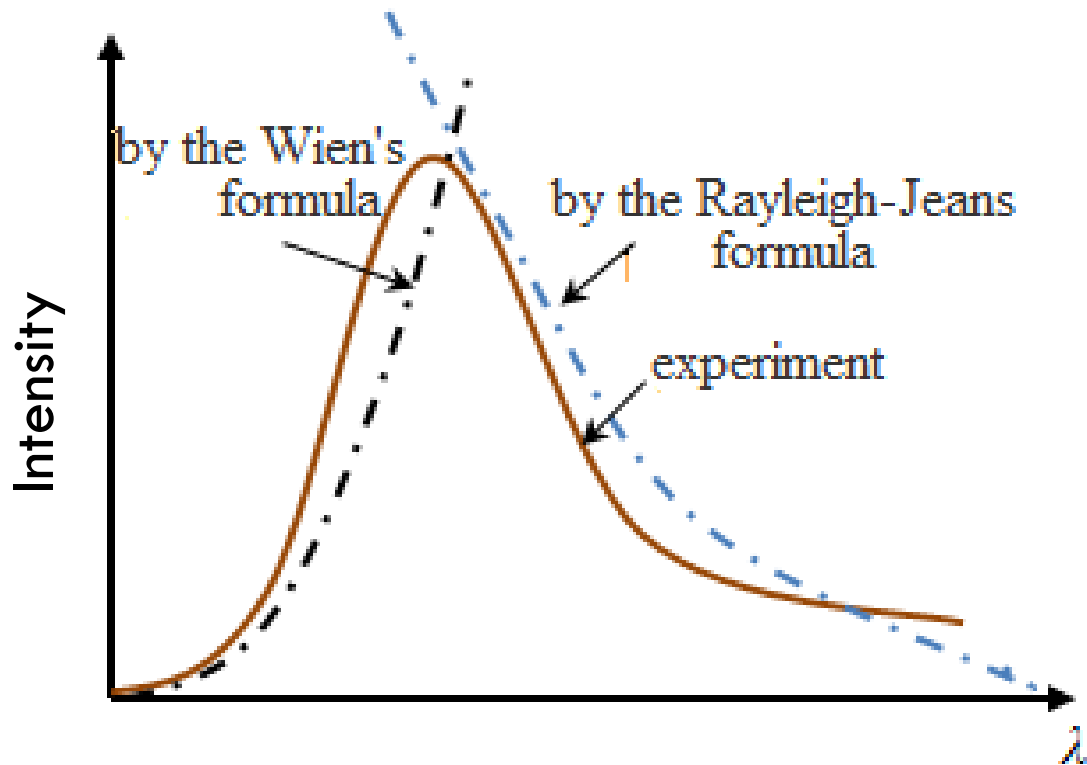
The total energy $u(\nu)d\nu$ per unit volume in the cavity in the frequency interval from ν to $(\nu+d\nu)$ is therefore

Rayleigh-Jeans Formula

$$u(\nu)d\nu = \bar{\epsilon} G(\nu)d\nu = \frac{8\pi kT}{c^3} \nu^2 d\nu$$

- This radiation rate is proportional to this energy density for frequencies ν to $(\nu+d\nu)$. In above equation, the Rayleigh-Jeans formula, contains everything that classical physics can say about the spectrum of blackbody radiation.
- Even a glance at Eq. shows that it cannot possibly be correct. As the frequency increases toward the ultraviolet end of the spectrum, this formula predicts that the energy density should increase as ν^2 .
- In the limit of infinitely high frequencies, $u(\nu)d\nu$ therefore should also go to infinity. In reality, of course, the energy density (and radiation rate) falls to 0 as ν tends to infinity. This discrepancy became known as the [ultraviolet catastrophe of classical physics](#).
- Where did Rayleigh and Jeans go wrong?

DISCREPANCY BETWEEN THEORETICAL AND EXPERIMENTAL CURVES



The Ultraviolet Catastrophe

PLANCK'S THEORY OF BLACKBODY RADIATION

In 1900, Max Planck developed a theory of blackbody radiation that leads to an equation for the intensity of the radiation.

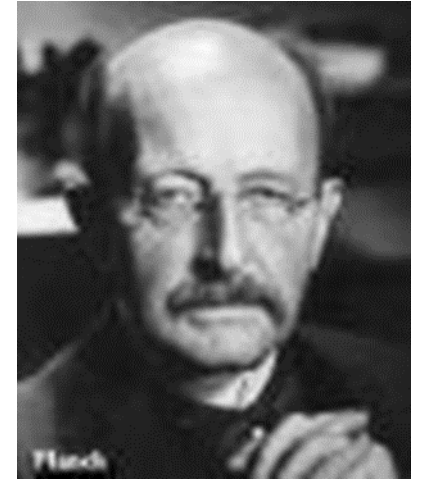
This equation is in complete agreement with experimental observations.

He assumed the cavity radiation came from atomic oscillations in the cavity walls

Planck made following assumptions about the nature of the oscillators in the cavity walls

A black body contains a **large number of atomic oscillators**:

- Each oscillator is oscillating with a characteristic frequency.
- The frequency of radiation emitted by the oscillator is the same as the oscillator **frequency**.
- The oscillator can absorb energy in multiples of small unit called quanta.
- This **quantum of radiation** is **photon**.



Max Planck
1858-1947

A German theoretical physicist whose discovery of energy quanta won him the Nobel Prize in Physics in 1918

CONT'D....

- The energy of a **photon** is directly proportional to the **frequency of radiation** emitted.
- An oscillator **vibrating with frequency**, can only emit energy in integral multiples of $h\nu$, where $n = 1, 2, 3, 4, \dots, n$. n is **principal quantum number**.
- The oscillators emit or absorb energy when making a transition from one quantum state to another.
 - The entire energy difference between the initial and final states in the transition is emitted or absorbed as a single quantum of radiation
 - An oscillator emits or absorbs energy only when it changes quantum states
- Einstein supported, implemented and modified the concept of quantized energy transfer in any interaction to explain the photoelectric effect. He considered that the light consists of massless (zero rest mass) particles called photons.
- He further assumed that the electromagnetic field was quantized and light consists of energy bundles, called quanta or photons and each photon traveling with velocity c and having energy $h\nu$.

PLANCK'S QUANTUM IS SMALL FOR "ORDINARY-SIZED" OBJECTS BUT LARGE FOR ATOMS

"ordinary" pendulum
 $\nu = 1 \text{ Hz}$

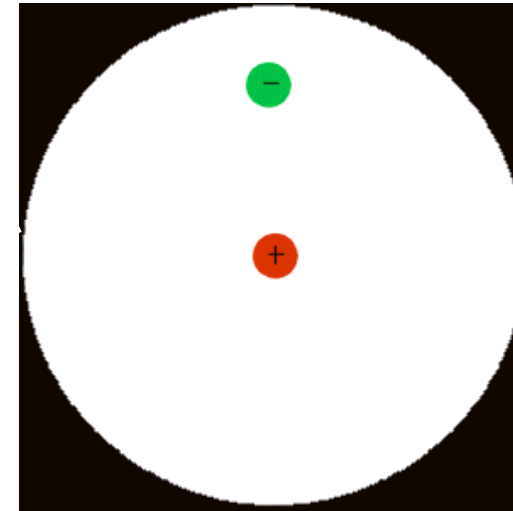


$$E_{\text{quant}} = h\nu = 6.6 \times 10^{-34} \text{ J s} \times 1 \text{ Hz} \\ = 6.6 \times 10^{-34} \text{ J}$$

very tiny

*about the same as
the electron's KE*

Hydrogen atom, $\nu \approx 2 \times 10^{14} \text{ Hz}$



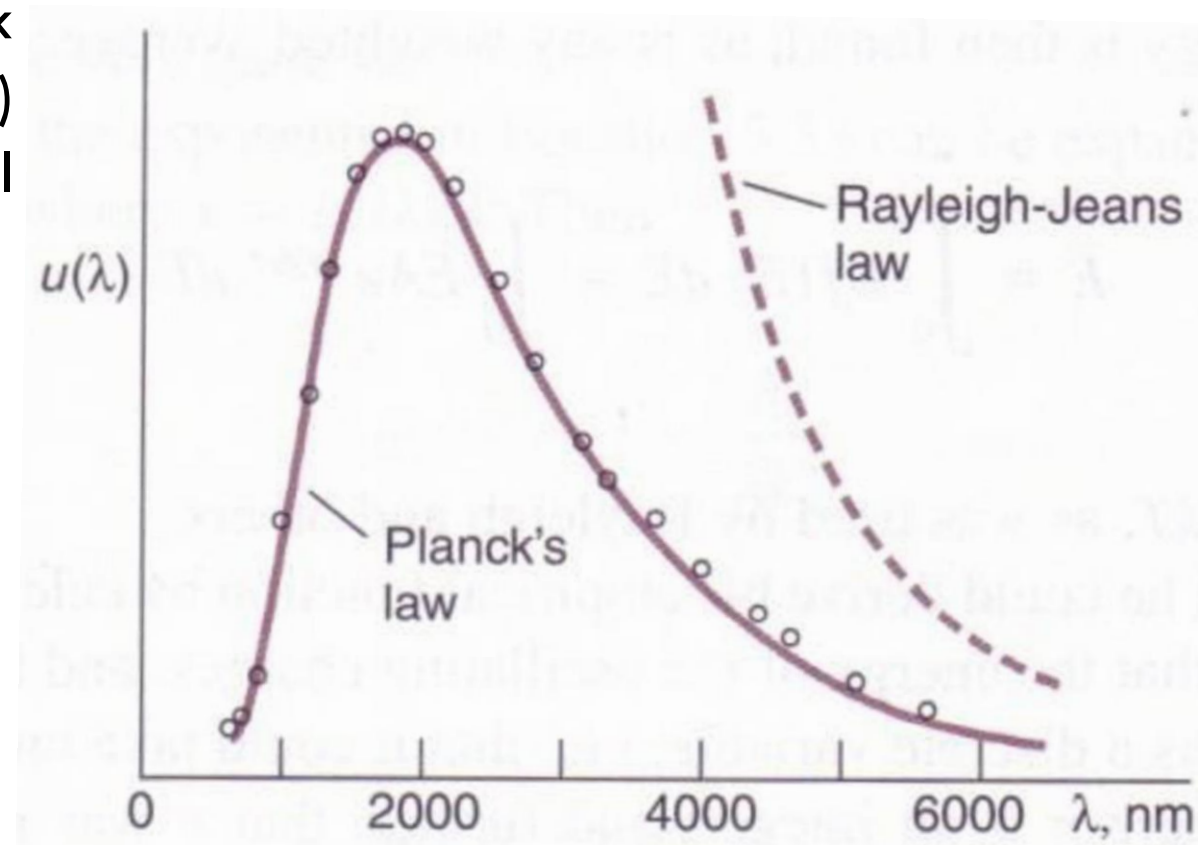
$$E_{\text{quant}} = h\nu \\ = (6.6 \times 10^{-34} \text{ J s}) \times (2 \times 10^{14} \text{ Hz}) \\ = (6.6 \times 2) \times 10^{-20} \text{ J} \\ = 1.3 \times 10^{-19} \text{ J}$$

THE PLANCK'S RADIATION FORMULA

In 1900 the German physicist Max Planck used “lucky guesswork” (as he later called it) to come up with a formula for the spectral energy density of blackbody radiation:

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

Blackbody radiation follows the Planck's formula for all the wavelengths range



CONT'D....

Planck's formula was applicable with practical results at both low and high frequencies.
It is important to note that:

- At high frequencies, $h\nu \gg kT$ and $e^{h\nu/kT} \rightarrow \infty$, which means that $u(\nu)d\nu \rightarrow 0$ as observed. No more ultraviolet catastrophe.
- At low frequencies, where the Rayleigh- Jeans formula is a good approximation to the data $h\nu \ll kT$ and $h\nu/kT \ll 1$. In general,

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$$

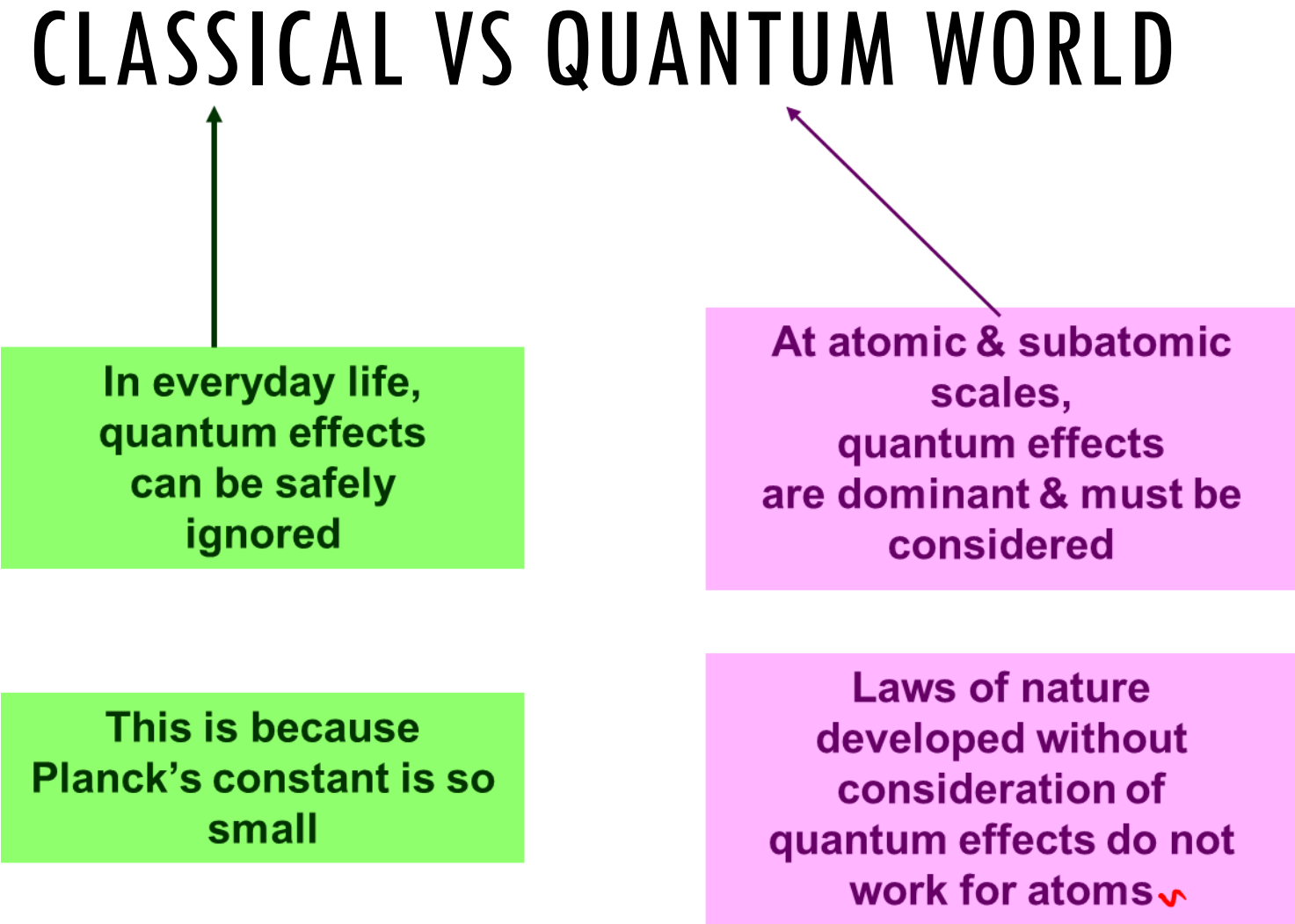
If x is small, $e^x \approx 1 + x$, and so for $h\nu/kT \ll 1$ we have $\frac{1}{e^{h\nu/kT} - 1} \approx \frac{1}{1 + \frac{h\nu}{kT} - 1} \approx \frac{kT}{h\nu} \quad h\nu \ll kT$

Thus at low frequencies Planck's formula becomes

$$u(\nu) d\nu \approx \frac{8\pi h}{c^3} \nu^3 \left(\frac{kT}{h\nu} \right) d\nu \approx \frac{8\pi kT}{c^3} \nu^2 d\nu$$

Rayleigh-Jeans Formula

CLASSICAL VS QUANTUM WORLD



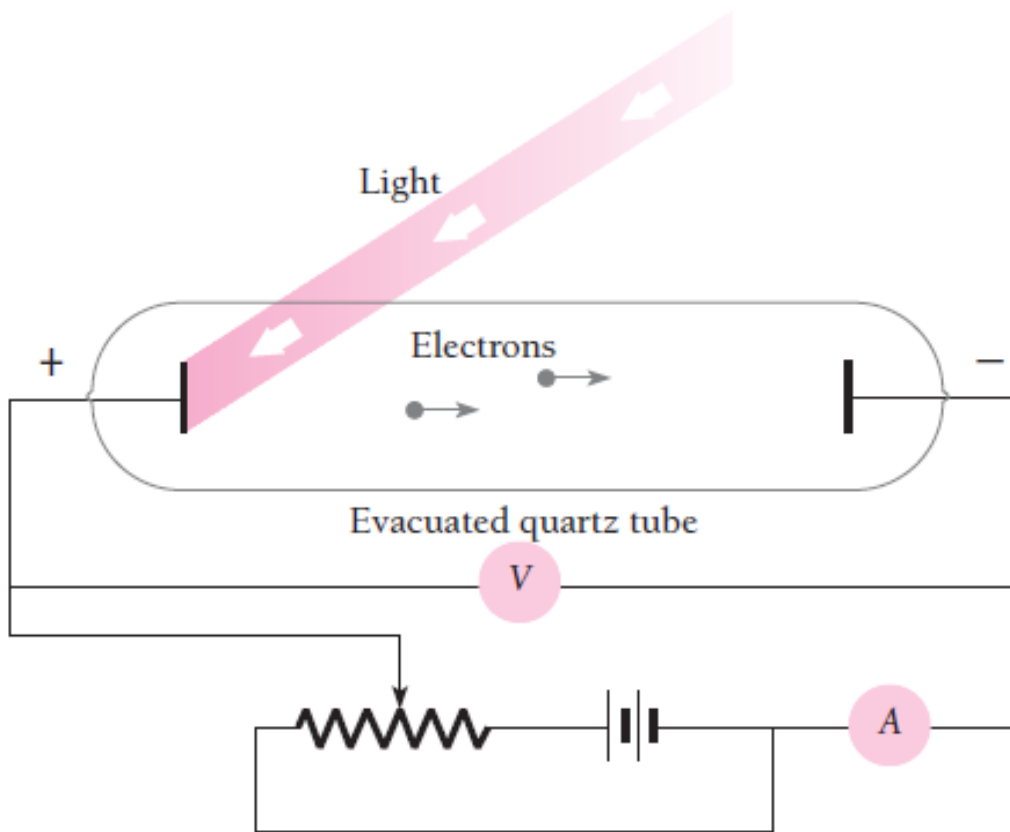
In everyday life,
quantum effects
can be safely
ignored

This is because
Planck's constant is so
small

At atomic & subatomic
scales,
quantum effects
are dominant & must be
considered

Laws of nature
developed without
consideration of
quantum effects do not
work for atoms~

EINSTEIN'S IDEA OF QUANTIZATION-PHOTOELECTRIC EFFECT

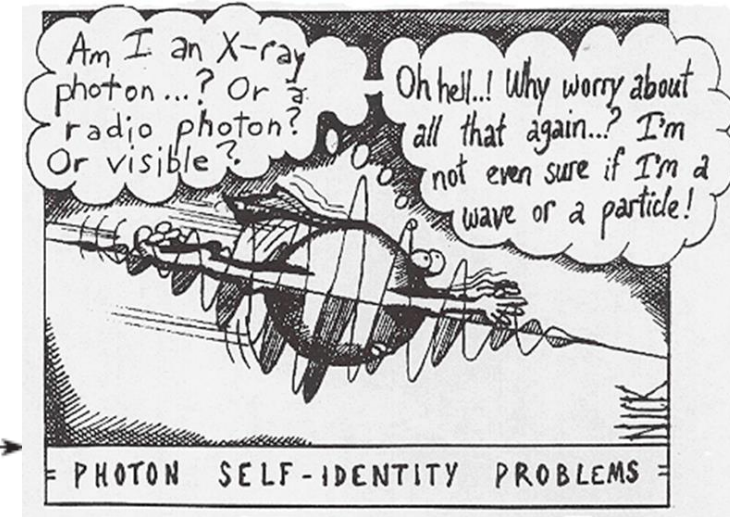
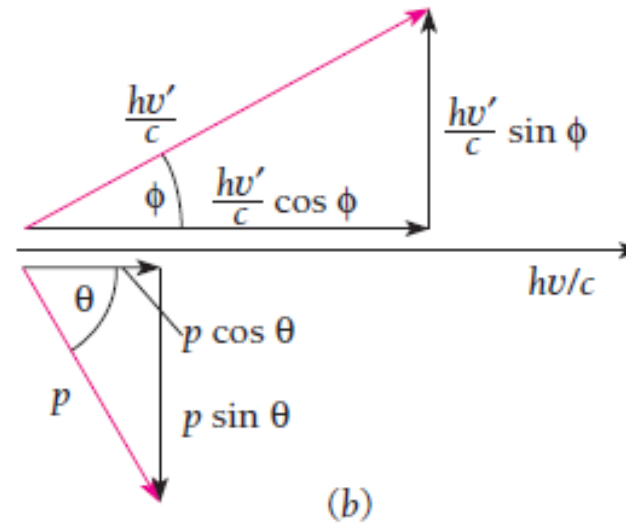
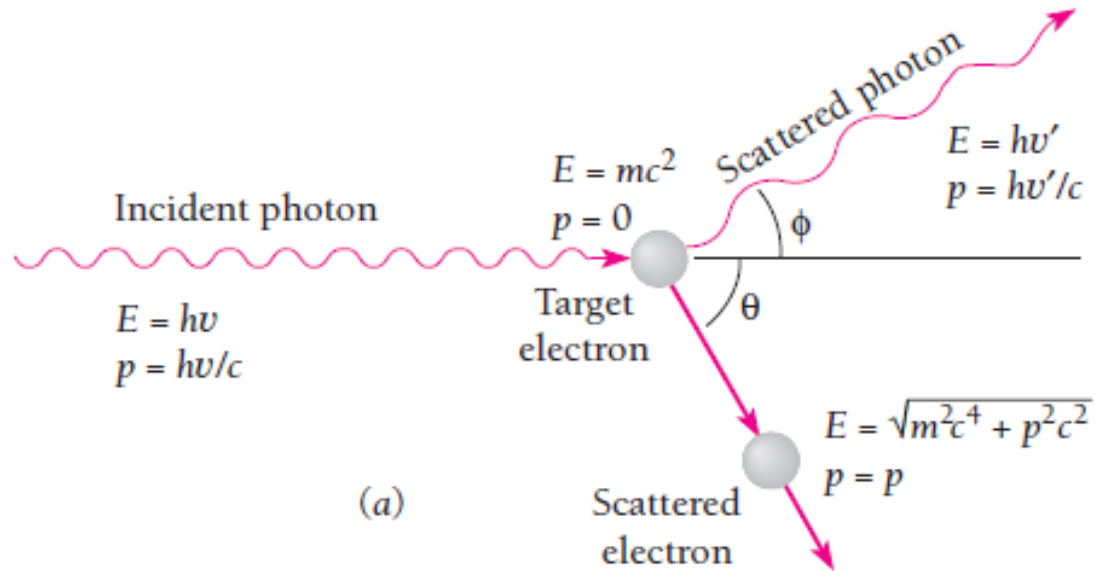


- Within the limits of experimental accuracy (about 10^{-9} s), there is no time interval between the arrival of light at a metal surface and the emission of photoelectrons.
- However, because the energy in an em wave is supposed to be spread across the wavefronts, a period of time should elapse before an individual electron accumulates enough energy (several eV) to leave the metal.
- A detectable photoelectron current results when 10^{-6} W/m^2 of em energy is absorbed by a sodium surface. A layer of sodium 1 atom thick and 1 m^2 in area contains about 10^{19} atoms, so if the incident light is absorbed in the uppermost atomic layer, each atom receives energy at an average rate of 10^{-25} W .
- At this rate over a month would be needed for an atom to accumulate energy of the magnitude that photoelectrons from a sodium surface are observed to have.

CONT'D....

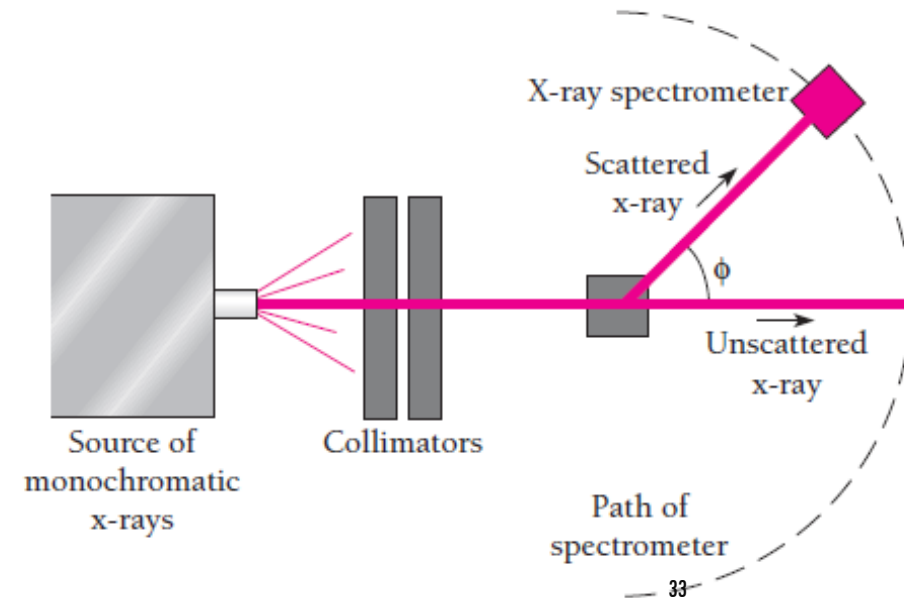
- A bright light yields more photoelectrons than a dim one of the same frequency, but the electron energies remain the same.
- The EM theory of light, on the contrary, predicts that the more intense the light, the greater the energies of the electrons.
- The higher the frequency of the light, the more energy the photoelectrons have. Blue light results in faster electrons than red light.
- At frequencies below a certain critical frequency ν_0 , which is characteristic of each particular metal, no electrons are emitted.
- Above ν_0 the photoelectrons range in energy from 0 to a maximum value that increases linearly with increasing frequency.
- This observation, also, cannot be explained by the EM theory of light.
- Thus, he concluded that light is made up of particles which have quantized energies.

COMPTON EFFECT (QUALITATIVE IDEA)

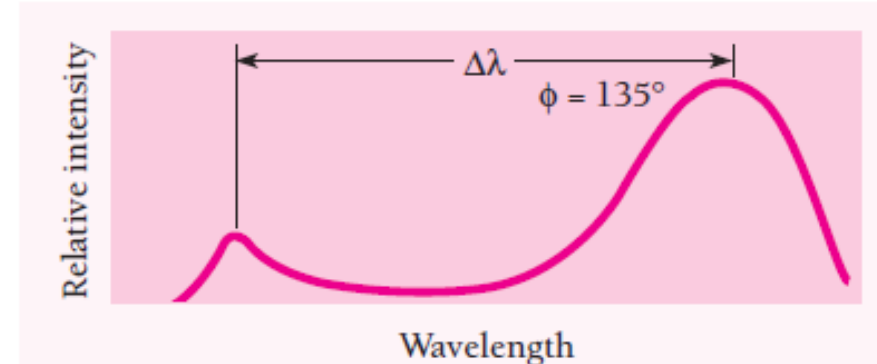
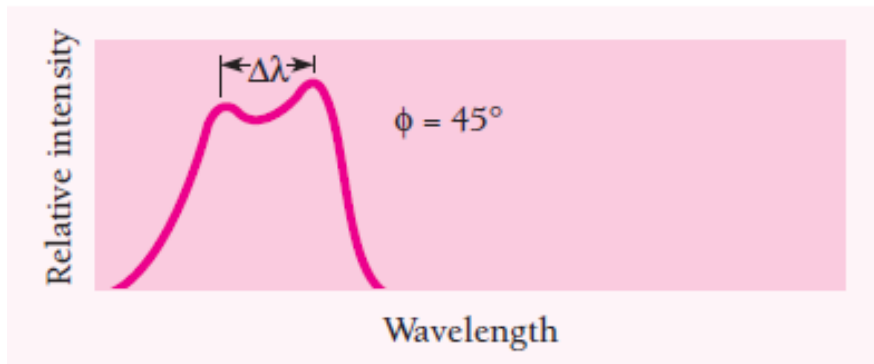
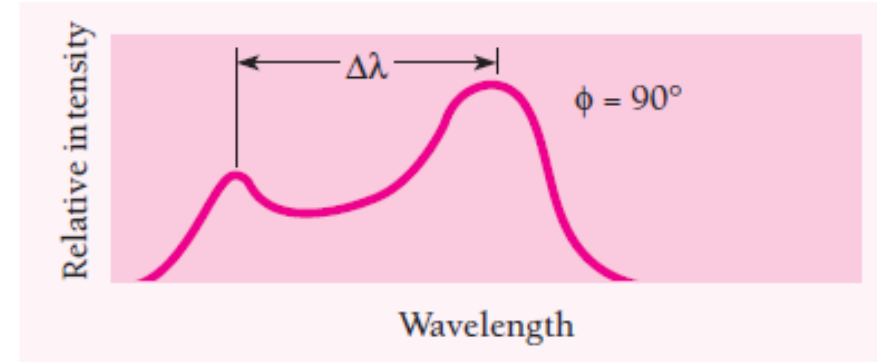
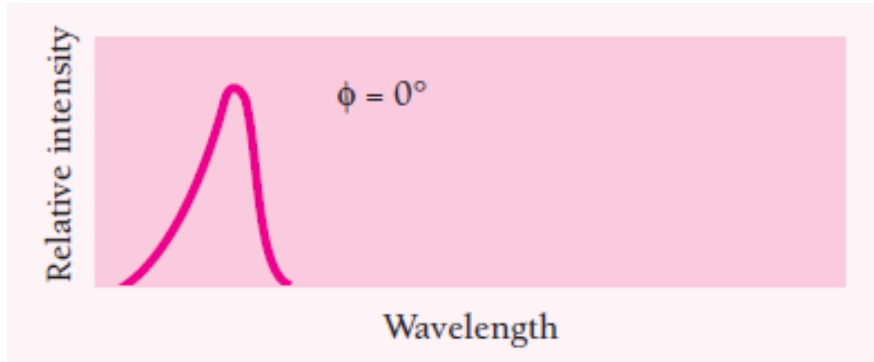
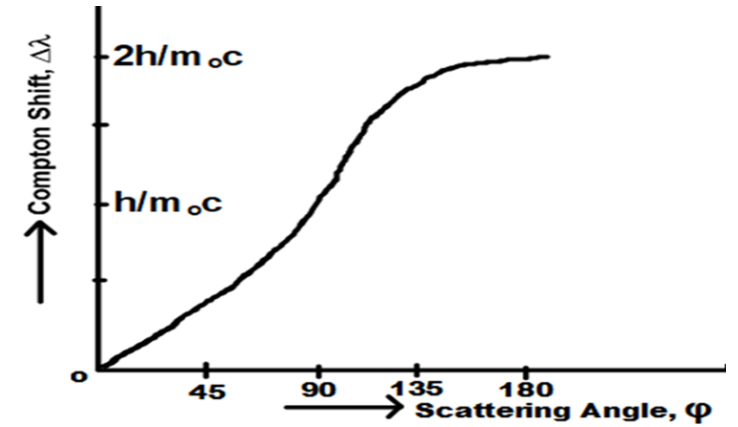


$$\lambda' - \lambda = \frac{h}{mc}(1 - \cos \phi)$$

Compton's Shift



CONT'D....



DE BROGLIE'S HYPOTHESIS-WAVE PARTICLE DUALITY OF MATTER



Louis de Broglie
(1892-1987)

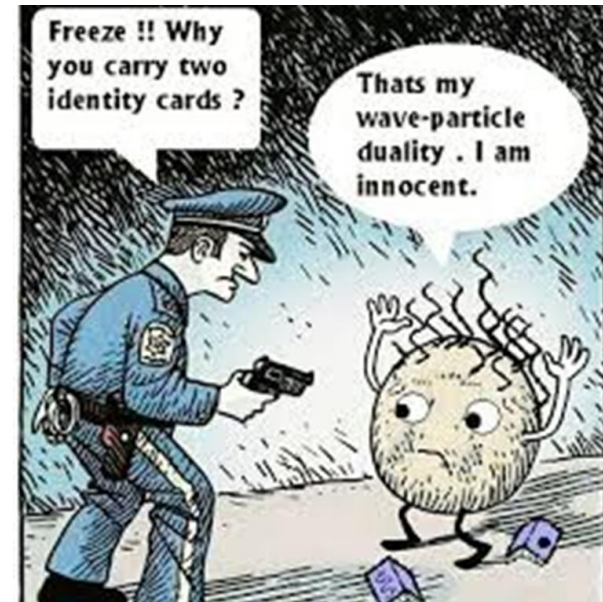
- ❑ We have seen that light comes in discrete units (photons) with particle properties (energy and momentum) that are related to the wave-like properties of frequency and wavelength.
- ❑ In 1923, Prince Louis de Broglie postulated that ordinary matter can have wave-like properties, with the wavelength λ related to momentum p in the same way as for light

de Broglie's relation

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

Wavelength depends on momentum, not on the physical size of the particle

Prediction: We should see diffraction and interference of matter waves!!!



Louis de Broglie received the Nobel prize in Physics in 1929.

DOES DUAL NATURE EXIST IN NATURE?



Platypus

“Australia's unique duck-billed platypus is part bird, part reptile and part mammal according to its gene map.

The platypus is classed as a mammal because it has fur and feeds its young with milk. It flaps a beaver-like tail. But it also has bird and reptile features — a duck-like bill and webbed feet, and lives mostly underwater. Males have venom-filled spurs on their heels.”

CALCULATION OF DE BROGLIE'S WAVELENGTH

- Wavelength of electron with 50 eV kinetic energy

$$K = \frac{p^2}{2m_e} = \frac{h^2}{2m_e\lambda^2} \Rightarrow \lambda = \frac{h}{\sqrt{2m_e K}} = 1.7 \times 10^{-10} \text{ m}$$

Here, K is kinetic energy

- Wavelength of Nitrogen molecule at room temperature

$$K = \frac{3kT}{2}, \quad \text{Mass} = 28m_u$$
$$\lambda = \frac{h}{\sqrt{3MkT}} = 2.8 \times 10^{-11} \text{ m}$$

- Wavelength of Rubidium (87) atom at 50 nK

$$\lambda = \frac{h}{\sqrt{3MkT}} = 1.2 \times 10^{-6} \text{ m}$$

DE BROGLIE'S EXPLANATION OF ANGULAR MOMENTUM QUANTIZATION IN THE BOHR MODEL

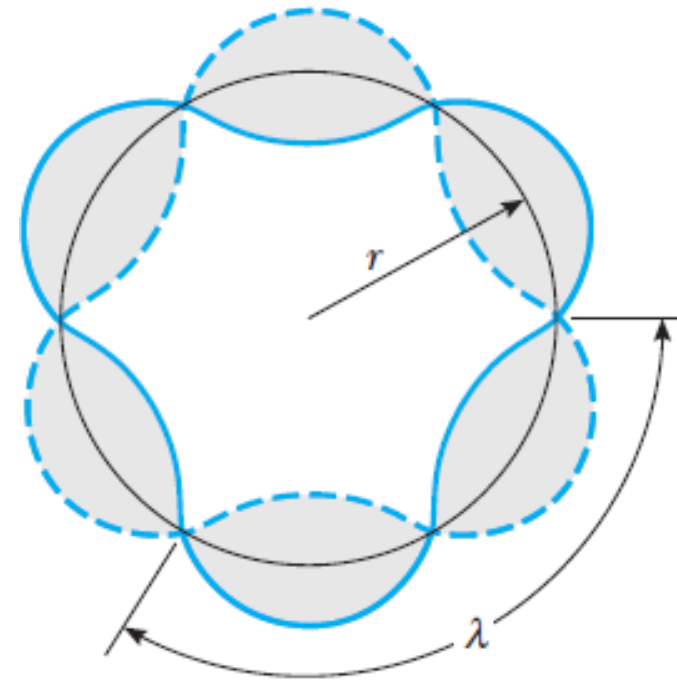
- Using de Broglie's hypothesis, an aspect of Bohr theory that is the quantization of angular momentum can be easily visualized physically.
- According to Bohr theory, the allowed orbits are those for which the electron's orbital angular momentum about the nucleus is an integral multiple of $h/2\pi$
- One simply assumes that the allowed Bohr orbits arise because the electron matter waves interfere constructively when an integral number of wavelengths exactly fits into the circumference of a circular orbit. Thus

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

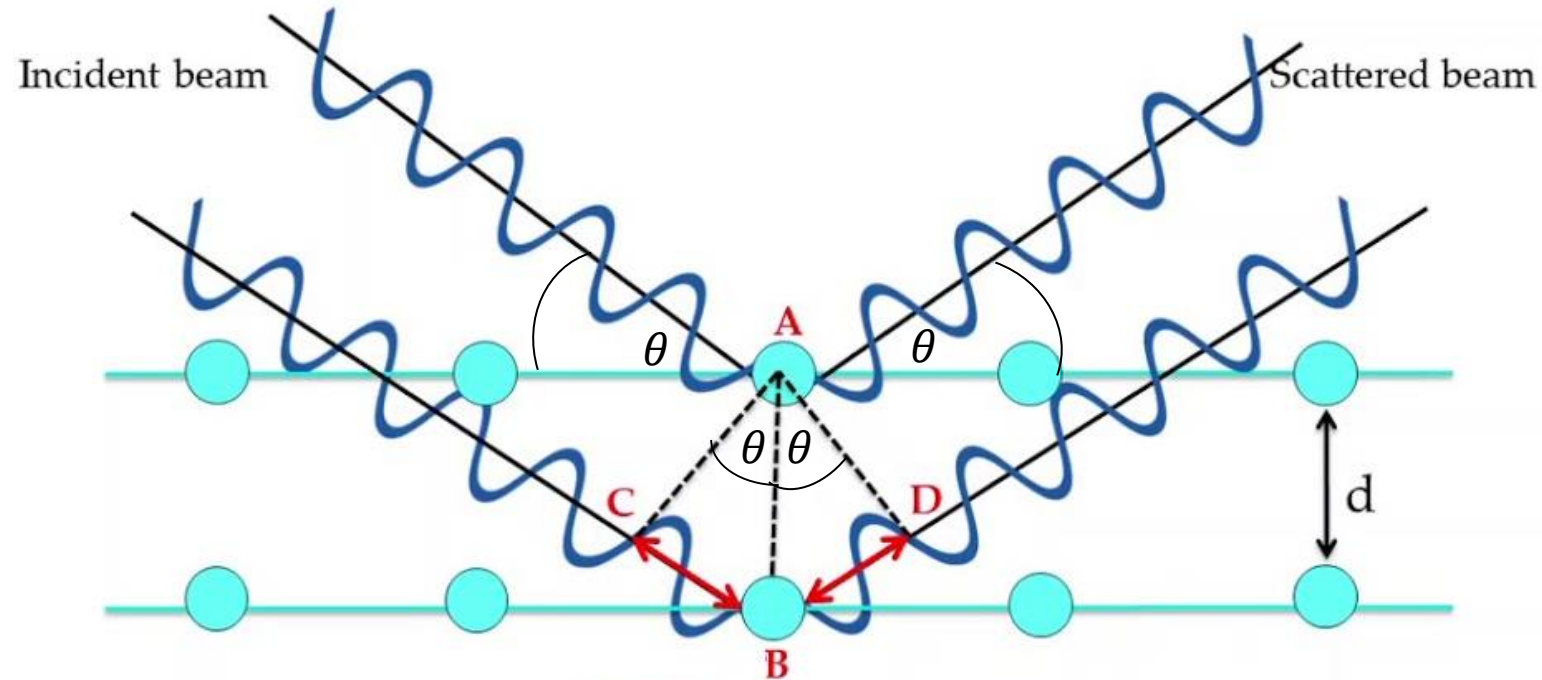
$$\text{Since } \lambda = \frac{h}{p} = \frac{h}{mv}$$

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

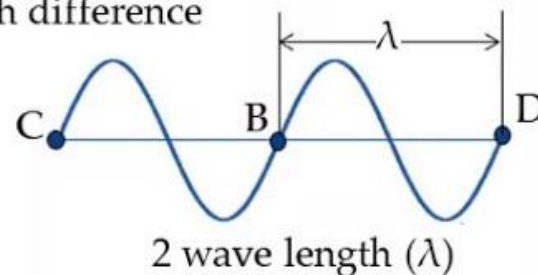
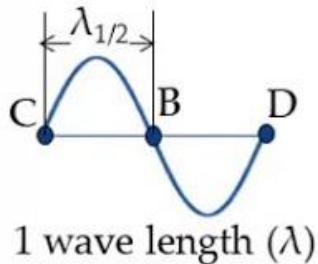
Angular Momentum Quantization Condition!



LIGHT AS A WAVE: X-RAY DIFFRACTION (BRAGG'S LAW): REVISITED



CB+BD = Path difference



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

THE DAVISSON-GERMER EXPERIMENT (1927): ELECTRON DIFFRACTION

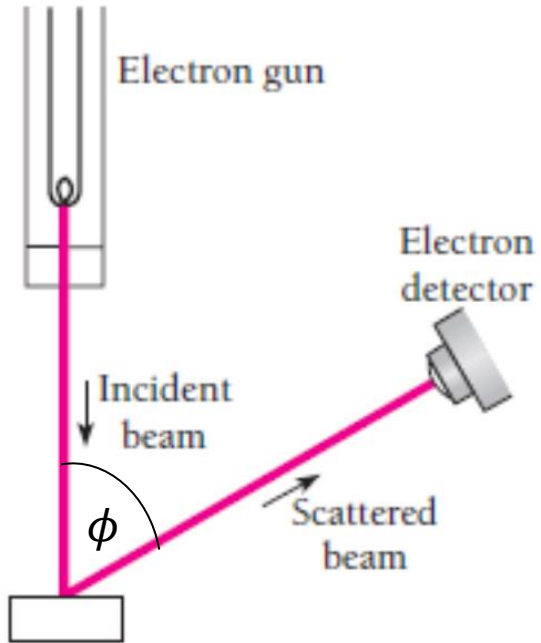
- A wave effect with no analog in the behavior of Newtonian particles is diffraction.
- In 1927 Clinton Davisson and Lester Germer in the United States and G. P. Thomson in England independently confirmed de Broglie's hypothesis by demonstrating that electron beams are diffracted when they are scattered by the regular atomic arrays of crystals.
- We shall look at the experiment of Davisson and Germer because its interpretation is more direct.



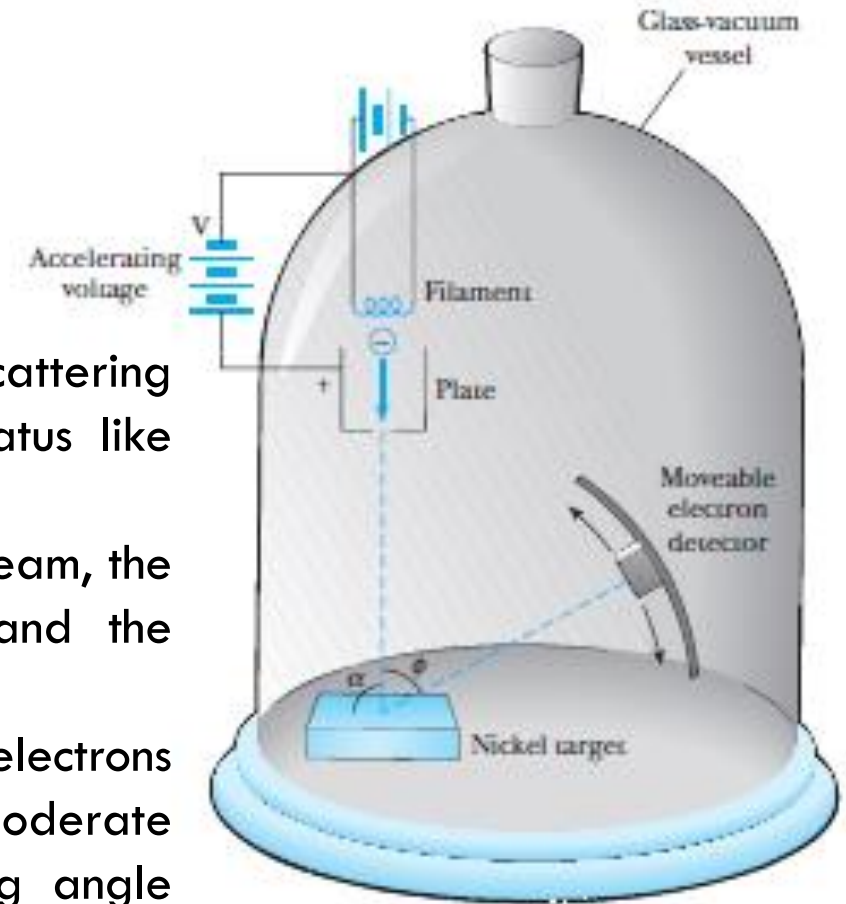
Clinton J. Davisson (left) and Lester H. Germer (centre) at Bell Laboratories in New York City.

*(All three received Nobel Prizes for their work. J. J. Thomson, G. P.'s father, had earlier won a Nobel Prize for verifying the particle nature of the electron: the wave-particle duality seems to have been the family business.)

CONT'D...



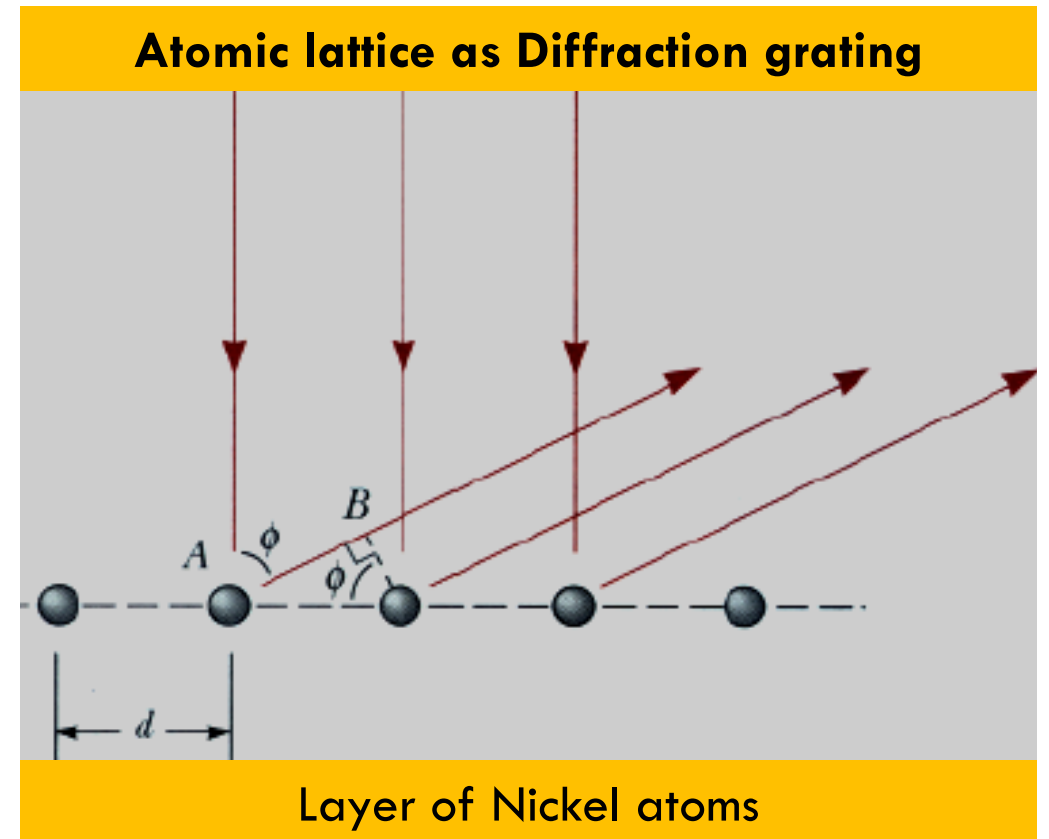
- Davisson and Germer were studying the scattering of electrons from a solid using an apparatus like shown in Fig (left).
- The energy of the electrons in the primary beam, the angle at which they reach the target, and the position of the detector could all be varied.
- Classical physics predicts that the scattered electrons will emerge in all directions with only a moderate dependence of their intensity on scattering angle and even less on the energy of the primary electrons.
- Using a block of nickel as the target, Davisson and Germer verified these predictions



CONT'D....

If electrons have associated wave like properties then we expect interference pattern when incident on a layer of atoms (reflection diffraction grating) with interatomic spacing such that

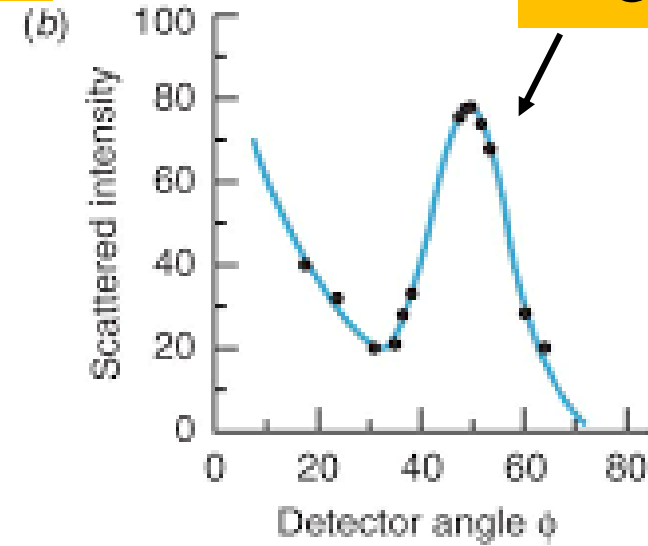
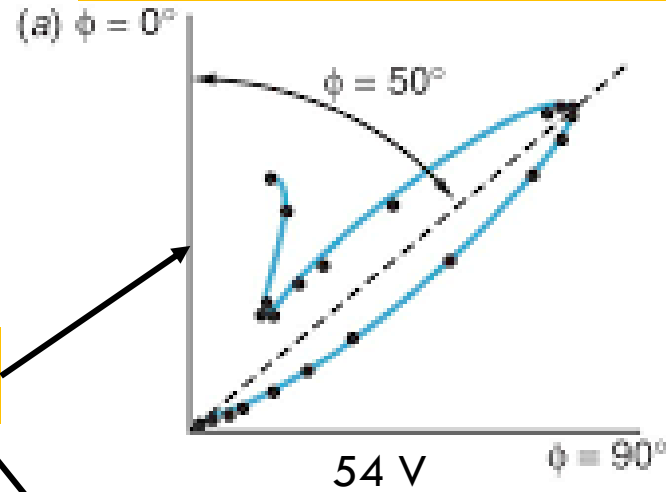
Path difference, $AB = d \sin\phi = n\lambda$



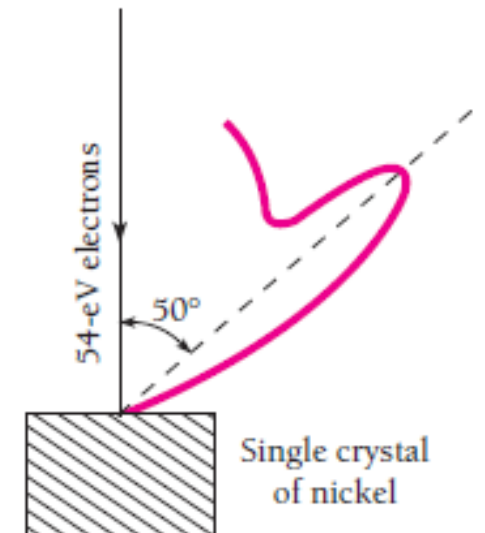
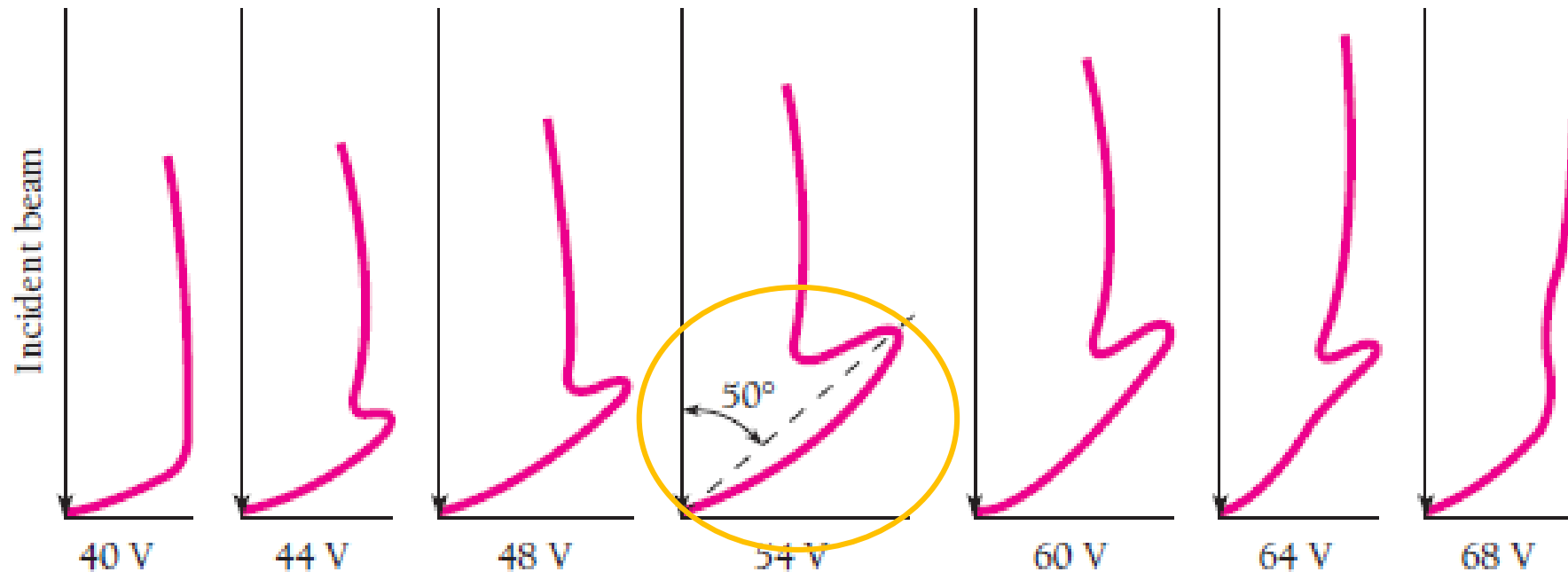
CONT'D....

Peak Intensity at $\phi = 50^\circ$
Accelerating Voltage = 54 V

Polar Plots



Cartesian Plot



ANALYSING DAVISSON GERMER EXPERIMENT USING DE BROGLIE'S HYPOTHESIS

De Broglie wavelength of an electron accelerated through 54 V, $\lambda = \frac{12.26}{\sqrt{54}} = 1.67 \text{ \AA}$

$$\lambda_{predicted} = 1.67 \text{ \AA}$$

Experimental data from Davisson- Germer experiment observations:

$$d_{Nickel} = 2.15 \text{ \AA} \quad (\text{Found from X-ray diffraction using Bragg's law})$$

$$\phi = 50^\circ \quad (\text{from scattering intensity plots})$$

Therefore,

by using Diffraction rule, $d \sin \phi = n \lambda$

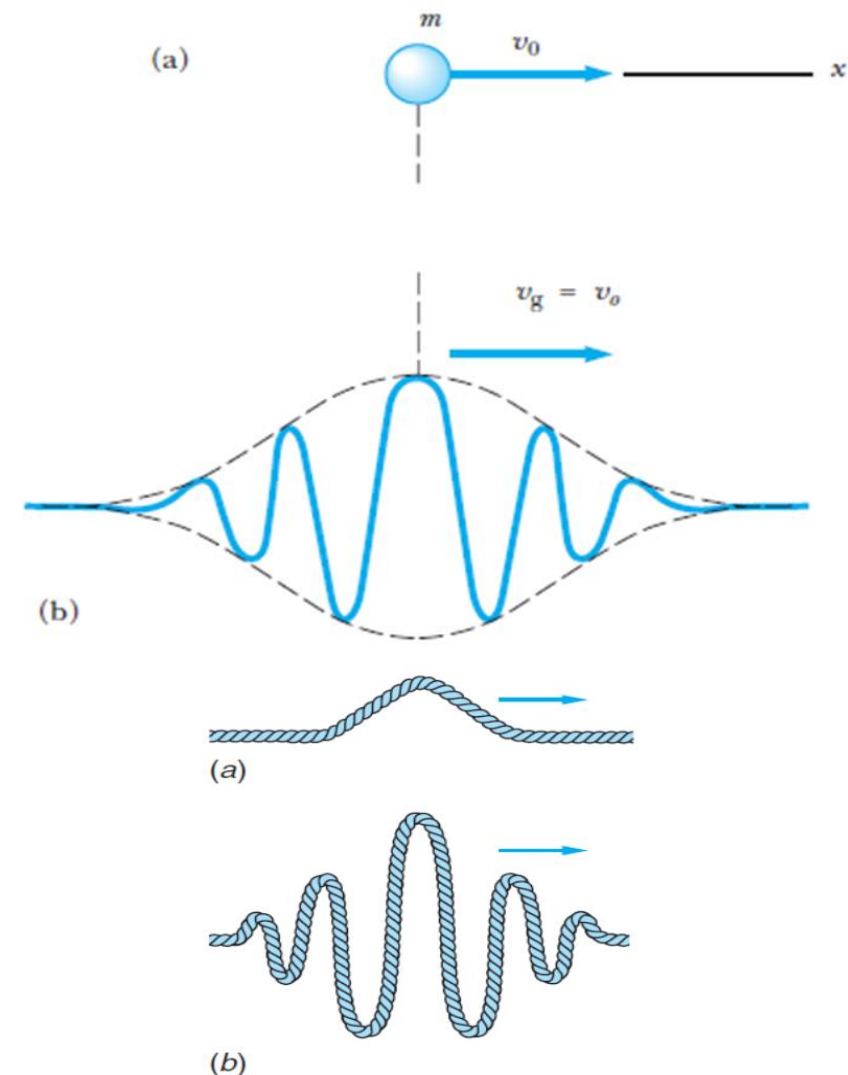
For first principal maximum, $n = 1 \Rightarrow 2.15 \times \sin 50^\circ = 1 \times \lambda = 1.65 \text{ \AA}$

$$\lambda_{observed} = 1.65 \text{ \AA}$$

Excellent agreement!

MATTER WAVES: WAVES OF WHAT?

- The matter wave representing a moving particle must reflect the fact that the particle has a large probability of being found in a small region of space only at a specific time.
- This means that a traveling sinusoidal matter wave of infinite extent and constant amplitude cannot properly represent a localized moving particle.
- What is needed is a pulse, or “wave group”, of limited spatial extent. Such a pulse can be formed by adding sinusoidal waves with different wavelengths.
- The resulting wave group can then be shown to move with a speed v_g (the group speed) identical to the classical particle speed.



(a) Wave pulse moving along a string. A pulse has a beginning and an end: i.e. it is localized unlike a pure harmonic wave, which goes on forever in space and time.
(b) A wave packet formed by superposition harmonic waves

MATTER WAVES VELOCITY

Phase velocity is the velocity with which a wave travels. It is denoted by v_p .

For matter waves, it is given by

$$v_p = \frac{c^2}{v}$$

where c is velocity of light and v is velocity of the particle.

This can be proved as : We know that $E = h\nu$ and $E = mc^2$

$$\text{Thus, } h\nu = mc^2 \text{ or } \nu = \frac{mc^2}{h}$$

$$\text{Phase velocity of a wave is given by, } v_p = \nu \times \lambda = \frac{mc^2}{h} \times \frac{h}{mv} = \frac{c^2}{v}$$

QED

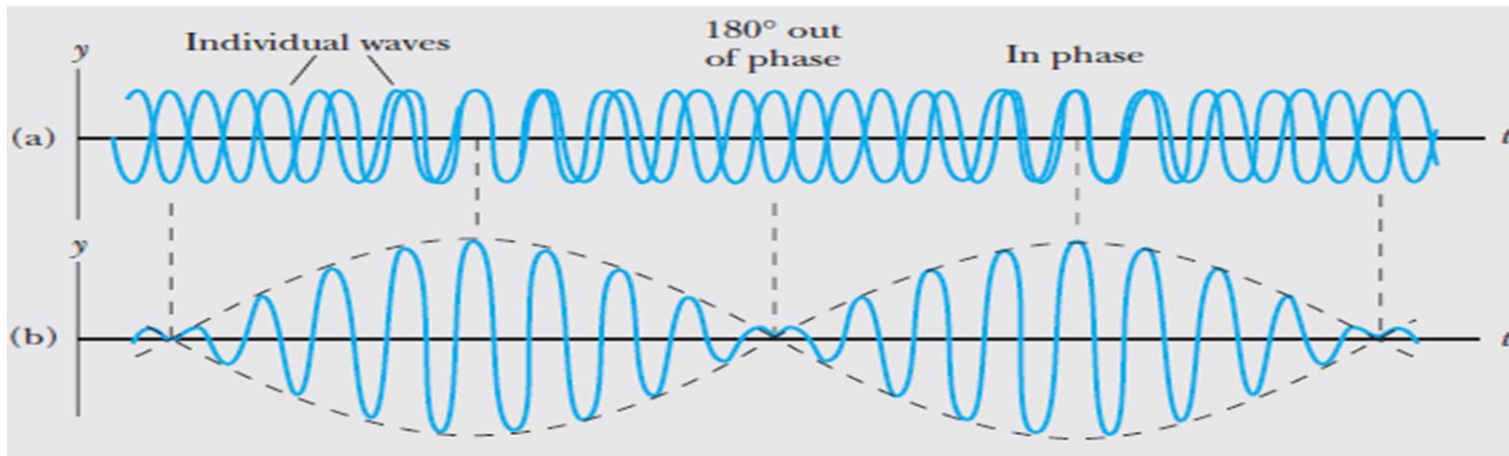
- The above equation gives the relationship between the phase velocity and particle velocity.
- It is clear from the above equation that, Phase velocity is not only greater than the velocity of the particle but also greater than the velocity of light which can never happen.
- Therefore phase velocity has no physical meaning in case of matter waves. Thus a concept of group velocity was introduced.

CONT'D....

Since phase velocity has no meaning in case of matter waves, the concept of group velocity was introduced which is as follows.

“Matter wave is regarded as the resultant of the superposition of large number of component waves all traveling with different velocities. The resultant is in the form of a packet called wave packet or wave group. The velocity with which this wave group travels is called group velocity.” The group velocity is represented by v_g ”

$$v_g = \frac{d\omega}{dk}$$



RELATION BETWEEN GROUP VELOCITY AND PARTICLE VELOCITY (FOR A FREE PARTICLE)

Group Velocity is given by, $v_g = \frac{d\omega}{dk}$

Energy of a wave of frequency ν is given by,

$$E = h\nu = \frac{2\pi h\nu}{2\pi} = \hbar\omega \quad \text{where } \frac{h}{2\pi} = \hbar$$

On differentiating

$$dE = \hbar d\omega \quad \text{————— (1)}$$

From de Broglie's relation. We have $p = \frac{h}{\lambda} = \frac{2\pi h}{\lambda 2\pi} = \hbar k$

$$dp = \hbar dk \quad \text{————— (2)}$$

From Eqns (1) and (2) we get, $\frac{dE}{dp} = \frac{d\omega}{dk} = v_g \quad \text{————— (3)}$

Group Velocity

CONT'D....

For a free particle, Total energy, $E = \frac{p^2}{2m}$

(Total energy equals to kinetic energy of the particle as potential energy is zero for a free particle)

Differentiating both sides we get w.r.t. p , we get

$$\frac{dE}{dp} = \frac{2p}{2m} = \frac{2mv}{2m} = v \quad (4)$$

Particle velocity

Hence, Group velocity = Particle velocity

UNCERTAINTY PRINCIPLE: A CONSEQUENCE OF DE BROGLIE'S HYPOTHESIS!

We cannot know the future because we cannot know the present!

To regard a moving particle as a wave group implies that there are fundamental limits to the accuracy with which we can measure such “particle” properties as position and momentum.

It is impossible to know both the exact position and exact momentum of an object at the same time.

$$\Delta x \Delta p_x \geq \frac{h}{4\pi} \text{ or } \frac{\hbar}{2}$$

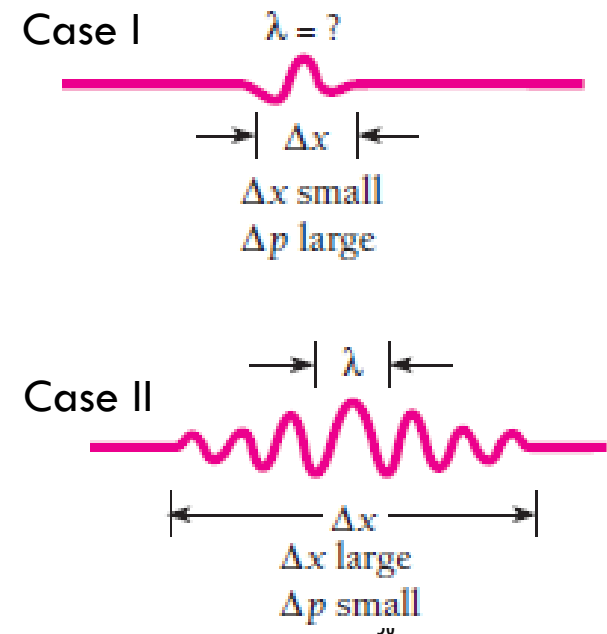
Uncertainty Principle!

This principle, which was discovered by Werner Heisenberg in 1927, is one of the most significant of physical laws.

Heisenberg received the Nobel Prize in Physics in 1932.



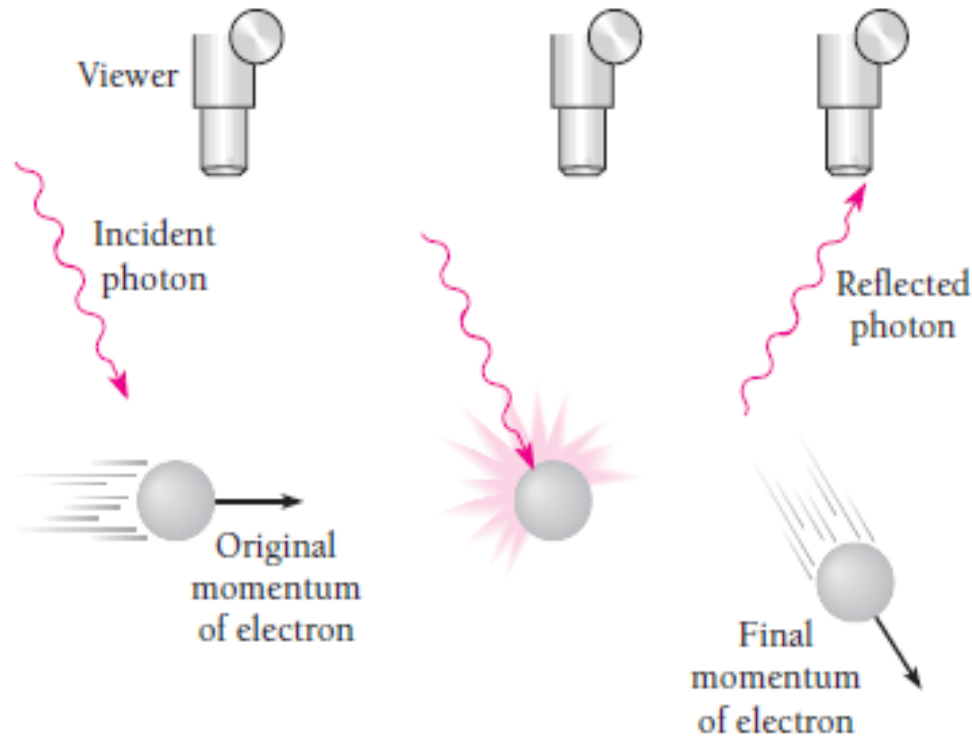
Werner Heisenberg
1901-1976



CONT'D....

- Uncertainty principle states that the product of the uncertainty Δx in the position of an object at some instant and the uncertainty Δp in its momentum component in the x direction at the same instant is equal to or greater than $h/4\pi$.
- If we arrange matters so that Δx is small, corresponding to a narrow wave group, then Δp will be large. If we reduce Δp in some way, a broad wave group is inevitable and Δx will be large.
- These uncertainties are due not to inadequate apparatus but to the imprecise character in nature of the quantities involved.
- Any instrumental or statistical uncertainties that arise during a measurement only increase the product $\Delta x \Delta p$.
- Since we cannot know exactly both where a particle is right now and what its momentum is, we cannot say anything definite about where it will be in the future or how fast it will be moving then.
- We cannot know the future for sure because we cannot know the present for sure.
- But our ignorance is not total: we can still say that the particle is more likely to be in one place than another and that its momentum is more likely to have a certain value than another.

GEDANKEN EXPERIMENT (HEISENBERG'S MICROSCOPE)



- Suppose we look at an electron using light of wavelength λ , as shown in Fig.
- Each photon of this light has the momentum h/λ .
- When one of these photons bounces off the electron (which must happen if we are to “see” the electron), the electron’s original momentum will be changed.
- The exact amount of the change in p cannot be predicted, but it will be of the same order of magnitude as the photon momentum h/λ .

Hence,
$$\Delta p \approx \frac{h}{\lambda} \quad \text{—————} \quad (1)$$

- The longer the wavelength of the observing photon, the smaller the uncertainty in the electron’s momentum.

CONT'D....

- Light being both wave and particle phenomena, we cannot expect to determine the exact location of the electron regardless of the instrument used.
- A reasonable estimate of the minimum uncertainty in the measurement might be one photon wavelength, so that

$$\Delta x \geq \lambda \quad \text{—————} \quad (2)$$

- The shorter the wavelength, the smaller the uncertainty in location.
- However, if we use light of short wavelength to increase the accuracy of the position measurement, there will be a corresponding decrease in the accuracy of the momentum measurement because the higher photon momentum will disturb the electron's motion to a greater extent.
- Light of long wavelength will give a more accurate momentum but a less accurate position.
- Combining Eqs. (1) and (2) gives

$$\Delta x \Delta p \geq h$$

- This result is consistent with the uncertainty principle, $\Delta x \Delta p \geq \frac{h}{2}$

CONT'D....

The argument above implies that the electron can possess a definite position and momentum at any instant and that it is the measurement process that introduces the indeterminacy in Δx and Δp .

On the contrary, this indeterminacy is inherent in the nature of a moving body.

THE WAVE FUNCTION, Ψ

- The quantity with which quantum mechanics is concerned is the wave function ψ of a body.
- While ψ itself has no physical interpretation, the square of its absolute magnitude $|\psi|^2$ evaluated at a particular place at a particular time is proportional to the probability of finding the body there at that time.
- The linear momentum, angular momentum, and energy of the body are the other quantities that can be established from ψ .
- The problem of quantum mechanics is to determine ψ for a body when its freedom of motion is limited by the action of external forces.

CONT'D....

- The general form of the 1-dimensional wave function is $\psi(x, t) = Ae^{i(kx - \omega t)}$ which describes a wave moving in the x direction.
- Wave functions are usually complex with both real and imaginary parts e.g. $\psi = A + iB$.
- 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^* .

$$|\psi|^2 = \psi\psi^* = (A + iB)(A - iB) = A^2 + B^2$$

- Hence $|\psi|^2 = \psi\psi^*$ is always a positive real quantity, as required.

NORMALIZATION OF WAVE FUNCTION

If the particle has to exist somewhere then the integral of $|\psi|^2$ over all space must be finite i.e.

In 3-dimensions
$$\int_{-\infty}^{\infty} |\psi|^2 dV = 1$$
 Where $dV = dx dy dz$

This is called normalization condition.

In 1-dimension
$$\int_{-\infty}^{\infty} |\psi|^2 dx = 1$$

However, If $\int_{-\infty}^{\infty} |\psi|^2 dV = 0$, that means particle does not exist.

Every acceptable wave function has to be normalized if it is not.

By using the above integral , every acceptable wave function can be normalized by multiplying it by an appropriate constant.

PROBABILITY

The probability $P(x)$ of a particle being between x and $(x + dx)$ can be found by multiplying probability density $|\psi|^2$ with dx i.e.

$$P(x) = |\psi|^2 dx$$

The probability of the particle being between x_1 and x_2 is given by

$$P(x) = \int_{x_1}^{x_2} |\psi|^2 dx = \int_{x_1}^{x_2} \psi \psi^* dx$$

The wave function must also be normalized so that the probability of the particle being somewhere on the x axis is 1.

$$\int_{-\infty}^{\infty} |\psi|^2 dx = \int_{-\infty}^{\infty} \psi \psi^* dx = 1$$

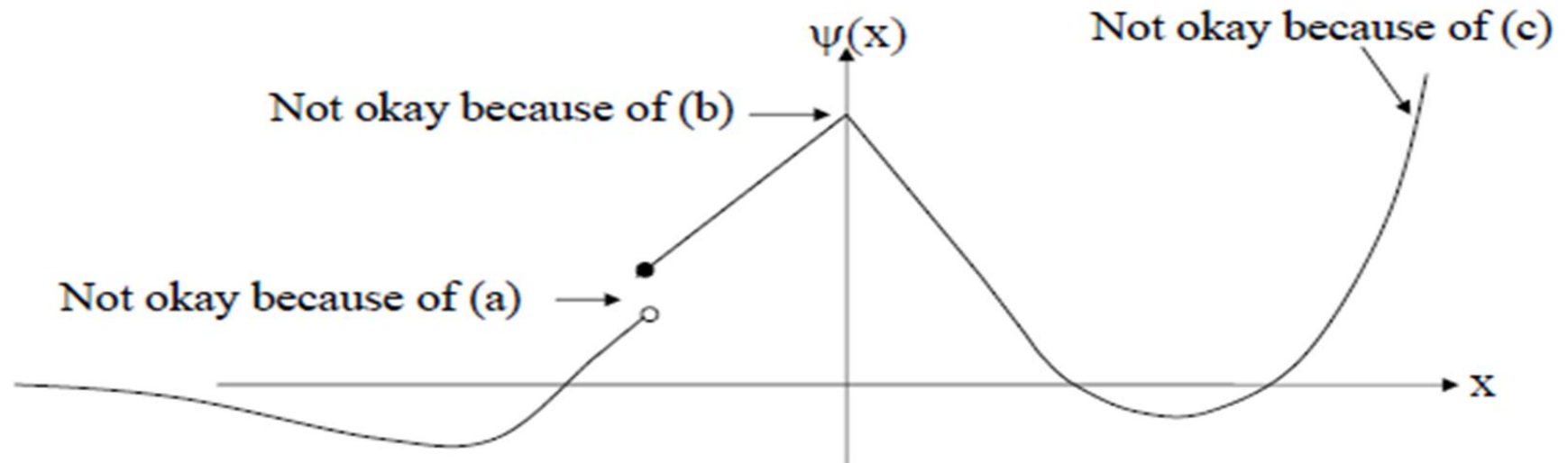
PROPERTIES OF WELL BEHAVED WAVE FUNCTIONS

Besides being normalizable, ψ needs to satisfy certain properties which are :

- a) ψ must be continuous and single-valued everywhere.
- b) $\partial\psi/\partial x, \partial\psi/\partial y, \partial\psi/\partial z$ must be continuous and single-valued everywhere.
- c) ψ must be normalizable, which means that ψ must go to 0 as $x \rightarrow \infty, y \rightarrow \infty, z \rightarrow \infty$ in order that $\int_{-\infty}^{\infty} |\psi|^2 dV$ over all space be a finite constant.

Only wave functions with all these properties can yield physically meaningful results when used in calculations, so only such “well-behaved” wave functions are admissible as mathematical representations of real bodies.

CONT'D...



a) ψ must be continuous and single-valued everywhere.

b) $\partial\psi/\partial x, \partial\psi/\partial y, \partial\psi/\partial z$ must be continuous and single-valued everywhere.

c) ψ must be normalizable, which means that ψ must go to 0 as $x \rightarrow \infty, y \rightarrow \infty, z \rightarrow \infty$ in order that

$\int_{-\infty}^{\infty} |\psi|^2 dV$ over all space be a finite constant.

EXAMPLE: HOW TO NORMALIZE A WAVE FUNCTION?

We are given a wave function of a particle confined in a 1-dimensional box of length L , i.e. $0 \leq x \leq L$

$$\psi = A \sin\left(\frac{n\pi x}{L}\right)$$

We have to find the value of A which is our normalization constant.

Solution: According to normalization condition in 1-dimension, $\int_{-\infty}^{\infty} |\psi|^2 dx = 1$

Now

$$|\psi|^2 = \psi\psi^* = A^2 \sin^2\left(\frac{n\pi x}{L}\right)$$

(As given wave function is a real one so its multiplication with its complex conjugate will yield square of the function itself)

$$\therefore \int_0^L A^2 \sin^2\left(\frac{n\pi x}{L}\right) dx = 1$$

CONT'D....

$$\therefore A^2 \int_0^L \sin^2 \left(\frac{n\pi x}{L} \right) dx = 1 \Rightarrow A^2 \int_0^L \frac{1 - \cos \left(\frac{2n\pi x}{L} \right)}{2} dx = 1 \Rightarrow \frac{A^2}{2} \int_0^L \left[1 - \cos \left(\frac{2n\pi x}{L} \right) \right] dx = 1$$

On integrating w.r.t. x , we get $\frac{A^2}{2} \left[x - \frac{L}{2\pi n} \sin \left(\frac{2n\pi x}{L} \right) \right]_0^L = 1$

On substituting the limits, we get, $\frac{A^2}{2} L = 1 \Rightarrow A^2 = \frac{2}{L}$

$$\therefore A = \sqrt{\frac{2}{L}}$$

Thus the normalized wave function becomes, $\psi = \sqrt{\frac{2}{L}} \sin \left(\frac{n\pi x}{L} \right)$

PROBLEM:

The wave function of a certain particle is $\psi = A \cos^2 x$ for $-\pi/2 \leq x \leq \pi/2$.

- (a) Find the value of A.
- (b) Find the probability that the particle be found between $x = 0$ and $x = \pi/4$.

Ans: (a) $\sqrt{8/3\pi}$ (b) 0.462

EQUATION OF MOTION OF MATTER WAVES



Erwin Schrodinger
1887-1961

According to de-Broglie's hypothesis, a moving particle of mass, m is associated with matter waves whose wavelength is given by $\lambda = \frac{h}{mv}$. To describe the motion of these waves we have to have a wave equation.

The Schrödinger wave equation in its time-dependent form for a particle of energy E moving in a potential U in one dimension is

In 1-dimension

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + U\psi$$

Schrödinger's Equation: Time-dependent Form

In 3-dimensions

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + U\psi$$

$$\text{Where } \nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

The Laplacian Operator

$$i\hbar \frac{\partial \psi}{\partial t} = \left(-\frac{\hbar^2}{2m} \nabla^2 + U \right) \psi(x, y, z, t)$$

Schrodinger received the Nobel Prize in Physics in 1933.

TIME-DEPENDENT SCHRÖDINGER WAVE EQUATION

A basic physical principle that cannot be derived from anything else

- In quantum mechanics the wave function ψ corresponds to the wave variable y of wave motion in general.
- However, ψ , unlike y , is not itself a measurable quantity and may therefore be complex.
- For this reason we assume that ψ for a particle moving freely in the $+x$ direction is specified by

$$\psi = Ae^{i(kx-\omega t)} \quad \text{—————} \quad (1)$$

It is convenient since we already know what ω and k are in terms of the total energy E and momentum p of the particle being described by ψ .

$$E = h\nu = \frac{2\pi h\nu}{2\pi} = \hbar\omega \Rightarrow \omega = \frac{E}{\hbar} \quad \text{and} \quad p = \frac{h}{\lambda} = \frac{2\pi h}{\lambda 2\pi} = \hbar k \Rightarrow k = \frac{p}{\hbar}$$

Which gives

$$\psi = Ae^{i/\hbar(px-Et)} \quad \text{—————} \quad (2)$$

This equation describes the wave equivalent of an unrestricted particle of total energy E and momentum p moving in the $+x$ direction.

CONT'D....

Differentiating equation (2) w.r.t. x twice, we get $\frac{\partial^2 \psi}{\partial x^2} = \frac{p^2}{\hbar^2} \psi$

$$p^2 \psi = -\hbar^2 \frac{\partial^2 \psi}{\partial x^2} \quad \text{—————} \quad (3)$$

Differentiating equation (2) w.r.t. t once, we get $\frac{\partial \psi}{\partial t} = -\frac{iE}{\hbar} \psi$

$$E \psi = i\hbar \frac{\partial \psi}{\partial t} \quad \text{—————} \quad (4)$$

At speeds small compared with that of light, the total energy E of a particle is the sum of its kinetic energy $p^2/2m$ and its potential energy U , where U is in general a function of position x and time t :

$$\therefore E = \frac{p^2}{2m} + U(x, t) \quad \text{—————} \quad (5)$$

The function U represents the influence of the rest of the universe on the particle. Of course, only a small part of the universe interacts with the particle to any extent; for instance, in the case of the electron in a hydrogen atom, only the electric field of the nucleus must be taken into account.

CONT'D....

Multiplying equation (5) by ψ on both sides, we get $E\psi = \frac{p^2}{2m}\psi + U(x, t)\psi$ ————— (6)

Now we substitute for $p^2\psi$ and $E\psi$ from Eqs. (3) and (4) in eqn. (6) to obtain the time dependent form of Schrödinger's equation:

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + U\psi$$

Time-dependent Schrödinger equation in one dimension

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + U\psi$$

Time-dependent Schrödinger equation in 3- dimensions

where the particle's potential energy U is some function of x , y , z , and t .

- Any restrictions that may be present on the particle's motion will affect the potential energy function U .
- Once U is known, Schrödinger's equation may be solved for the wave function of the particle, from which its probability density may be determined for a specified x , y , z , t .

CONT'D....

Schrödinger's equation cannot be derived from other basic principles of physics; it is a basic principle in itself.

TIME-INDEPENDENT SCHRÖDINGER WAVE EQUATION: STEADY STATE FORM

- The potential in many cases will not depend explicitly on time.
- To describe those cases Schrodinger time independent equation is used.
- The Schrödinger wave equation for a particle of energy E moving in a constant potential U in one dimension is

In 1-dimension

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} \{E - U(x)\}\psi(x) = 0$$

In 3-dimensions

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{\hbar^2} \{E - U(x, y, z)\}\psi(x, y, z) = 0$$

$$\nabla^2\psi + \frac{2m}{\hbar^2} \{E - U(x, y, z)\}\psi(x, y, z) = 0$$

$$\text{Where } \nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

The Laplacian Operator

CONT'D....

We begin with the one-dimensional wave function of an unrestricted particle which is given by

$$\psi = Ae^{i/\hbar(px-Et)} = Ae^{+(ip/\hbar)x}e^{-(iE/\hbar)t} = \psi e^{-(iE/\hbar)t} \quad \text{————— (1)}$$

Evidently ψ is the product of a time-dependent function $e^{-(iE/\hbar)t}$ and a position dependent function, $\psi = Ae^{+(ip/\hbar)x}$.

As it happens, the time variations of all wave functions of particles acted on by forces independent of time have the same form as that of an unrestricted particle.

Substituting the ψ of Eq. (1) into the time-dependent form of Schrödinger's equation, we find that

$$E\psi e^{-(iE/\hbar)t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} e^{-(iE/\hbar)t} + U\psi e^{-(iE/\hbar)t}$$

Dividing through by the common exponential factor gives $E\psi = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + U\psi$

On rearranging the terms we get

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

**Time independent Schrödinger
equation in one dimension**

STEADY STATE FORM OF WAVE FUNCTION

The wave function can be written as: $\psi = \psi e^{-(iE/\hbar)t}$

Where $\psi(x) = Ae^{+(ip/\hbar)x} = \psi(x) = Ae^{+ikx}$

The probability density becomes: $\psi\psi^* = \psi^2(x)$

The probability distributions are constant in time. This is a standing wave phenomena that is called the stationary state.