QC-2 QUANTUM CHEMISTRY (Classical Concept)

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I. CLASSICAL MECHANICS (*Newtonian Mechanics*)

- Based on *Newton's laws of motion* :**I- *law*** (*inertia*), **II- *law*** (*force*), **III- *law*** (*action and reaction*)
- Classical mechanics considers a system as a particle which can be ***localized*** (its position is known) having ***continuous energy*** *i.e., closely spaced & appears as band*). e.g., KE = ½ mv^2 (no defined value for velocity)
- *Classical mechanics*–Applicable to ***macroscopic*** particles-Fails when applied to microscopic particles (e , p , n, atoms & molecules)
- *The wave length of a bigger particle will be very less i.e., As mass increases, λ decreases* **λ α (1/m) ; λ = h/p**
- *Classical mechanics fails to explain some modern experiments* (Photoelectric effect, Blackbody radiation and Atomic spectrum of hydrogen).
- **Wave:** Delocalized **–** characterized by **λ** and **υ.**
- Particle has a wave nature- ***de Broglie relation*** λ = h/p = h / mv.

II. PHOTOELECTRIC EFFECT

- *Electromagnetic radiation* (X-ray or UV) – incident on metals like alkali metals(because of low ionization energy), Cs, Fr- emit electrons.(E = hν)
- $h\upsilon = w_o + KE$; $h\upsilon = h\upsilon_o + \frac{1}{2} mv^2$, $\mathbf{w_o}$ = work function ; $\boldsymbol{\upsilon_o}$ = Threshold frequency

Observations

1. A metal emits electrons only if a certain radiation is used.
2. The KE of emitted electron is proportional frequency of light used.
3. Energy of the radiation applied = energy used to remove electron + energy used by the electron to possess kinetic energy
4. Number of electrons emitted is directly proportional to the intensity, I of the light.
   - *Threshold frequency,* υ_o (around-10^{14} Hz) – which is needed to exhibit photoelectric effect-Quantization of energy.
   - *Work function* (**w_o**)**:** The electromagnetic energy used to do work against electrostatic force of attraction between electron and nucleus.
   - *Photoelectric effect explains the quantization of energy & particle nature of light.*

Metal	υ_o , Hz	$\lambda_o = (c/\ \upsilon_o)$, nm	$w_o = h\ \upsilon_o$, J	w_o , eV
K	5.8×10^{14}	517	3.843×10^{-19}	2.398
Mg	9.0×10^{14}	333	5.963×10^{-19}	3.722
Ca	4.8×10^{14}	625	$3.18\ 0 \times 10^{-19}$	1.985
Ni	12.5×10^{14}	240	8.281×10^{-19}	5.169
Zn	10.7×10^{14}	280	7.084×10^{-19}	4.422
Pt	13.5×10^{14}	222	8.943×10^{-19}	5.58

- 1eV = 1.602×10^{-19} J molecule^{-1} = 96485 J mol^{-1} = 8065.5 cm^{-1}
- 1nm = 10^{-9} m
- 1A = 10^{-8} cm = 10^{-10} m = 0.10 nm

Conclusions

1. Energy of electron is discontinuous. **Reason:** Only frequency equal to or greater than threshold frequency can cause **PE** effect
2. In favor of particle nature. **Reason:** Light behaves as particle & transfers energy to electrons and the electrons are ejected with certain KE.

III. COMPTON EFFECT

Light falling on a beam of electron undergoes scattering. The scattered light has longer wavelength than the incident radiation.

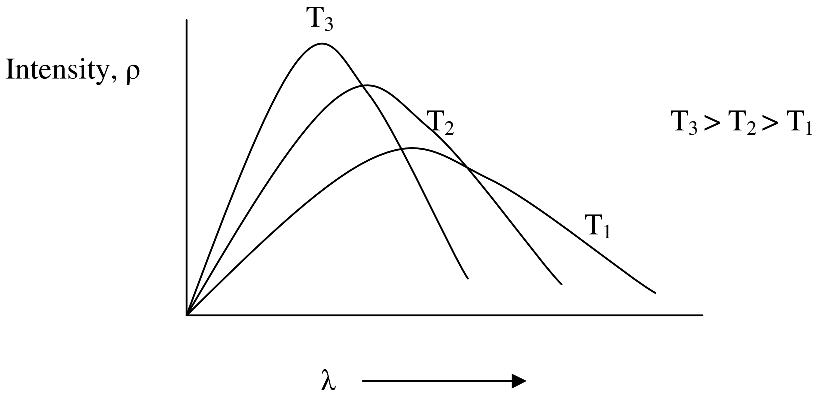
IV. DIFFRACTION*:*

1. *Phenomenon characteristic of wave*
2. *Bending of wave through a narrow slight*
3. *Diffraction obeys Bragg's law* $n\lambda = 2d\sin\theta$
4. *Suggest the wave nature of electron*

V. BLACK BODY RADIATION– Black body = Perfect emitter and absorber of radiation.(Energy vs Wavelength).

- λ_{max} wave length corresponding to maximum intensity
- λ_{max} shifted to lesser value as temperature increases (visible to uv).
- λ of emitted light decreases with the increase in temperature.
- $\lambda_{max}\ \alpha\ 1/T$; $\lambda_{max}\ T$ = constant (***Wien's law***)
- The area under the curve is proportional to the total energy emitted & represents the intensity of light emitted.

- Energy emitted by unit area of cross section , $U \propto T^4$ (***Stefen displacement law***)



Classical Theory: Rayleigh's Concept

$$\text{Intensity, } \rho = \frac{8\pi v^2 kT}{c^2}$$

Energy is continuous according to the classical frequency, ν

Planck's Theory:

$$\text{Intensity, } \rho = \frac{8\pi hc}{\lambda^3}\left[e^{h\nu/kT} - 1\right]^{-1}$$

Energy is discontinuous in units of hν/kT

VI. ATOMIC SPECTRUM OF HYDROGEN–Emission spectrum-Line spectrum-Lymann (Transition from higher to 1^{st} orbit).

Balmer, Paschen, Brackett, Pfund Series of lines transition from higher to 2^{nd} , 3^{rd} 4^{th} 5^{th} orbit, respectively.

$$\text{Wave number , } \bar{\upsilon} = R_H \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\} m^{-1}$$

NB: $1\ cm^{-1} = 100\ m^{-1}$

- R_H = Rydberg's constant for hydrogen = $1.097 \times 10^7\ m^{-1} = 1.097 \times 10^9\ cm^{-1}$;

  NB: $1\ m^{-1} = 100\ cm^{-1}$

- The λ of light emitted increases from Lyman to Pfund series.

- ***Lyman Series***

  $\mathbf{n_1} = 1$; $\mathbf{n_2} = 2,3,4,5$ …….......… **UV** region

- ***Balmer Series***

  n_1 = 2 ; **n_2** = 3, 4, 5 , 6 , 7 ……… **Visible** region

- ***Paschen Series***

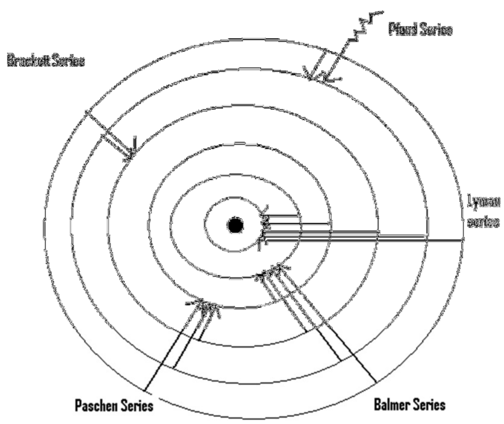
  n_1 = 3 ; **n_2** = 4, 5, 6, 7, 8 ……… .**Near IR** region

- ***Brackett Series***

  n_1 = 4 ; **n_2** = 5 , 6 , 7 , 8 ,9 ……… **Far IR** region

- ***Pfund Series***

  n_1 = 5 ; **n_2** = 5 , 6 , 7 , 8 ,9 ……… **Far IR** region



- Shortest wave length (highest energy) in each series can be obtained by putting **n_2** = ∞
- Longest wave length (least energy) in each series can be obtained by putting **n_2** = the next number in that series.
- **IE of H *atom*:** 13.6 eV = 1.312×10^6 J mol^{-1} = 1312 $kJmol^{-1}$

  n_1 = 1 ; **n_2** = ∞ ; get wave number and then E

$$E = h\upsilon = \frac{hc}{\lambda} = hc\bar{\upsilon} \text{ , J atom}^{-1}$$

- Splitting of spectral lines when recorded using a high resolving spectrophotometer- presence of sub-energy levels called **orbitals**.
- ***Zeemann Effect*** -Splitting of spectral lines in the presence of magnetic field- Directional properties of orbitals-Magnetic quantum number.
- ***"H" like*** species: He^+ , Li^{2+} are isoelectronic & should give emission spectrum similar to hydrogen atom.

VII. BOHR'S THEORY OF "H" ATOM (Neil Bohr-1913)

1. The electron revolves around the nucleus only in allowed (fixed) circular orbits.
2. The angular momentum of the electron is an integral multiple of $h/2\pi$.

   mvr = n (h/2π), $h = 6.625 \times 10^{-34}$ Js.
3. These orbits are called stationary orbits and an electron revolving in these orbits does not radiate or absorb energy.
4. An atom radiates energy when the electron in it jumps from higher energy to lower energy.

$$E = \frac{-2\pi^2 m z^2 e^4}{n^2 h^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The radius of the **orbit** is proportional to the square of the principal quantum number. Therefore the radii of the orbit are in the ratio 1:4:9:25 etc.

The negative sign in equation for energy indicates that the energy of the electron increases as **n** increases. Equation-11 also suggests that to remove an electron from the first orbit(n = 1)of the hydrogen atom i.e. to ionize an atom, the energy required is **13.6 eV**. This is known as **ionization energy** or the **ionization potential of the atom.**

According to Bohr's second postulate, when an electron jumps from an outer orbit to an inner orbit the frequency of the photon emitted is given by,

$$E_1 - E_2 = h\upsilon$$

$$\upsilon = \frac{2\pi^2 m Z^2 e^4}{h^3}\left\{\frac{1}{n_1^2} - \frac{1}{n_2^2}\right\} \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The wave number (ύ) of a radiation is defined as the reciprocal of its wavelength

Where c is the velocity of light.

Therefore from equation-2

$$\bar{\upsilon} = \frac{2\pi^2 m Z^2 e^4}{ch^3}\left\{\frac{1}{n^2_1} - \frac{1}{n^2_2}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

$$R_H \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(4)}$$

Rydberg's constant for hydrogen, $R_H = 1.094 \times 10^7\ m^{-1}$

The value of **R_H for helium** is **$4 \times 1.094 \times 10^7\ m^{-1}$**

Quantum numbers-n,l,m,s (Concept of orbitals)