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Principles of Quantum Mechanics

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Basics of Quantum Mechanics
- Classical Point of View -

- In classical (Newtonian) mechanics, the laws are written in terms of PARTICLE TRAJECTORIES.
- A PARTICLE is an indivisible mass point object that has a variety of properties that can be measured, which we call observables. The observables specify the state of the particle (position and momentum).
- A SYSTEM is a collection of particles, which interact among themselves via internal forces, and can also interact with the outside world via external forces. The STATE OF A SYSTEM is a collection of the states of the particles that comprise the system.
- All properties of a particle can be known to infinite precision.
- Conclusions:
  - TRAJECTORY → state descriptor of Newtonian physics,
  - EVOLUTION OF THE STATE → Use Newton's second law
  - PRINCIPLE OF CAUSALITY → Two identical systems with the same initial conditions, subject to the same measurement will yield the same result.

INADEQUACIES OF CLASSICAL MECHANICS

Due to certain limitation of classical mechanics and its wrong assumption this theory could not explain following physical phenomena.

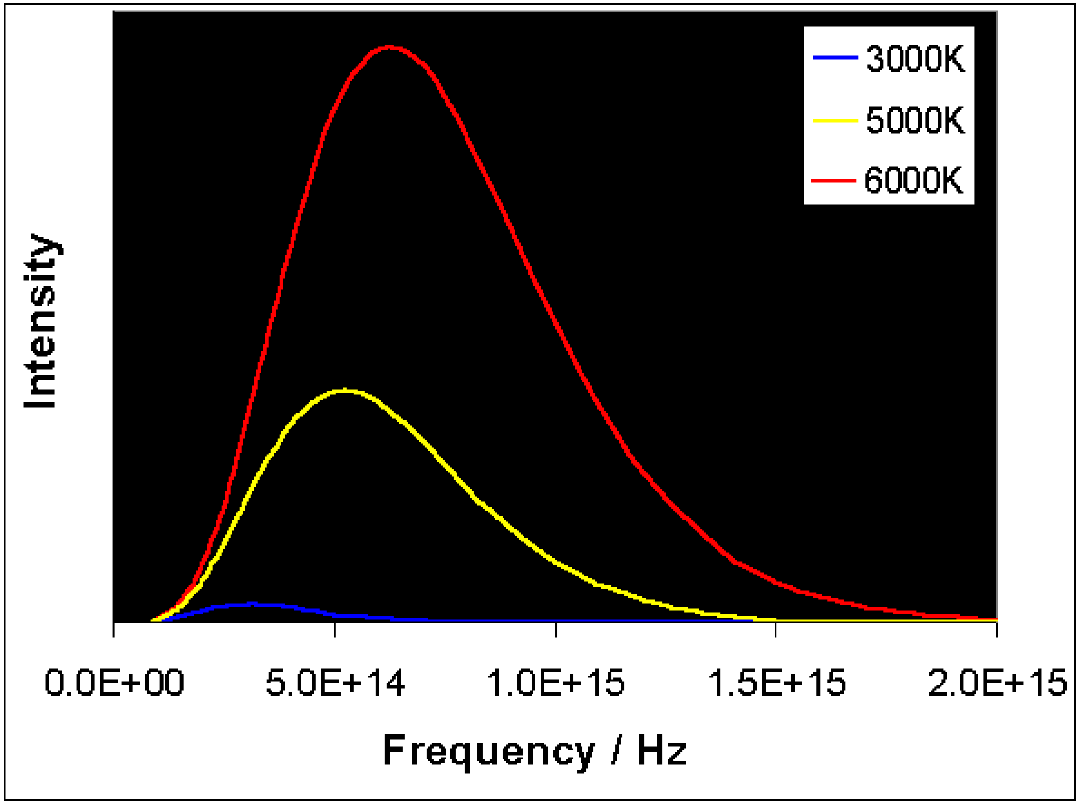
1. It fails to explain the spectrum of black body radiation.
2. It fails to explain the stability of atoms.
3. It fails to explain discrete atomic spectrum
4. It fails not to explain photoelectric effect.
5. It fails to explain the phenomena of pair production
6. It fails to explain the phenomena of Compton scattering.
7. It fails to explain the variation of electric conductivity of solid
8. (super conductivity).
9. It could not explain the phenomena associated with spinning motion of electron.
10. It could not explain Zeeman effect, Stark effect, Raman effect etc
11. It could not explain the phenomena of radioactivity like β-decay and α- decay .

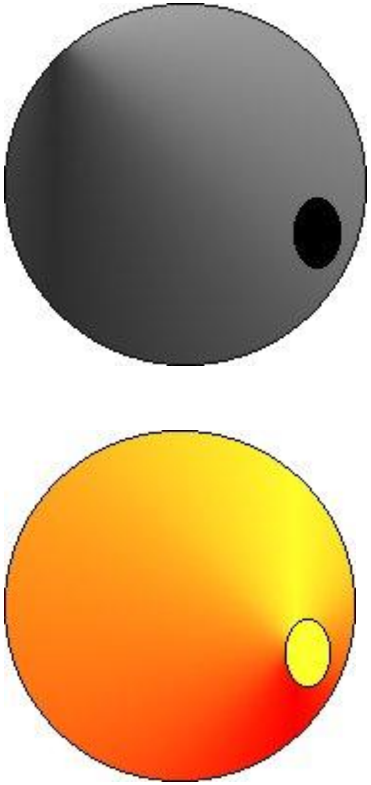
Basics of Quantum Mechanics
- Quantum Point of View -

- **Quantum particles can act as both particles and waves → WAVE-PARTICLE DUALITY**
- **Quantum state is a conglomeration of several possible outcomes of measurement of physical properties → Quantum mechanics uses the language of PROBABILITY theory (random chance)**
- **An observer cannot observe a microscopic system without altering some of its properties. Neither one can predict how the state of the system will change.**
- **QUANTIZATION of energy is yet another property of "microscopic" particles.**

Black-body Radiation

A black body is a *perfect absorber* of electromagnetic radiation - also a perfect emitter

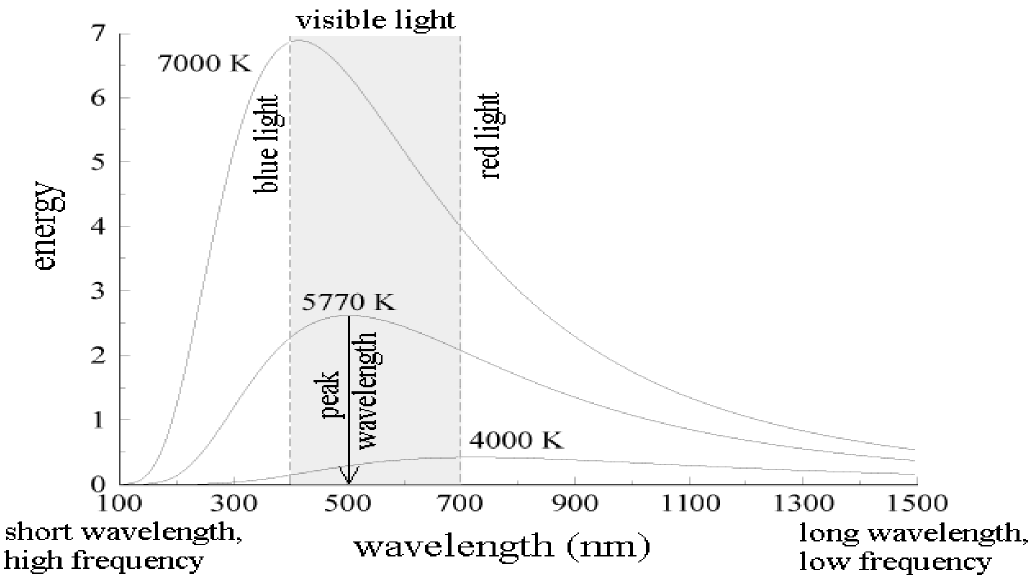




Height increases with T, as in Stefan-Boltzmann equation.

Black Body Radiation

- The energy of blackbody radiation is not shared evenly by all Wavelengths of light.
- The spectrum of blackbody Radiation shows that some wavelengths get more energy than others.
- Three spectra are shown, for three different temperatures.
- Here are some experimental facts about blackbody radiation:



1. The blackbody spectrum depends only on the temperature of the object, it does not depend on the type of material, ie all materials emit the same blackbody spectrum if their temperatures are the same.
2. As the temperature of an object increases, it emits more blackbody energy at all wavelengths.
3. As the temperature of an object increases, the peak wavelength of the blackbody spectrum shifts toward shorter wavelength. For example, blue stars are hotter than red stars.
4. The blackbody spectrum always becomes small at the left-hand side (the short wavelength, high frequency side).

RAYLEIGH'S ENERGY DENSITY DISTRIBUTION

Rayleigh–Jeans formula:

$$u(\nu, T) = \frac{8\pi \nu^2}{c^3} kT.$$

•Illustrates that this law is in complete disagreement with experimental data, except for low frequencies .

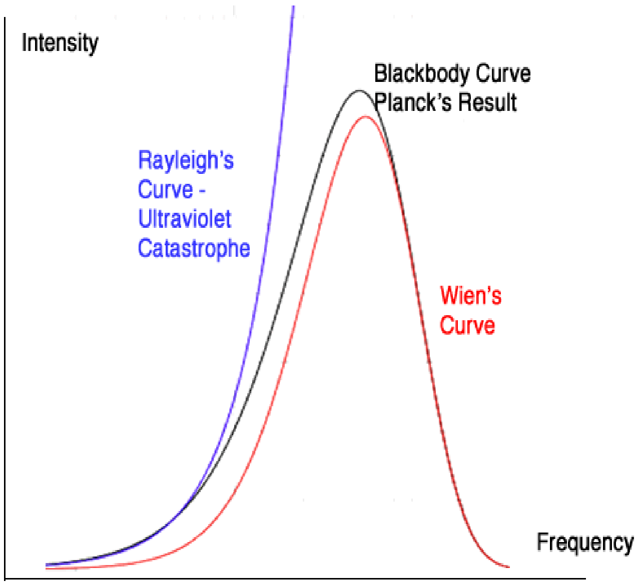
• The electromagnetic energy density *u* (ν, T) diverges for high frequencies ν , whereas experimentally it must be finite as shown in adjacent figure.

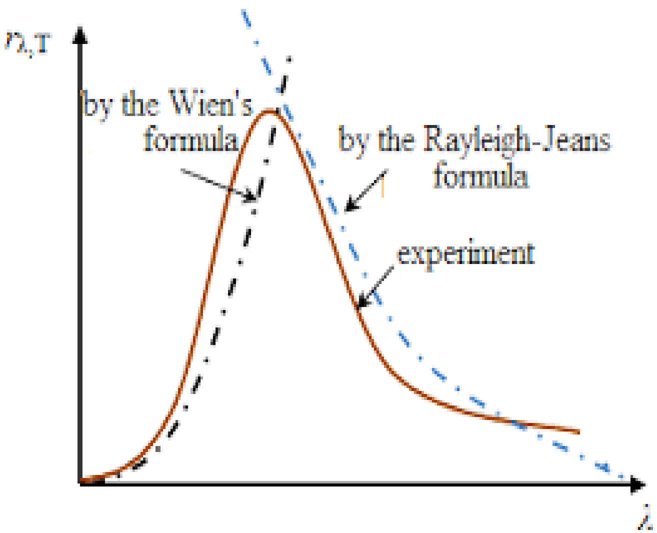
• The integration of this equation over all frequencies *diverges*, implies that the cavity contains an *infinite* amount of energy.

• This result is absurd. Divergence of this equation for *high* frequencies (i.e., in the *ultraviolet* range) is called the *ultraviolet catastrophe*.

• It is a real catastrophically failure of classical physics indeed!

• It was founded on an erroneous premise:
the energy exchange between radiation and matter is *continuous; any amount of energy can be* Exchanged.

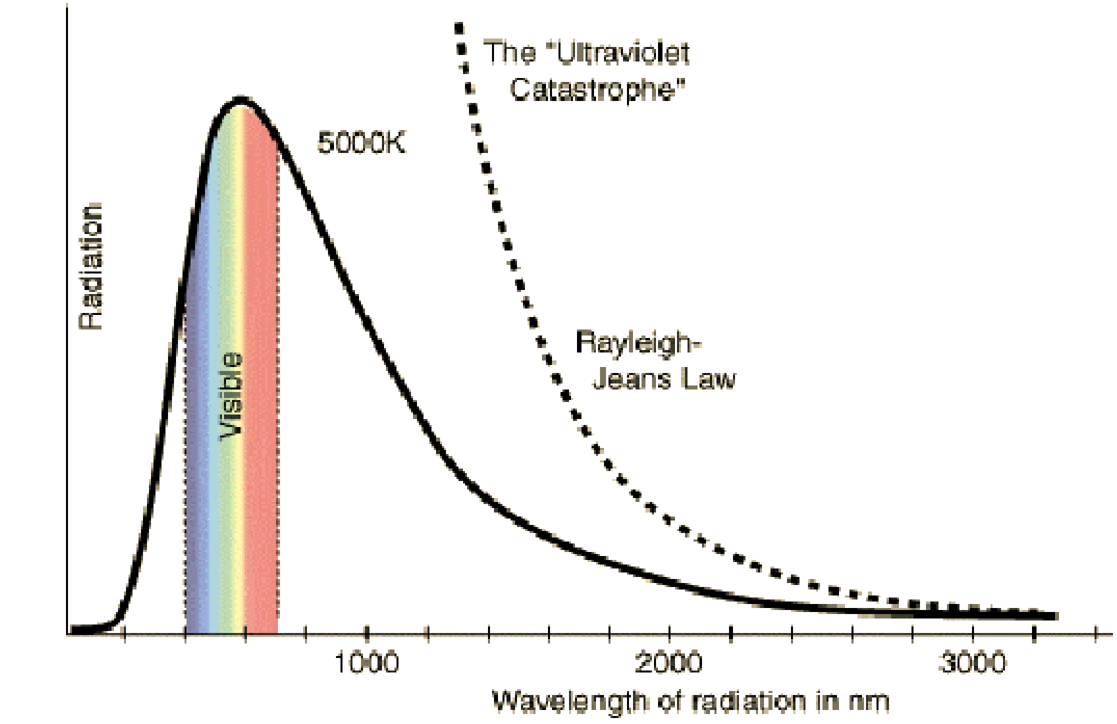




THE 'ULTRAVIOLET CATASTROPHE'

1900 - Rayleigh

Predicted infinite intensity for the UV region



- This was a CLASSICAL prediction, first made in the late 19th century, that an IDEAL BLACK BODY at thermal equilibrium will emit radiation with INFINITE POWER.

- Max Planck resolved this issue by postulating that electromagnetic energy did <u>not</u> follow the classical description, but could <u>only</u> oscillate or be emitted in DISCRETE PACKETS OF ENERGY proportional to the frequency. He called these packets 'QUANTA'.

Note: $h = 6.626x10^{-34} J.s$

$$E = h\upsilon$$

Planck's energy density distribution

- **The problem of ultraviolet catastrophe has been resolved by Max Planck.**
- **An accurate description of blackbody radiation has been put forward accordingly.**
- **Planck considered that the energy exchange between radiation and matter must be *discrete not continuous.***
- **He derived the radiation law by using the following assumptions.**

1. **A black body chamber is filled up not only with radiation, but also with simple harmonic oscillators or harmonic oscillators or resonators of molecular dimensions. They can vibrate with all possible frequencies.**
2. **The frequency of radiation emitted by an oscillator is the same as the frequency of its vibration.**
3. **An oscillator cannot emit energy in a continuous manner. It can emit energy in the multiples of a small unit called Quantum (Photon).**

- **Planck *postulated* that the energy of the radiation (of frequency ν) emitted by the oscillating charges (from the walls of the cavity) must come *only in integer multiples of h* ν *:***
- ***E = nh*ν (n= 1, 2, 3………) where *h is a universal constant and h*ν *is the energy of a "quantum" of radiation.***
- ***E = nh*ν is known as *Planck's quantization rule for energy or Planck's postulate.***

PLANK'S RADIATION LAW

Planck showed that the *correct* thermodynamic relation for the average energy is given by

$$\overline{E} = \frac{\sum_0^\infty nh\nu e^{-nh\nu/kT} dE}{\sum_0^\infty e^{-nh\nu/kT} dE} = \frac{h\nu}{e^{h\nu/kT} - 1}$$

- So the energy density per unit frequency of the radiation emitted from the hole of a cavity is given by

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

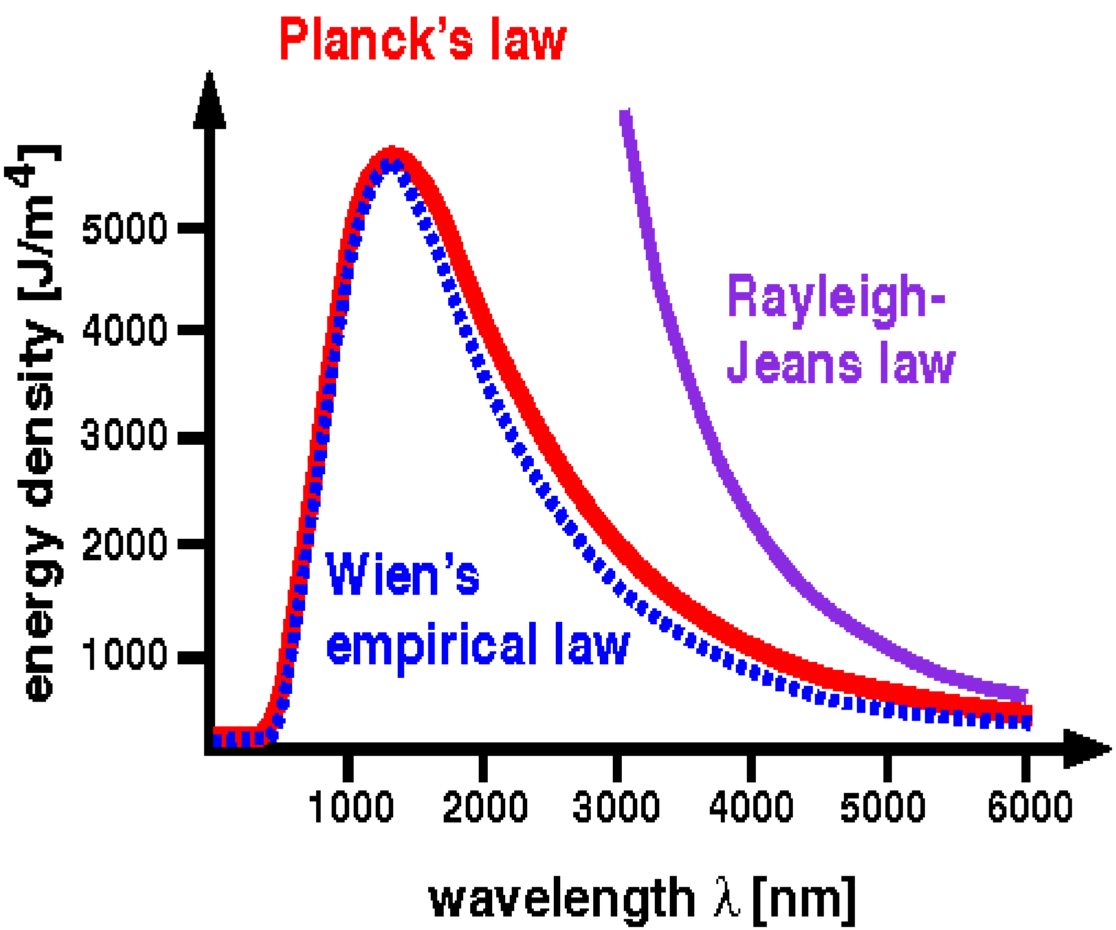
- This is known as *Planck's distribution relation.*
- This relation can be rewritten in terms of wavelength.
- So, the Planck's energy density or the energy density per unit wavelength

$$\boxed{\tilde{u}(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}.}$$

- The introduction of the constant *h had indeed heralded the end of classical physics and the* dawn of a new era: physics of the microphysical world namely the quantum physics.
- Assuming that the energy of an oscillator is quantized.

$$E_{min} = h\nu$$

$h = 6.626 \times 10^{-34}\ Js^{-1}$ - Planck's constant



Max Planck: 1858-1947

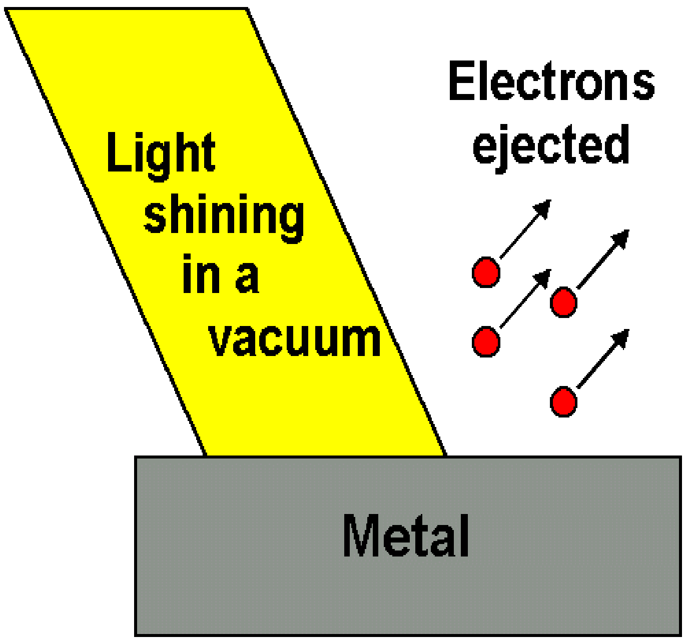
- **The energy in electromagnetic radiation is *quantized.***
- ***Quantum means "how much" in Latin.***
- **Remember this was all being done before anyone had a clue about atomic structure so "atomic oscillators" were an abstract concept.**

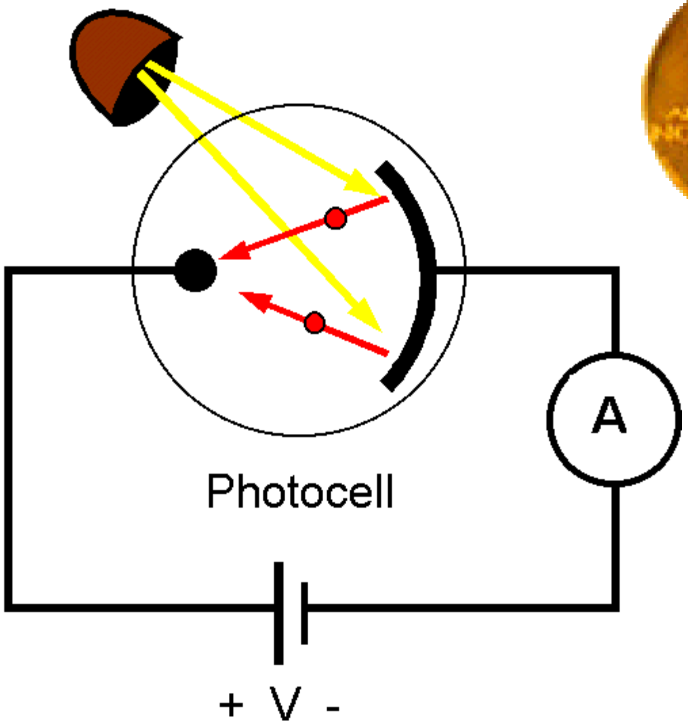
Photoelectric effect

- Noted by Hertz in 1887 (“pre-electron”).
- Characterised by Lenard in 1902
- Light shining on surface – electrons ejected
- The photoelectric effect provides a direct confirmation for the energy quantization of light.

Phillip Lénard

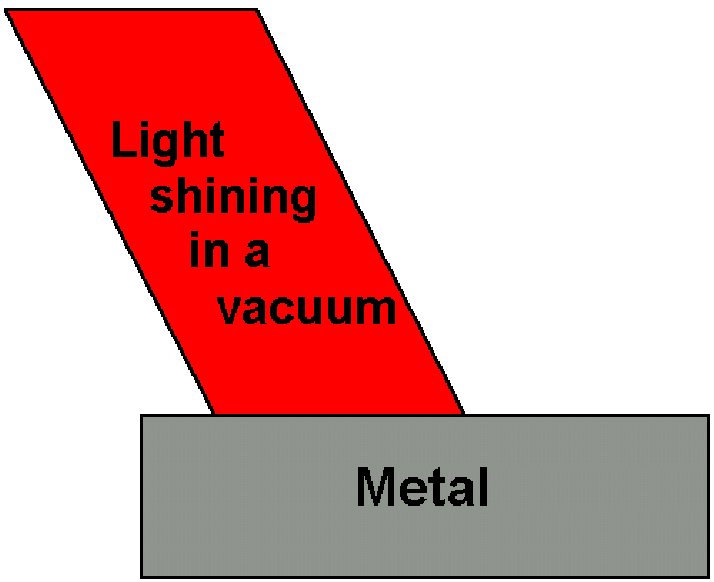
1862-1947

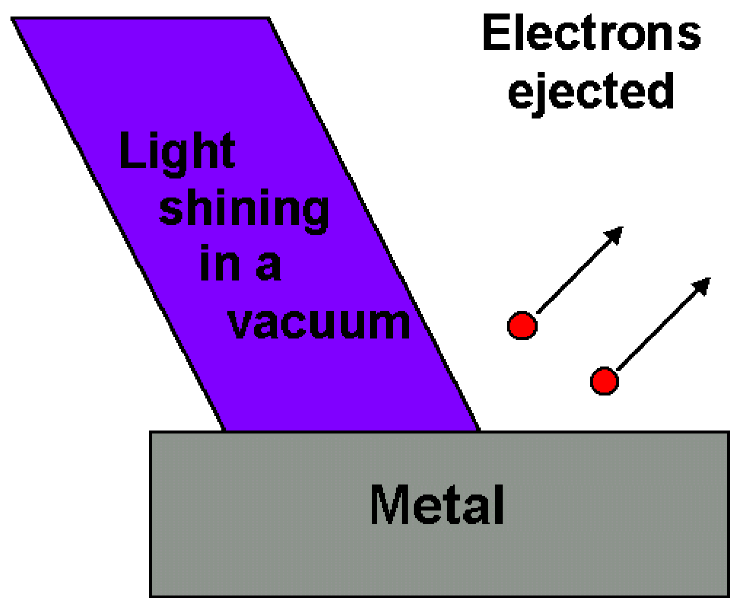




Comments

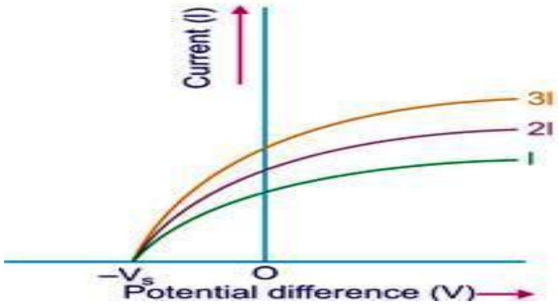
- Increasing the intensity of the light increased the number of photoelectrons, but not their energy.
- Red light (low ν) would not cause ejection of electrons.
- Weak high frequency (violet) light would result in few, high energy electrons



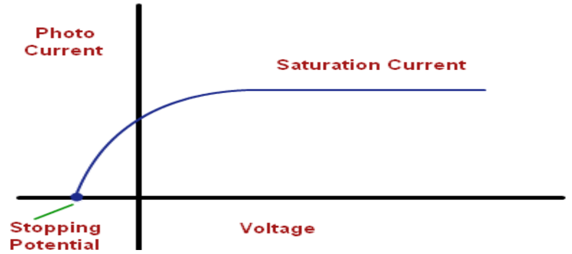


CHARACTERISTICS OF PHOTOELECTRIC EFFECT

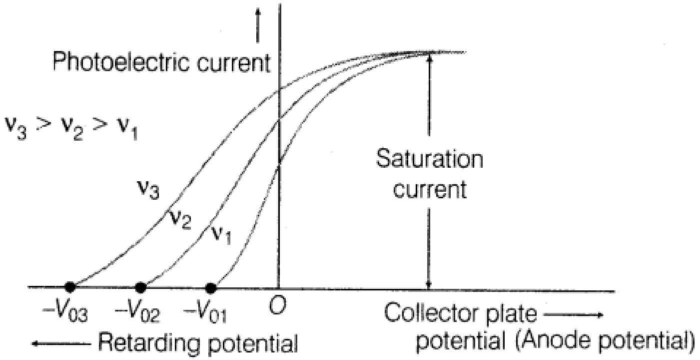
1. Effect of Intensity : ***The intensity of incident light affects the photoelectric current but leaves the maximum kinetic energy (The stopping potential) of photoelectrons unchanged.***



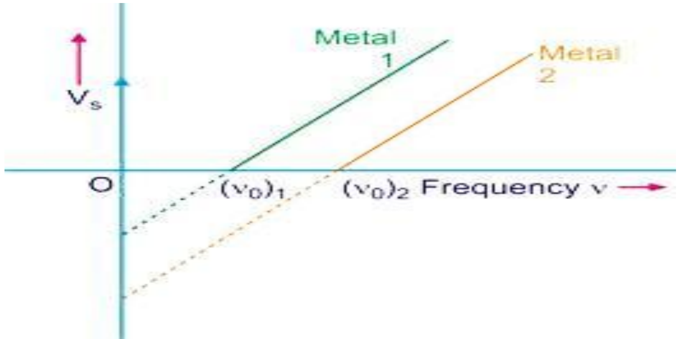
2. Effect of Frequency : The frequency affects the maximum kinetic energy (or stopping potential)of photoelectrons but leaves the photoelectric current unchanged



3. Effect of metal : The threshold frequencies are different for different metals, the slope (V_s/ν) for all the metals is same and hence a universal constant.



4. Effect of Time : There is no time lag between the incidence of light and the emission of photoelectrons.



Einstein, 1905

- Proposed that light consisted of quanta called *photons*
- Each incident photon has E = hv
- Thus increasing v increases E of emitted electrons
- Increasing *intensity* does just gives more photons
- Generalised Planck's result to light

EINSTEIN`S EXPLANATION OF PHOTOELECTRIC EFFECT

- Accordingly, if *hv* is the energy of incident photon, then the kinetic energy of ejected photo electron is given by *Einstein's photoelectric equation*

$$K = h\nu - W = h(\nu - \nu_0)$$

- where W= $h\nu_0$ is work function depending upon the threshold frequency (cut of frequency) of metal.
- The stopping potential is

$$V_s = \frac{h\nu}{e} - \frac{W}{e}$$

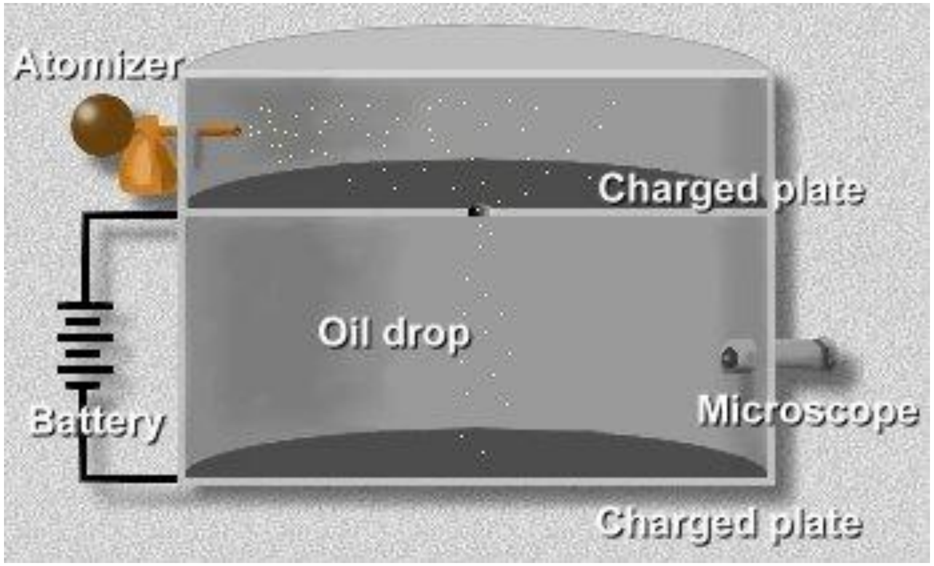
- Here *the magnitude of the photoelectric current thus generated is proportional to the intensity of the incident radiation, yet the speed of the electrons does not depend on the radiation's intensity, but on its frequency.*
- In nutshell, the photoelectric effect does provide compelling evidence for the corpuscular nature of the electromagnetic radiation.

Basics of Quantum Mechanics
- Photoelectric Effect -

- The photoelectric effect provides evidence for the particle nature of light.
- It also provides evidence for quantization.
- If light shines on the surface of a metal, there is a point at which electrons are ejected from the metal.
- The electrons will only be ejected once the threshold frequency is reached .
- Below the threshold frequency, no electrons are ejected.
- Above the threshold frequency, the number of electrons ejected depend on the intensity of the light.

MILLIKAN'S OIL DROP EXPERIMENT

1909 - Robert Millikan



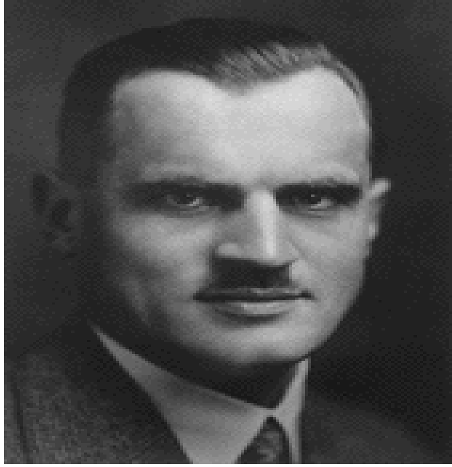
- This experiment determined the magnitude of the electronic charge, and that it was QUANTISED.

- This value is approximately

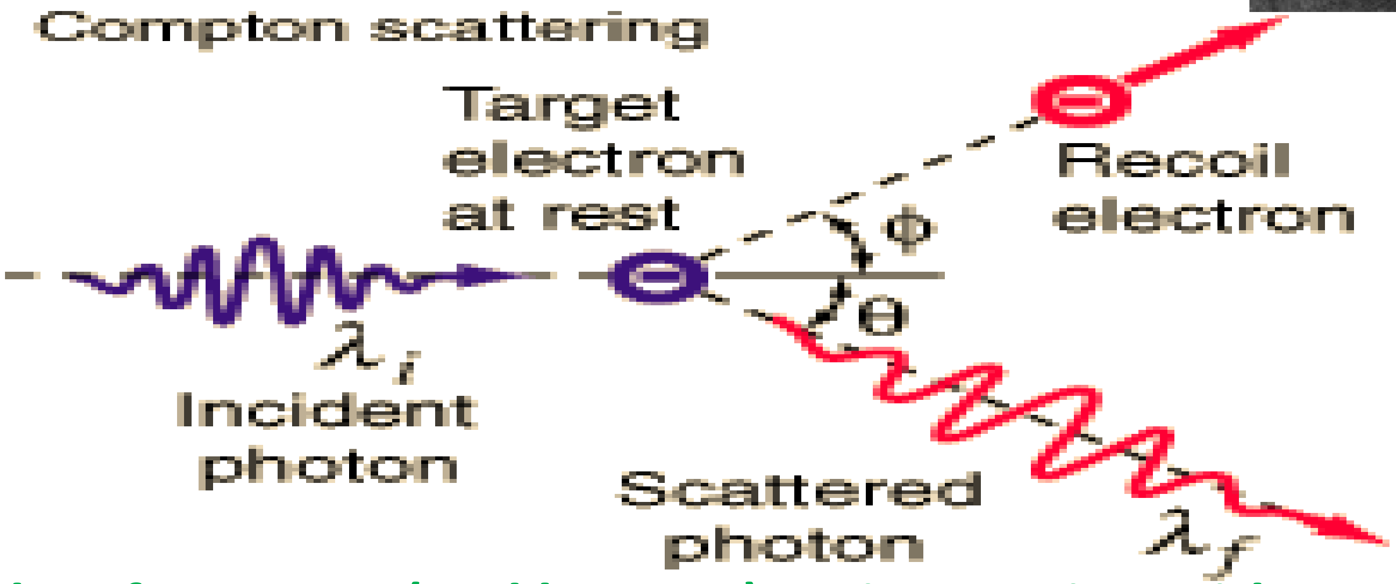
$$1.6x10^{-19}C$$

Note: An electron volt (eV) is the amount of energy it takes to accelerate one electron through a potential of one volt. Thus, 1eV $\equiv 1.6x10^{-19}J$

Compton Effect



- Compton provided the most conclusive confirmation of the particle aspect of radiation.
- Compton effect is a process in which x-rays collide with electrons and are scattered



- X-rays lost frequency (and hence E) on interaction with material
- Wavelength of the scattered radiation is larger than the wavelength of the incident radiation.
- Classically there would have been no frequency shift - confirmed photon theory

Compton Effect ……

- Wavelength of the scattered radiation does not depend on the intensity of incident radiation.
- It depends on the angle of scattering and the wavelength of the incident beam.
- The wavelength of the radiation scattered at an angle ɵ is given by

$$\lambda_s = \lambda_0 + \frac{h}{m_0 c}(1 - \cos\theta)$$

- Where m_0 is the rest mass of the electron. And the constant $\frac{h}{m_0 c}$ is known as the Compton wavelength of the electron and it has a value 0.0024 nm.
- Wavelength shift is

$$\Delta\lambda = \lambda_s - \lambda_0 = \frac{h}{m_0 c}(1 - \cos\vartheta) = 2\frac{h}{m_0 c}\sin^2\frac{\vartheta}{2}$$

- This relation, which connects the initial and final wavelengths to the scattering angle, confirms Compton's experimental observation:
- The wavelength shift of the X-rays depends only on the angle at which they are scattered and not on the frequency (or wavelength) of the incident photons.
- *Compton effect thus confirms that photons behave like particles: they collide with electrons like material particles.*

Wave – Particle Duality

- Newton thought light consisted of "corpuscles".
- Huygens believed that it was a wave.
- By the end of the 19^{th} century, everyone "knew" it was a wave : Young's Slits:

Thomas Young (1773-1829)

- Photoelectric effect – photons (particles!).
- Compton Effect: particles!

	Waves	Particles
Reflection	✓	✓
Refraction	✓	✓
Interference	✓	✗
Diffraction	✓	✗
Photoelectric effect	✗	✓

- **Bohr - principle of complementarity:** It is impossible to observe both the wave and particle aspects simultaneously.

Niels Bohr

1885-1962

- Light can be used as either wave or particle explanation : Need to be aware of both (Wave particle duality).

Matter Waves

Louis de Broglie

1892-1987

- In 1923 de Broglie proposed that particles should display wave like properties.: matter waves

- The de Broglie wavelength of a particle depends on its momentum, ***p .***

- *A*ccording to the de Broglie relation,

particle wavelength is ***λ = h / p = λ = h / mv***

- This shows that the wavelength of a particle can be altered by changing its velocity.

- ***So, for an electron***

$$\because \frac{p^2}{2m} = e\mathrm{V}, \;\; \therefore p = \sqrt{2meV} \Rightarrow \lambda = \frac{h}{\sqrt{2meV}} = \frac{2.27}{\sqrt{V}}$$

- In 1929 de Broglie was awarded the Nobel Prize in Physics for his discovery of the wave nature of electrons.

Basics of Quantum Mechanics
- The Correspondence Principle -

When Quantum physics is applied to macroscopic systems, it must reduce to the classical physics. Therefore, the non-classical phenomena, such as uncertainty and duality, must become undetectable. Niels Bohr codified this requirement into his Correspondence principle:

10^{-10} m → >0.01 m

(atoms, molecules) (us, etc.)

Quantum Physics ··········► **Classical Physics**

- Laws
- Physical models
- Predictions

Basics of Quantum Mechanics
- Particle-Wave Duality -

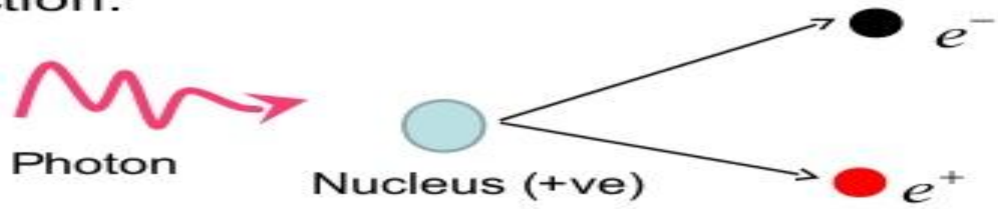
- The behavior of a "microscopic" particle is very different from that of a classical particle:
  - ➔ in some experiments it resembles the behavior of a classical wave (not localized in space)
  - ➔ in other experiments it behaves as a classical particle (localized in space)
- Corpuscular theories of light treat light as though it were composed of particles, but can not explain DIFRACTION and INTERFERENCE.
- Maxwell's theory of electromagnetic radiation can explain these two phenomena, which was the reason why the corpuscular theory of light was abandoned.

Summary
- Particle-Wave Duality -

- **Waves as particles:**
  - **Max Plank work on black-body radiation, in which he assumed that the molecules of the cavity walls, described using a simple oscillator model, can only exchange energy in quantized units.**
  - **1905 Einstein proposed that the energy in an electromagnetic field is not spread out over a spherical wavefront, but instead is localized in individual clumbs - quanta. Each quantum of frequency n travels through space with speed of light, carrying a discrete amount of energy and momentum =photon => used to explain the photoelectric effect, later to be confirmed by the *x*-ray experiments of Compton.**
- **Particles as waves**
  - **Double-slit experiment, in which instead of using a light source, one uses the electron gun. The electrons are diffracted by the slit and then interfere in the region between the diaphragm and the detector.**
  - **Aharonov-Bohm effect**

Pair Production

When a photon (electromagnetic energy) of sufficient energy passes near the field of nucleus, it materializes into an electron and positron. This phenomenon is known as pair production.



In this process charge, energy and momentum remains conserved prior and after the production of pair.

The rest mass energy of an electron or positron is 0.51 MeV (according to $E = mc^2$).

The minimum energy required for pair production is 1.02 MeV.

Any additional photon energy becomes the kinetic energy of the electron and positron.

The corresponding maximum photon wavelength is 1.2 pm. Electromagnetic waves with such wavelengths are called gamma rays (γ).

Heat Capacity of Solids

- A year after his photon proposal, Einstein (1907) came to the conclusion that his quantum idea was compatible with Planck's energy quanta.
- Einstein argued that the quantum idea should be applicable to thermal properties of matter, as well as to radiation.
- His theory of specific heat is historically important because it clarified the confused situation that had cast doubt on the kinetic theory of gases and even the molecular structure of matter.
- This is also the first instance when the quantum idea was shown to be relevant to physical systems well beyond the esoteric case of blackbody radiation.
- Einstein model for the thermal properties of solids has been modified by Debye model invoking the notion of quanta of sound waves (phonons).
- So, the birth of the quantum mechanics has begun new insights in the theory of specific heat followed by solid state physics.

Basics of Quantum Mechanics
- Quantum Point of View -

- **Quantum particles can act as both particles and waves ➔ WAVE-PARTICLE DUALITY**
- **Quantum state is a conglomeration of several possible outcomes of measurement of physical properties ➔ Quantum mechanics uses the language of PROBABILITY theory (random chance)**
- **An observer cannot observe a microscopic system without altering some of its properties. Neither one can predict how the state of the system will change.**
- **QUANTIZATION of energy is yet another property of "microscopic" particles.**

Postulates of Quantum Mechanics

Quantum physicists are interested in all kinds of physical systems (photons, conduction electrons in metals and semiconductors, atoms, etc.). State of these rather diverse systems are represented by the same type of functions ➔ STATE FUNCTIONS.

First postulate of Quantum mechanics:

- The state of a quantum mechanical system is completely specified by a function Ψ (x ,t) that depends on the coordinates of the particle(s) and on time.
- **This function, called the wave function or state function**
- **So, Every physically-realizable state of the system is described in quantum mechanics by a state function ψ that contains all accessible physical information about the system in that state.**
  - **Physically realizable states ➔ states that can be studied in laboratory**
  - **Accessible information ➔ the information we can extract from the wave-function**
  - **State function ➔ function of position, momentum, energy that is spatially localized.**

Postulates of Quantum Mechanics: Definition of $\Psi(r,t)$

- **The probability of funding a particle somewhere in a volume *V* of space is**
  - **Since the probability to find particle anywhere in space is 1, we have condition of normalization**
- **For one-dimensional case, the probability of funding the particle in the arbitrary interval *a* ≤ *x* ≤ *b* is**
- **It is customary to also normalize many-particle wave-functions to 1.**
- **The wave-function must also be single-valued, continuous, and finite.**

$$P_V = \int_V P(\mathbf{r},t)\,dV = \int_V \left|\Psi(\mathbf{r},t)\right|^2 dV$$

$$\int_{-\infty}^{\infty} \psi^*(\vec{r},t)\,\psi(\vec{r},t)\,d\tau = 1$$

$$\int_{all\,space} \left|\Psi(\mathbf{r},t)\right|^2 dV = 1$$

$$P_{ab} = \int_a^b \left|\Psi(x,t)\right|^2 dx$$

$$P_{everywhere} = \int_{-\infty}^{+\infty} \left|\Psi(x,t)\right|^2 dx$$

Postulates of Quantum Mechanics : Operators

Postulate 2:- To every observable in classical mechanics there corresponds a linear, Hermitian operator in quantum mechanics.

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Motivation?

- **Physical Quantity → Operators**
- **symbol ↔ actual operation**

Momentum

$$p_x \longrightarrow \hat{p}_x \longleftrightarrow \frac{\hbar}{i}\frac{\partial}{\partial x}$$

Total Energy

$$E \longrightarrow \hat{E} \longleftrightarrow i\hbar\frac{\partial}{\partial t}$$

Coordinate

$$x \longrightarrow \hat{x} \longleftrightarrow x$$

Potential Energy

$$U(x) \longrightarrow \hat{U}(x) \longleftrightarrow U(x)$$

Postulates of *Quantum Mechanics*

Postulate 3:- In any measurement of the observable associated with operator Â, the only values that will ever be observed are the eigen-values λ, which satisfy the eigen-value equation

$$\hat{A}\,\Psi(x,t) = \lambda\,\Psi(x,t)$$

- **This postulate captures the central point of quantum mechanics--the values of dynamical variables can be quantized (although it is still possible to have a continuum of eigen-values in the case of unbound states).**
- **Postulate 4:- If a system is in a state described by a normalized wave function Ψ(x,t) , then the average (expected) value of the observable corresponding to operator Â is given by**

$$\left\langle \hat{A} \right\rangle = \int_{-\infty}^{+\infty} \psi^{*}(\vec{r},t)\,\hat{A}\,\psi(\vec{r},t)\,d\tau$$

- **Postulate 5:- The wave-function or state function of a system evolves in time according to the time-dependent Schrödinger equation**

$$\hat{H}\,\psi(\vec{r},t) = i\hbar\,\frac{\partial\psi(\vec{r},t)}{\partial t}$$

- **Postulate 6:- The total wave-function must be anti-symmetric with respect to the interchange of all coordinates of one fermion with those of another. Electronic spin must be included in this set of coordinates.**
- **The Pauli exclusion principle is a direct result of this *anti-symmetry principle*.**

Eigen-values and Eigen-functions

- **QM: Observables are represented by linear Hermitian operators.**
  - **Q-What is an observable?: Ans- Operator**
  - **Q- Who is observing? Ans- Eigen function**
  - **What do you need to satisfy to be an observer?: Eigen value**

Observables are represented by linear Hermitian operators'

- What does 'Hermitian' imply?

$$Any\ operator\ \hat{A}\ is\ Hermitian \Leftrightarrow \left\langle \hat{A} \right\rangle is\ real \Leftrightarrow \left\langle \hat{A} \right\rangle = \left\langle \hat{A}^{*} \right\rangle$$

$$where\ the\ \exp ectation\ value\ \left\langle \hat{A} \right\rangle = \int \psi^{*} \hat{A} \psi\, d\tau$$

- **Equation Â Ψ(x,t)= λ Ψ(x,t) shows that Â is an operator, Ψ(x,t) is eigen function and λ is eigen value.**
- **If two eigen functions have the same eigen-value, we say that "the spectrum is degenerate".**
- **An operator does not change the 'direction' of its eigenvector.**
- **An operator does not change the state of its eigenvectors ('eigen-states', 'eigen-functions', 'eigen-kets' …) '.**
- **if the spectrum is non-degenerate then the eigen-functions are orthogonal if the spectrum is discrete, then the Ψ's are normalizable if the spectrum is continuous, then the Ψ's are not normalizable**

Properties of the Wave-function and its First (Partial) Derivative

1. must be ***finite*** for all x
2. must be ***single-valued*** for all x
3. must be ***continuous*** for all x.
4. *always obey the Schrödinger equation.*

$$\boxed{\langle U(x)\rangle = \int_{-\infty}^{+\infty} \psi^*(x)U(x)\psi(x)dx}$$

$$\boxed{\langle p_x\rangle = \int_{-\infty}^{+\infty} \psi^*(x)\left(-i\hbar\frac{\partial}{\partial x}\right)\psi(x)dx}$$

$$\boxed{\langle E\rangle = \int_{-\infty}^{+\infty} \psi^*(x,t)\left(i\hbar\frac{\partial}{\partial t}\right)\psi(x,t)dx}$$

Schrödinger Equation

- Schrödinger developed the wave equation which can be solved to find the wave-function by translating the equation for energy of classical physics into the language of waves

$$\frac{p^2}{2m} + U(x) = E \quad \longleftrightarrow \quad -\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x)}{\partial^2 x} + U(x)\psi(x) = i\hbar\frac{\partial}{\partial t}\psi(x)$$

- This is called as the time-dependent Schrödinger equation.
- For fixed energy, we obtain the time-independent Schrödinger equation, which describes stationary states

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

- the energy of such states does not change with time
  - $\psi_n(x)$ is an eigen-function or eigen-state
  - U is a potential function representing the particle interaction with the environment

The Uncertainty Principle (back ground)

- **Since we deal with probabilities we have to ask ourselves:**

  "How precise is our knowledge?"
- **Specifically, we want to know *Coordinate* and *Momentum* of a particle at time $t = 0$**
  - **If we know the forces acting upon the particle than, *according to classical physics*, we know everything about a particle at any moment in the future.**
- **But it is impossible to give the precise position of a wave**
- **A wave is naturally spread out**
- **Consider the case of diffraction**
- **Most of the energy arriving at a distant screen falls within the first maximum.**
- ***Can we know Coordinate and Momentum (velocity) at some exactly, if we deal here with probabilities?***
- **The answer in Quantum Mechanics is different from that in Classical Physics, and is encapsulated in the Heisenberg's *Uncertainty Principle***

So what is UP

"We can't measure complementary variable of matter/particle at same time to certainly."

Complementary variables are :

* Energy and time
* Any two Cartesian components of angular momentum
* Position and momentum
* Spin on different axis
* Wave and particle
* Value of a field and its change (at a certain position)
* Entanglement and coherence

The Uncertainty Principle

- *An experiment cannot simultaneously determine a component of the momentum of a particle (e.g., p_x) and the exact value of the corresponding coordinate, x.*

$$\boxed{(\Delta p_x)(\Delta x) \geq \frac{\hbar}{2}}$$

- Position and momentum are, therefore, considered as incompatible variables.
- The Heisenberg uncertainty principle strikes at the very heart of the classical physics => the particle trajectory.
- **The more accurately we know the energy of a body, the less accurately we know how long it possessed that energy**

$$\boxed{(\Delta E)(\Delta t) \geq \frac{\hbar}{2}}$$

The Uncertainty Principle

1. ***The limitations imposed by the uncertainty principle have nothing to do with quality of the experimental equipment***
2. ***The uncertainty principle does imply that one cannot determine the position or the momentum with arbitrary accuracy***
   - ***It refers to the impossibility of precise knowledge about both: e.g. if $\Delta x = 0$, then $\Delta\ p_x$ is infinity, and vice versa***
3. ***The uncertainty principle is confirmed by experiment, and is a direct consequence of the de Broglie's hypothesis.***
4. ***Quantum mechanically, the uncertainty principle forces the electron to have non-zero momentum and non-zero expectation value of position.***

Significance:-

- **Based on early estimates of the size of a hydrogen atom and the uncertainty principle, the ground-state energy of a hydrogen atom is in the eV range. The ionization energy of an electron in the ground-state energy is approximately 10 eV, so this prediction is roughly confirmed.**
- **Because the emitted photons have their frequencies within 1.1×10^{-6} percent of the average frequency, the emitted radiation can be considered monochromatic.**

Expectation Values

- **Only average values of physical quantities can be determined (can't determine value of a quantity at a point)**
- **These average values are called** *Expectation Values*
  - *These are values of physical quantities that quantum mechanics predicts and which, from experimental point of view, are averages of multiple measurements*
- *Example, [expected] position of the particle*

$$\boxed{\langle x\rangle = \int_{-\infty}^{+\infty} x P(x)\,dx, \text{ with } \int_{-\infty}^{+\infty} P(x)\,dx = 1}$$

Expectation Values

- **Since** $P(\mathbf{r},t)dV = |\Psi(\mathbf{r},t)|^2 dV$, *we have a way to calculate expectation values if the wave-function for the system (or particle) is known*

$$\langle x \rangle = \int_{-\infty}^{+\infty} x P(x,t) dx = \int_{-\infty}^{+\infty} x |\Psi(x,t)|^2 dx, \text{ since} |\Psi(x,t)|^2 = \Psi^*(x,t)\Psi(x,t)$$

$$\langle x \rangle = \int_{-\infty}^{+\infty} \Psi^*(x,t) x \Psi(x,t) dx$$

- In General for a Physical Quantity *W*
  - ***Below*** $\hat{W}$ ***is an operator (discussed later) acting on wave-function*** $\Psi(r,t)$

$$\langle W \rangle = \int_{-\infty}^{+\infty} \Psi^*(x,t) \left[\hat{W} \Psi(x,t) \right] dx$$

Expectation Value for Momentum of a Free Particle

- Generally

$$\langle p \rangle = \int_{-\infty}^{+\infty} \psi(x)^* \left[\hat{p}\,\psi(x)\right] dx = \int_{-\infty}^{+\infty} \psi(x)^* \left[\left(-i\hbar \frac{\partial}{\partial x} \right) \psi(x) \right] dx$$

$$\langle p \rangle = -i\hbar \int_{-\infty}^{+\infty} \psi(x)^* \cdot \frac{\partial \psi(x)}{\partial x}\, dx$$

- Free Particle

$$\psi(x) = Ae^{ikx} \quad \text{with} \quad \int_{-\infty}^{+\infty} \left|\psi(x)\right|^2 dx = \int_{-\infty}^{+\infty} \left[Ae^{ikx}\right]^* \left[Ae^{ikx}\right] dx = 1,$$

$$\text{where } A \to 0 \text{ as limits of integration} \to \infty$$

$$\langle p \rangle = \int_{-\infty}^{+\infty} \left[Ae^{ikx}\right]^* \left[\frac{\hbar}{i} \frac{\partial}{\partial x} Ae^{ikx} \right] dx$$

$$\langle p \rangle = \int_{-\infty}^{+\infty} \left[Ae^{ikx}\right]^* \frac{\hbar}{i} ik \left[Ae^{ikx}\right] dx = \hbar k \int_{-\infty}^{+\infty} \left[Ae^{ikx}\right]^* \left[Ae^{ikx}\right] dx = \hbar k = p$$

Dirac’s bra and ket vectors

- The Dirac Bra-Ket notation is a concise and convenient way to describe quantum states.
- A symbol $|\alpha>$ denoting quantum state is called a ket, or a ket vector.
- It is an abstract entity, and describes the "state" of the quantum system.
- We say that a physical system is in quantum state , where α represents some physical quantity, such as momentum, spin etc, when represented by the ket $|\alpha>$.
- For two distinct quantum states $|\alpha>$ and $|\beta>$, there combination describes a ket
- $|\psi>= a\ |\alpha> + b\ |\beta>$ where a and b are complex coefficients.
- So, the number of linear independent kets required to express any other ket, is called the dimension of the vector space.
- In quantum mechanics the vector space of kets is usually non denumerable infinite.
- Such a vector space is known as Hilbert space and any physical state is described by a ket in Hilbert space.
- Dirac also defined another vector called a bra vector, designated by $<\alpha|$.
- This is not a ket, and does not belong in ket space e.g. $<\alpha| + |\beta>$ has no meaning.
- For every ket $|\beta>$, there exists a bra labelled $<\beta|$.
- The bra $<\beta|$ is said to be the dual of the ket $|\beta>$.
- The dual of $|\psi>= a\ |\alpha> + b\ |\beta>$ is a bra $<\psi|= a^*<\alpha| + b^* <\beta|$.
- The ‘bra-ket’ is the inner product defined as $<\alpha|\beta>= (|\alpha> , |\beta>)= (<\beta|\alpha>)^*$

Bra-ket: Dirac notation

•The scalar (inner) product is defined by the symbol <|>, called a a *bra-ket.*

• The scalar product (ϕ,ψ) is denoted by the bra-ket < ϕ|ψ> analogous to

$$\langle \varphi | \psi \rangle = \int \varphi^{*}(\vec{r},t)(\vec{r},t)d\tau$$

• Wave-functions is denoted as ψ(r,t) in wave mechanics *, but in the more general* formalism of quantum mechanics its role is played by abstract kets | ψ >.

•Note: When a ket (or bra) is multiplied by a complex number, we get a ket (or bra).

• Properties of kets, bras, and bra-kets:

- Every ket has a corresponding bra
- A scalar product <ϕ|ψ> must be distinguished from its complex conjugate.
- Here product <ψ|ϕ> is not the same thing as <ϕ|ψ> : i.e. <ϕ|ψ> *= <ψ|ϕ> .
- The norm is real and positive.
- Existence of Schwarz inequality, $\left|\langle \psi | \varphi \rangle\right|^{2} \leq \langle \psi | \psi \rangle \langle \varphi | \varphi \rangle \Leftrightarrow \left|\vec{A}\cdot\vec{B}\right|^{2} \leq \left|\vec{A}\right|^{2}\left|\vec{B}\right|^{2}$
- Existence of Triangle inequality $\sqrt{\langle(\psi+\varphi)(\psi+\varphi)\rangle} \leq \sqrt{\langle \psi | \psi \rangle} + \sqrt{\langle \varphi | \varphi \rangle} \Rightarrow \left|\vec{A}+\vec{B}\right| \leq \left|\vec{A}\right| + \left|\vec{B}\right|$
- Orthogonality property of eigen states <ψ|ϕ> =0.
- Orthonormality property of states : <ψ|ϕ> =0, <ψ| ψ > =1, < ϕ |ϕ> =1.
- If |ψ > and |ϕ > belong to the same vector (Hilbert) space, products of the type <ψ| <ϕ| and | ψ > | ϕ > are forbidden.
- Eigen ket |ψ > may also be written as $|\psi\rangle = \sum_{n} c_n |a_n\rangle;\ c_n = \langle a_n | \psi \rangle; \sum_{n} |a_n\rangle\langle a_n = 1|$