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Content

ATOMIC STRUCTURE, BONDING, GENERAL ORGANIC CHEMISTRY AND ALIPHATIC HYDROCARBONS

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BLOCK I: ATOMIC STRUCTURE

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BLOCK IV: HYDROCARBONS

■■

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QUESTION PAPER

June – 2024

(Solved)

BCHCT-131

ATOMIC STRUCTURE, BONDING, GENERAL ORGANIC CHEMISTRY AND ALIPHATIC HYDROCARBONS

Time: 2 Hours] *[Maximum Marks: 50*

Note: *Attempt any* ***five*** *questions from Part-A and any* ***five*** *questions from Part-B. All questions carry equal marks.*

PART-A

Q. 1. ***(a)*** **What are the main postulates of Bohr's atomic theory?**

Ans. Ref.: See Chapter-1, Page No. 2, 'Bohr's Atom Model'.

(b) **What is the energy value of an electron if** $n = \infty$ **?**

Ans. At $n = \infty$, the energy of the electron is 0 eV. This corresponds to the point where the electron has been completely removed from the atom, meaning it is at an infinite distance from the nucleus and is no longer bound to the atom.

Q. 2. ***(a)*** **State the Heisenberg's uncertainty principle.**

Ans. Ref.: See Chapter-2, Page No. 12, 'Heisenberg Uncertainty Principle'.

(b) **Write the resonance structures of nitrate ion.**

Ans. Ref.: See Chapter-8, Page No. 78, Q. No. 3.

Q. 3. Write the electronic configuration of Niobium (At. no. = 41). Does it follow Aufbau's principle? Explain giving reasons.

Ans. Ref.: See Chapter-5, Page No. 37, 'Anomalous Electronic Configuration'.

Q. 4. ***(a)*** **What is ionisation energy?**

Ans. Ref.: See Chapter-6, Page No. 45, 'Ionisation Energy'.

(b) **Which one has lower ionisation energy-oxygen or nitrogen? Give reason in support of your answer.**

Ans. Nitrogen has a higher ionization energy than oxygen. Nitrogen's electron configuration ($1s^2 2s^2 2p^3$) has a stable half-filled 2p subshell, making it harder to remove an electron. Oxygen ($1s^2 2s^2 2p^4$) has one extra electron in the 2p subshell, leading to electron-electron repulsion, which makes it easier to remove an electron. Thus, oxygen has lower ionization energy than nitrogen due to reduced stability from electron pairing.

Q. 5. Giving all the steps, write the Lewis structure of CO_2**.**

Ans. Ref.: See Chapter-7, Page No. 69, Q. No. 2.

Q. 6. List the different types of quantum numbers and give the significance of quantum numbers.

Ans. Ref.: See Chapter-4, Page No. 30, Q. No. 1.

Q. 7. Write short notes on the following:

(a) **Linear Combination of Atomic Orbital (LCAO).**

Ans. Ref.: See Chapter-9, Page No. 84, 'LCAO Method'.

(b) **Applications of Schrodinger Equation.**

Ans. Ref.: See Chapter-3, Page No. 21, 'Applications of Schrodinger Equation'.

PART-B

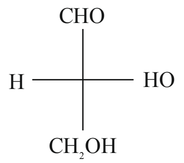
Q. 8. ***(a)*** **What is the difference between enantiomers and diastereomers? Give one example of each.**

Ans. Ref.: See Chapter-10, Page No. 100, 'Enantiomers' and 'Diastereomers'.

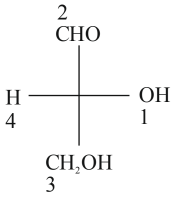
(b) **Why is the staggered conformation of ethane more stable than its eclipsed conformation?**

Ans. Ref.: See Chapter-12, Page No. 124, Q. No. 2, (Terminal Questions).

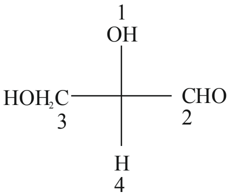
Q. 9. What are the rules for assigning R or S configuration of a molecule? Assign R or S configuration to the following molecule:



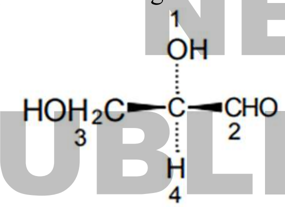
Ans. The Fischer projection formula of D-(+)-glyceraldehyde can be written as follows:



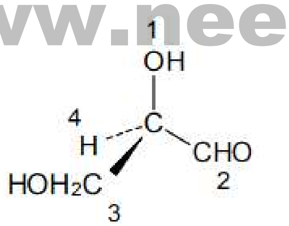
The four substituents attached to the chiral centre have the order or priorities as shown by the numbers 1>2>3>4. Fischer projection into another Fischer projection as shown below:



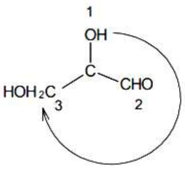
This new Fischer projection corresponds to the following perspective drawing.



The molecule is then projected in such a way that H is at the back:



Then, by overlooking this H, path from 1 → 2 → 3 is traced as illustrated below.



Since, this path is clockwise, hence, D-(+)-glyceraldehyde is assigned R configuration.

Q. 10. What is the difference between basicity and nucleophilicity? Explain with the help of an example.

Ans. Ref.: See Chapter-14, Page No. 146, 'Basicity and Nucleophilicity'.

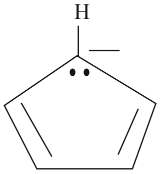
Q. 11. What is Huckel's rule? Classify the following compounds as aromatic or non-aromatic and justify your answer:

Ans. Ref.: See Chapter-19, Page No. 200, 'Huckel's Rule'.

(i)

Ans. Ref.: See Chapter-19, Page No. 200, 'Cyclobutadiene'.

(ii)



Ans. Ref.: See Chapter-19, Page No. 201, Q. No. 6*(c)*.

Q. 12. Arrange the following acids in the increasing order of their acid strength. Give reasons for your answer:

CH_3COOH; $Cl_2CHCOOH$; $ClCH_2COOH$; Cl_3CCOOH

Ans. Ref.: See Chapter-13, Page No. 132, 'Factors Affecting Strength of Acids and Bases'.

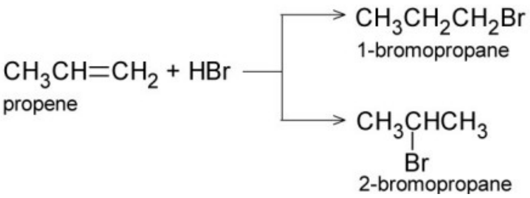
Q. 13. Complete any *two* of the following reactions and give their mechanism:

(i) $CH_3CH = CH_2 + HBr \longrightarrow$

(ii) $CH_3CH = CH_2 + HBr \xrightarrow{\text{Peroxide}}$

(iii) $CH = CH + H_2O \xrightarrow{\text{Catalyst}}$

Ans. *(i)*



Ans. Ref.: See Chapter-17, Page No. 180, 'Markownikoff's Rule'.

Ans. Ref.: See Chapter-17, Page No. 180, 'Peroxide Effect'.

Ans. Ref.: See Chapter-17, Page No. 181, 'Hydration' and 'Mechanism'.

Q. 14. Predict the main product of any *five* of the following:

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Atomic Structure, Bonding, General Organic Chemistry and Aliphatic Hydrocarbons

Bohr's Theory

1

INTRODUCTION

In this first chapter on Atomic Structure earlier developments and models for the structure of the atom will be discussed. Atomic models proposed by Dalton, Thomson and Rutherford will be dealt initially.

This will be followed by Bohr's proposed model in detail enabling one to calculate the radius of orbits and energy of an electron in a particular orbit. An elementary idea about the atomic spectrum will help in understanding the spectrum of hydrogen atom on the basis of Bohr's theory then its achievments and limitations will be discussed. This follows the modifications in Bohr's theory proposed by Sommerfeld.

CHAPTER AT A GLANCE

EARLIER ATOMIC MODELS : DALTON, THOMSON AND RUTHERFORD MODELS

Greek philosophers in 400 B.C. held that atoms would be the ultimate result of continued sub-division of matter. The word 'atom' is derived from the Greek word 'atomos' which means 'uncut' or indivisible. Models proposed by Dalton, Thomson and Rutherford are presented now.

The postulates of Dalton's atomic theory are as follows:

1. Matter consists of small indivisible particles called atoms.
2. Atoms present in an element are similar.
3. When one or more elements combine they form a compound.
4. Atoms of various elements are of different masses.
5. When a chemical reaction takes place, atoms are neither created nor destroyed and new products are formed by exchange reaction.

Dalton's atomic theory needed revision after the discovery of sub-atomic particles like electron. Then Thomson in 1904 proposed 'plum pudding model' of the atom (Fig. 1.1) of uniform sphere of radius 10^{-8} cm having positive charge at the centre and electrons embedded in it to give it a stable electrostatic arrangement.

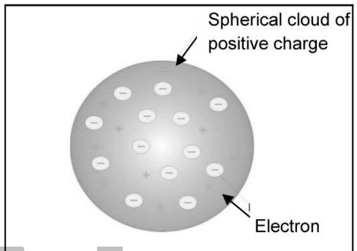
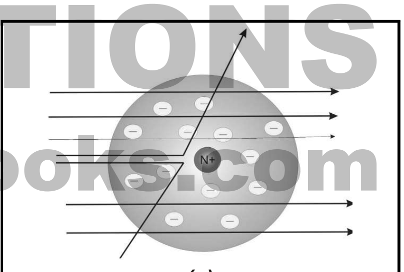


Fig. 1.1: Thomson plum pudding model

But this model failed to account for scattering of α-particles falling on thin gold foil as observed by Geiger and Marsden (1909).



(a)

Fig 1.2: Deflection of α-particles by nuclel of metal foil (a) Observed results

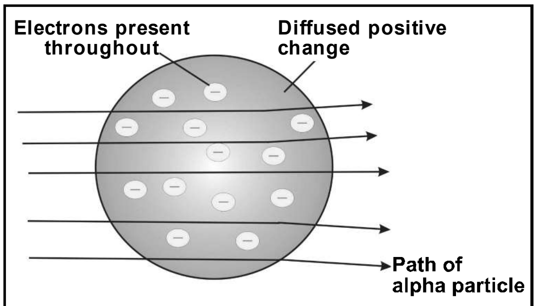


Fig 1.2: *(b)* Expected outcome of the experiment. Curved lines shows the path of extra straight lines indicate the path of those not deflected.

Thomson proposed an atom to be uniform sphere consisting of positively charged particles and electrons embedded in such a way to give it the most electrostatic arrangement.

Rutherford suggested a model, where nucleus accounted for the positive charge and mass, at the centre and negative particles surrounding it. The electrons rotated about the nucleus similar to the movement of planets around the Sun.

BOHR'S ATOM MODEL

Niels Bohr (1913) suggested an improved atomic model to explain the stability and spectrum of the hydrogen atom.

(i) An electron would rotate in stationary orbits is those having definite energy and angular momentum.

(ii) The electron does not radiate energy, while moving in selected orbit.

(iii) The angular momentum of the electron in an orbit is an integral multiple of $\frac{h}{2\pi}$ units.

$$mvr = \frac{nh}{2\pi} \qquad ...(1.1)$$

where, *m* and *v* are the mass and velocity of the electron, *r* is the radius of the orbit and *n* is an integer known as principal quantum number *h* is Planck's The constant orbits are called K, L, M, N ...corresponding to the values of *n viz,* 1, 2, 3, 4...

(iv) When an electron moves from one orbit to another, it emits or absorbs radiation of definite frequency, which is seen as spectral line. The change in energy, ΔE between this transition is related to the spectral line by the equation:

$$\Delta E = hv = hc\overline{v} \qquad ...(1.2)$$

where, c is the velocity of light and $\overline{v}$ is wave number. The radii of different orbits in hydrogen atom, the energy of the electron present in various orbits and the frequency of the spectral lines can thus, be calculated.

Calculation of Radius of Orbits

The radius of orbit is given by:

$$r = \frac{n^2 \in_0 h^2}{\pi mZe^2}$$

Radius of the first Bohr orbit (r_1) for hydrozen atom (n = 1, z = 1)

$$r_1 = \frac{1^2 \times 8.854 \times 10^{-12} \times (6.636 \times 10^{-34})^2}{3.142 \times 9.109 \times 10^{-31} \times 1 \times (1.602 \times 10^{-19})^2}$$

= 53 × 10^{-12} *m*

= 53 *pm* (approx).

Energy of an Electron in an Orbit

The total energy, E_n, of an electron in the n^{th} orbit, is equal to the sum of its Potential Energy (P.E.) and Kinetic Energy (K.E.) i.e. E_n = PE + KE. ...(1.3)

The potential energy of an electron is the amount of work done in removing the electron to inifinte distance from its equilibrium distance *r*, with respect to the nucleus. The force of attraction (f_a) between the nucleus and the electron is $\frac{-Ze^2}{4\pi \in_0 r^2}$ as in eq. 1.4

$$\text{P.E.} = \int_r^\infty f_a . dr = \int_0^\infty \frac{-Ze^2}{4\pi \in_0 r^2} dr = \frac{-Ze^2}{4\pi \in_0} \int_r^\infty \frac{dr}{r^2}$$

$$= \frac{-Ze^2}{4\pi \in_0} \left[\frac{1}{r}\right]_r^\infty$$

$$= \frac{-Ze^2}{4\pi \in_0 r}$$

The negative sign implies that work has to be done against the attractive force to remove electron to infinity.

$$\text{K.E.} = \frac{mv^2}{2}$$

Putting the values of PE and KE in eq. 1.3

$$E_n = \frac{Ze^2}{4\pi \in_0 r} + \frac{mv^2}{2} \qquad ...(1.4)$$

$$\text{We know } \frac{mv^2}{2} = \frac{Ze^2}{8\pi \in_0 r} \qquad ...(1.5)$$

$$\text{So, } E_n = \frac{Ze^2}{8\pi \in_0 r} - \frac{Ze^2}{4\pi \in_0 r} = \frac{-Ze^2}{8\pi \in_0 r} \qquad ...(1.6)$$

Substituting the value of *r*

$$E_n = \frac{-Ze^2}{8\pi \in_0} \bullet \frac{\pi mZe^2}{n^2 \in_0 h^2} = \frac{-Z^2 e^4 m}{8 \in_0^2 h^2 n^2} \qquad ...(1.7)$$

In the above eq. negative sign denotes that work must be done to remove the electron against the attractive force. The energy of the electron in the n^{th} orbit of the hydrogen atom is given by putting the values of *e*, *m*, $\in_0$ and *h* in Eq. 1.7.

$$E_n = \frac{-1^2 \times (1.602 \times 10^{-19} \text{C})^4 \times 9.109 \times 10^{-31} \text{ kg}}{8 \times (8.854 \times 10^{-12} \text{C}^2 \text{N}^{-1} m^{-2})^2 \times (6.26 \times 10^{-34} \text{Js})^2 \times n^2}$$

$$E_n = \frac{-2.178 \times 10^{-18}}{n^2} \text{J} \qquad ...(1.8)$$

When the electron is in the first orbit *n* = 1, *z* = 1 for hydrogen atom then its energy is – 2.178 × 10^{-18}J.

As 'n' becomes sufficiently large, the energy levels differs only slightly. This is called convergence of the energy levels.

HYDROGEN ATOM SPECTRUM AND BOHR'S THEORY

Atomic spectrum is obtained, when gases or vapours of a chemical substance are heated in a bunsen flame or an electric arc. A line spectrum is produced, when a ray of light passes through a prism. This spectrum consists of a limited number of coloured lines, each having different wavelength of light. Atomic spectra of elements have discrete spectral lines at lower frequencies followed by a continuous spectrum at very high frequencies.

Atomic spectrum of hydrogen shows three series of lines *viz.* Lyman, Balmer and Paschen.

Balmer series is given by eq. 1.9.

$$\bar{v} = \frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \qquad \text{... (1.9)}$$

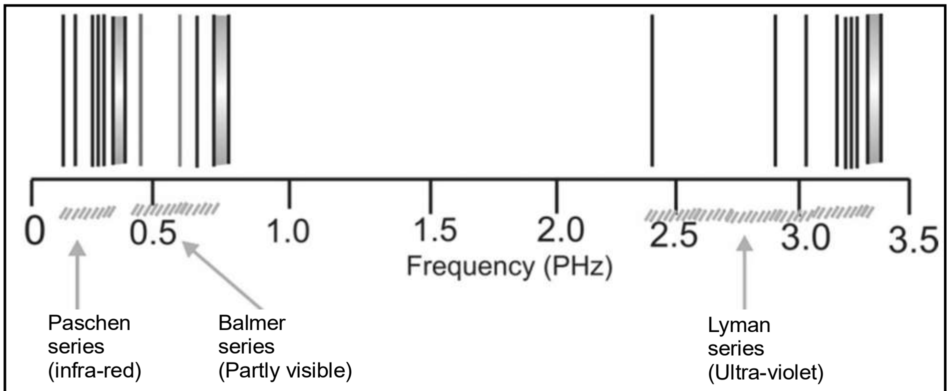


Fig. 1.3. Discrete lines followed by continuum in the atomic spectrum of hydrogen

Where R is Rydberg constant and its value is $1.097 \times 10^7 m^{-1}$ and *n* is an integer 3, 4, ..., etc.

$$\bar{v} - \bar{v}_\infty = \frac{R}{(n - d^2)} \qquad \text{...(1.10)}$$

It is observed that spacing between the lines decreases with increase in frequency. The spectral lines converge to form a continuous spectrum at very high frequencies. Lyman and Paschen series are seen in the ultraviolet and infrared regions, respectively.

Ritz proposed for hydrogen, new spectral series given by the eqn. $\bar{v} = R\left(\frac{1}{m^2} - \frac{1}{n^2}\right)$ ...(1.11)

Where *m* and *n* are integers and *m* is constant for a given series. Classical physics was unsuccessful in explaining discrete and continuous spectra discussed above. This was explained by Bohr's theory.

Assuming that E_1 and E_2 are the energies of the inner and outer orbits having quantum numbers n_1 and n_2 respectively.

$$E_1 = \frac{-Z^2 e^4 m}{8 \epsilon_0^2 h^2} \cdot \frac{1}{n_1^2} \qquad \text{...(1.12)}$$

$$E_2 = \frac{-Z^2 e^4 m}{8 \epsilon_0^2 h^2} \cdot \frac{1}{n_2^2} \qquad \text{...(1.13)}$$

Energy liberated, when transition of electron occurs from outer level n_2 to inner level n_1.

$$E_2 - E_1 = \frac{-Z^2 e^4 m}{8 \epsilon_0^2 h^2}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

$$\Delta E = \frac{Z^2 e^2 m}{8 \epsilon_0^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \text{...(1.14)}$$

$$\bar{v} = \frac{\Delta E}{hc} = \frac{Z^2 e^4 m}{8 \epsilon_0^2 h^3 c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \text{...(1.15)}$$

The term $\frac{Z^2 e^4 m}{8 \epsilon_0^2 h^3 c}$ is Rydberg constant (R_H) for hydrogen atom

$= 1.097 \times 10^7 m^{-1}$

Thus, $\bar{v} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ ...(1.16)

The frequencies of the spectral lines in Lyman, Balmer, Paschen, Brackett and Pfund series can be calculated. The values of n_1 and n_2 for the above series are tabulated in following table:

Table 1 : Series of spectral lines in the atomic spectrum of hydrogen

Name of the series	n_1	n_2	**Region**
Lyman	1	2,3,4,...	Ultraviolet
Balmer	2	3,4,5,...	Visible
Paschen	3	4,5,6,...	Infrared
Brackett	4	5,6,7,...	Infrared
Pfund	5	6,7,8,...	Infrared

From eq. 1.14 it was concluded that continous spectra is seen at a particular point. At this point the electron is beyond the sphere of influence of the nucleus ($n_2 = \infty$). This point is called the Ionisation energy of the hydrogen atom:

$$H(g) \rightarrow H^+(g) + e^-$$

CRITICAL ANALYSIS AND LIMITATIONS OF BOHR'S THEORY

Bohr's theory has been successful in explaining the *(a)* Atomic spectrum of the hydrogen, *(b)* Rydberg constant value, and *(c)* ionisation energy of hydrogen.

The theoretical and experimental values are in agreement with each other.

The ionisation energy for hydrogen atom is calculated as:

here $n = 1$, $n_2 = \infty$

$$\bar{\nu} = R_H\left(\frac{1}{1^2} - \frac{1}{\infty^2}\right) = R_H = 1.097 \times 10^7 m^{-1}$$

But in chemical reactions, ionisation energy of hydrogen is calculated on the basis of energy required to remove one mole of electrons i.e. 6.022×10^{23} electrons from one mole of hydrogen atoms in the ground state i.e. $= 6.022 \times 10^{23}\, hc\, \bar{\nu}$ J mol^{-1}

Putting the values of c, h, $\bar{\nu}$ in the above eq. we get,

$$= 6.022 \times 10^{23} \times 6.626 \times 10^{-34} \times 2.998 \times 10^8 \times 1.097 \times 10^7 \text{ J mol}^{-1}$$
$$= 1.312 \times 10^6 \text{ J mol}^{-1}$$
$$= 1312 \times 10^3 \text{ J mol}^{-1}$$
$$= 1312 \text{ KJ mol}^{-1}$$

Ionisation energies of other elements can be determined by the above method.

Limitations of Bohr's Theory

1. The angular momentum of the electron can never be zero as per Bohr's approach. This is contradicted later.
2. This theory is unable to give satisfactory explanation to the hyperfine structure in the atomic spectrum of hydrogen atom.
3. The spectra of multielectron atoms remained unanswered.
4. Formation of molecules from atoms could not be explained.
5. Wave properties of electrons is not considered as Bohr's theory is unsuccessful in explaining diffraction patterns.
6. Movement of electron in stationary orbits was based on the assumption that accurate and simultaneous determination of both position and velocity of the electron.

Sommerfeld Modification

Sommerfeld (1916) proposed the concept of elliptical orbits, where the nucleus was assumed to be present at one of the focii of the ellipse fig. 1.4 a, b.

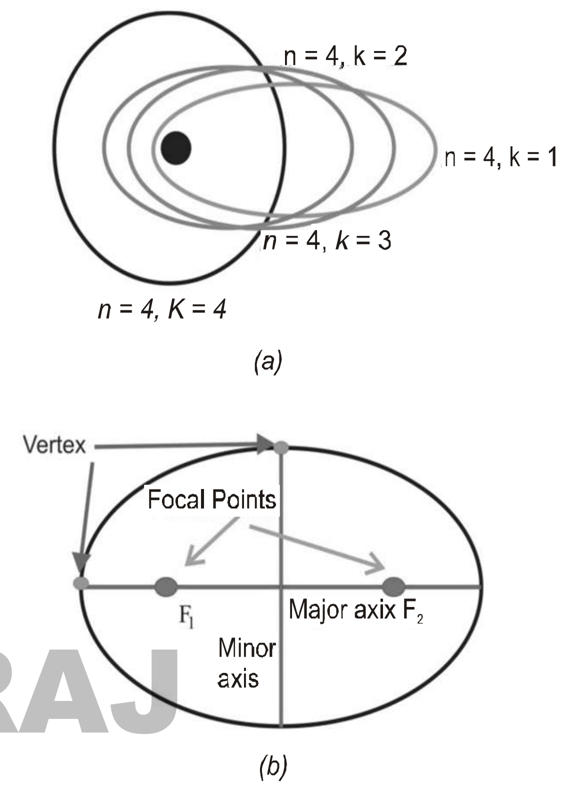


Fig 1.4 ***(a)*** **Eliptical orbits proposed by Sommerfeld, and** ***(b)*** **Major and Minor axes and focal points of an ellipse**

The motion of an electron in an elliptical orbit is described in terms of radial quantum number, n_r and azimuthal quantum number, k by the eq.

$$n = n_r + k$$

These quantum numbers are also related as

$$\frac{n}{k} = \frac{\text{Length of the major axis}}{\text{Length of the minor axis}}$$

The value of k varies from 1 to n for a given value of n. When $n = 4$, k can be 1, 2, 3 or 4, then value of $\frac{n}{k}$ will be

(i) $\frac{4}{1}$, *(ii)* $\frac{4}{2}$, *(iii)* $\frac{4}{3}$ and *(iv)* $\frac{4}{4}$

Where elliptical orbits are designated by *(i)*, *(ii)* and *(iii)* and circular orbit (where $n = k$) by *(iv).*

The energy of the electron in hydrogen atom according to Sommerfeld is given by:

$$E_n = \frac{2\pi^2 e^4 m}{(k + n_r)^2 h^2} \quad \text{... (1.17)}$$

Hence, it is seen that energy varies inversely with n and k. So, each principal level has sub-energy levels. Elliptical orbits are evidence of extra lines in the atomic