Quantum Mechanics

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Quantum Mechanics

- Classical Mechanics: The branch of science that is based on Newton's laws of motion is called as **Classical Mechanics.**
- These laws were found to explain the properties of all the macroscopic particles moving with speeds much less than the speed of light .
- Classical mechanics can be applied to only macroscopic particles as the position as well as momentum can be predicted accurately for these particles .

- Classical mechanics assumes that the energy is absorbed or emitted in a continuous manner. But according to Planck's theory , the transition of energy is in the form of packets called as quanta.
- There are four phenomenon which could not be explained on the basis of classical mechanics which are **Black body radiation, Photoelectric effect, Heat capacity of solids, Atomic spectra of hydrogen.**

- Black body radiation :When light falls on any body ,part of the light is absorbed and part is reflected. The body which absorbs the entire radiations incident on it is called as **perfectly black body.**
- Perfectly black body is not only a good absorber of light but is also a good emitter of radiations
- Black body is a hallow sphere blackened on the inside with lamp black.It has a small aperture on one side and small hump on the opposite wall so that the light should get reflected number of times inside the body.

- Stefan studied the radiations from black body and found that the amount of energy by a perfectly black body per unit area per unit time is directly proportional to fourth power of absolute temperature

$$E \alpha\ T^4 \text{ OR } E= \sigma T^4$$

Where σ = Stefan's constant and the law is called as Stefan-Boltzmann's fourth power law.

This energy emitted by a black body does not consist of a single wavelength but it is uniformly distributed along a spectrum.At different temperatures, the spectrum obtained is shown as

- Important features of the spectrum are

1. At a particular temperature ,the energy corresponding to all the wavelengths is not equal.
2. For each temperature,the maximum energy corresponds to a specific wavelength.This wavelength is denoted by λ_m and the energy E_m.

3. The area under the curve at any temperature gives the total amount of energy emitted per unit area per second.This is in accordance with Stefan’s law.

4. With increase in temperature,the maxima becomes sharper and shifts towards lower value of wavelength and also the area under curve increases. It means that, with increase in temperature, the total energy emitted increases and λ_m decreases.

5. The wavelength corresponding to maxima is inversely proportional to absolute temperature.

   That is , $\lambda_m \ \alpha \ \frac{1}{T}$:. λ_m T = Constant

This is called as Wien’s displacement law.This law explains why the colour of hot body changes on heating.

- In order to explain the black body radiation,Rayleigh and Jeans used classical mechanics

According to Wein's radiation law,

$$E_\lambda = \frac{8\pi hc}{\lambda^5} e^{-hc/kt\lambda} \text{.......................}(1)$$

According to Rayleigh-Jeans law, the equation is

$$E_\lambda = \frac{8\pi}{\lambda^4} Kt \text{..................................}(2)$$

Both of these equations failed to explain the entire spectrum of black body radiation.Wein’s law is obeyed at only shorter wavelengths while Rayleigh-Jean’s law is obeyed at only longer wavelengths.

Ultraviolet Catastrophe

- The emission of large amount of energy by black body radiation in high frequency region i.e. shorter wavelength. Is called as Ultraviolet Catastrophe.
- This phenomenon can not be explained on the basis of classical machanics.
- It is accurately explained by Max Planck on the basis of quantum theory.

- According to this theory-
- Energy is emitted or absorbed in the form of small packets called as quanta.
- Energy of each quantum is given by hv.
- Thus , the total energy emitted or absorbed is integral multiple of hv.

Based on these concepts,Planck deduced expression for the energy radiated by a black body at wavelength ⅄ as-

$$E_{⅄} = \frac{8\pi hc}{⅄^5} * \frac{1}{e^{hc/kt⅄} - 1} \quad \ldots\ldots\ldots\ldots(3)$$

This expression is called as Planck's Radiation Law.

- At shorter wavelength: When ⅄ is small, $e^{hc/kt\lambda} >> 1$.Hence, equation 3 becomes

$$E_{\lambda} = \frac{8\pi hc}{\lambda^5} e^{-hc/kt\lambda}$$

This is Wein's law. It is obeyed at shorter wavelengths.

- At longer wavelength: When ⅄ is larger, the binomial expansion of $e^{hc/kt\lambda}$ can be written as

$$e^{hc/kt\lambda} = (1 + x)^n = 1 + \frac{hc}{kT\lambda} + - - - - - - -$$

Eq.3 becomes

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

Neglecting the higher terms we get ,

$$E_\lambda = \frac{8\pi hc}{\lambda^5}\left[\frac{1}{\frac{hc}{kT\lambda}}\right] = \frac{8\pi hc}{\lambda^5}\left[\frac{kT\lambda}{hc}\right] = \frac{8\pi kT}{\lambda^4} \quad ....(5)$$

This is Rayleigh-Jean's law. It is obeyed at longer wavelengths. Hence Plank's quantum theory can explain the phenomenon of black body radiation over entire spectrum of wavelength.

Photoelectric effect

- When a beam of light of sufficiently high frequency is allowed to strike a metal surface , electrons are ejected from the metal surface. This phenomenon is called as photoelectric effect. The ejected electrons are called as photoelectrons.

Properties of Photoelectric effect

- Electrons are ejected only if frequency of incident light is equal to or greater than a minimum frequency called as threshold frequency (v_0).
- There is no time lag between incidence of light and ejection of electron.That is electrons are ejected instantaneously.
- Kinetic energy of ejected electrons depends upon the frequency of incident radiation
- The number of electrons ejected dependsupon the intensity of incident radiation.

- According to classical mechanics, the energy of light depends upon intensity and not on the frequency. Hence, if light of sufficiently high intensity is allowed to incident on the metal, electrons should have emitted irrespective of the frequency of light . But this is not the case. Hence, classical mechanics fails to explain these properties of photoelectric effect.

- According to Planck's Quantum Theory,light consists of small packets of energy called as photons. They have energy hv . When photon incidents on a metal surface , the energy equal to hv_0 is used for ejection of electron.This is called as work function(ϕ),which is fixed for a specific metal.Remaining energy is given to the emitted photoelectron in the form of kinetic energy.

- $hv = hv_0 + \frac{1}{2}mv^2$ ……………………..(1)

Where hv_0 =ϕ is called as work function. It is the minimum amount of energy required for observing photoelectric effect.

$\frac{1}{2}mv^2$ = kinetic energy of ejected photoelectron.

Kinetic energy = $(hv - hv_0)$

Heat capacity of solids

- The amount of heat required to raise the temperature of 1g of a solid through $1^{0}C$ is called as heat capacity of that solid.
- Dulong and Petit found that for all the monoatomic solids,the molar heat capacity is same with value of about 25 JK^{-1} mol^{-1} .
- According to classical mechanics,every molecule can be considered as an oscillator with vibrational energy 3kT(Boltzmann constant).

- Thus ,total vibrational energy of one mole of oscillators (N_A atoms) is given by –

  $E = N_A\ (3kT) = 3RT$

  $$\left(\frac{dE}{dT}\right) = 3R$$

From the definition of molar heat capacity at constant volume,

$$\left(\frac{dE}{dT}\right) = C_v$$

.: $C_v = 3R = 3 \times 8.314 = 24.9\ JK^{-1}\ mol^{-1}$

this shows that classical mechanics can very well explain the observed value of heat capacity of solids. However, at low temperature when $T \rightarrow 0$, the heat capacity is lower than 3R.

- This observation can be explained on the basis of quantum theory.
- Einstein applied quantum mechanics to the oscillator and suggested that the energy of all oscillators is not same, but they have energy values integral multiples of $h\nu_0$. The mean energy of oscillator is given by –

$$E_m = \frac{3h\nu 0}{e^{\frac{h\nu 0}{kT}} - 1} \qquad \text{..............................} \; 1$$

- For one mole of solid,

$$E = N_A E_m = \frac{3N_A h\nu_0}{e^{\frac{h\nu 0}{kT}} - 1} \quad \text{...........................2}$$