Atomic Structure

INTRODUCTION

In the beginning of nineteenth century, John Dalton (1766-1844) put forward his atomic theory, he regarded atom as hard and smallest indivisible particle of matter that takes part in chemical reactions; the atoms of one particular element are all identical in mass and atoms of different elements differ in mass and other properties. Later on, various investigators around the end of nineteenth century and beginning of twentieth century did several experiments and revealed the presence of much smaller negatively charged particles, named electrons by J.J. Thomson (1897) and positively charged particles, named protons by Rutherford (1911) within an atom. These tiny particles were called subatomic particles. It was also established by Rutherford that the whole positive charge and most of the mass of an atom lies at nucleus. The positive charge on the nucleus was attributed to the presence of protons called the atomic number by Moseley (1912). The electrons were said to be arranged around the nucleus in the extra nuclear region in certain well defined orbits called energy shells and were said to be in constant motion (N. Bohr, 1913). Chadwick's experiments (1932) also revealed the existence of yet another subatomic particle in the nucleus which did not have any charge and named as neutrons. Further investigations established that there were also present some other subatomic particles in the nucleus in addition to electrons, protons and neutrons. These particles are positrons, neutrinos, antineutrinos, pions (π-mesons) etc. The pions (Yukawa, 1935) are said to be continuously consumed and released by proton-neutron exchange processes. Thus, it is concluded that the atom no longer is an ultimate and indivisible particle of matter and the outer or valence shell electrons are responsible for chemical activity of the elements.

DE-BROGLIE'S MATTER WAVES: DUAL NATURE OF MATTER

This is based on wave mechanical concept of an electron in an atom. Albert Einstein proposed dual character of electromagnetic radiation in 1905, *viz*. wave character based on Maxwell's concept evidenced by diffraction, interference, polarisation kinds of phenomena and particle character based on Planck's quantum theory witnessed by quantization of energy and hence photoelectric effect, i.e. the ejection of photoelectrons from metal surface on striking electromagnetic radiation.

On the basis of above analogy, French Physicist Louis de Broglie (1924) postulated that not only light but all material objects (both micro and macroscopic) in motion such as electrons, protons, atoms, molecules etc. possess both, wave and the particle properties and thus have dual character, i.e. the wave character and particle (corpuscular) character. He called the waves associated with material particles as matter waves which are now named de Broglie's wave. These waves differ from electromagnetic or light waves in a sense that these are unable to travel through empty space and their speed is different form light waves.

❖ de Broglie's relation

de Broglie deduced a fundamental relation between the wave length of moving particle and its momentum by making use of Einstein's mass energy relationship and Planck's quantum theory. The material particle as a wave satisfies the Planck's relation for a photon, i.e.

$E = h\nu$ ……….. (1)

where h is Planck's constant and ν is the frequency of the wave. The frequency for light wave is ν .

At the same time, Einstein's mass energy relationship is applicable to it, i.e.

$E = mc^2$ (for a photon) ……….. (2)

or $h\nu = mc.\ c = p.c$ (p = momentum, p = m.c, mass x velocity)

Or, $h.c / \lambda = p.\ c$

Or, $\mathbf{p = h / \lambda}$

Here, λ corresponds to the wave character of matter and p its particle character. This is known as de Broglie's relation. From this relationship, it is concluded that "the momentum of a moving particle is inversely proportional to the wavelength of the wave associated with it".

It is important to note here from above discussion that de Broglie's relation is applicable to material particles of all sizes and dimensions but the wave character is significant only for micro objects like electrons and is negligible for macro objects hence cannot be measured properly. This infers that de Broglie's relation is more useful for smaller particles.

Reference: (a) Uttarakhand O. U. study material; (b) General and Inorganic Chemistry, Ramaprasad Sarkar, Volume 1 (c) Inorganic Chemistry, A.K. Das, Volume 1, (d) Biswasghatak, Narayan Sanyal, Bengali Novel

Lecture 2

HEISENBERG'S UNCERTAINTY PRINCIPLE

According to classical mechanics, a moving electron behaves as a particle whose position and momentum could be determined with accuracy. But according to de Broglie, a moving electron has wave as well as particle character whose precise position cannot be located because a wave is not

located at a particular point rather, it extends in space. To describe the character of a subatomic particle that behaves like a wave, Werner Heisenberg in 1927 formulated a principle known as Heisenberg's Uncertainty Principle. According to the principle "**It is impossible to determine simultaneously both the position as well as the momentum (or velocity) of a moving particle at the same time with certainty (or accurately)"**

He also proposed a mathematical relationship for the uncertainty principle by relating the uncertainty in position with the uncertainty in momentum which is given below:

$\Delta x \times \Delta p \geq h / 2\pi$

or $\Delta x \times m (\Delta v) \geq h / 2\pi$

–

(since $p = m v$)

where Δx is the uncertainty or error in the position of the particle, Δ p and Δ x are the uncertainties in its momentum and velocity and h is Planck's constant.

This equation states that the product of Δx and Δp can either be greater than or equal to (≥) but never smaller than h / 2π.

Atom Model of Rutherford:

3.5 THE NUCLEAR ATOM MODEL

Up to about the first decade of twentieth century (1910) the following major characteristics of atoms were recorded:

(i) Atoms are stable.

(ii) They are electrically neutral but they contain oppositely charged constituents.

(iii) They are exceedingly small. (The approximate radius of an atom was calculated to be in the range of 10^{-10} m from the kinetic theory of gases).

(iv) Atoms on excitation give rise to discontinuous line spectrum.

An early atom model suggested by J. J. Thomson (1904) considered the electrons as embedded in a sphere of uniform positive charge. This was unsatisfactory for many reasons, specially due to its failure to explain the atomic spectrum and was ultimately discarded.

3.5.1 The Atom Model of Rutherford

The first correct approach to atomic structure was made only when it was established that atoms posses a small nucleus. The corresponding atom model, first forwarded by Lord Rutherford

(1911), is called the nuclear model of the atom. In spite of several extensions and modifications, the basic idea of a nuclear atom is still maintained.

Experimental background

In Rutherford's laboratory, experiments were being carried out on the scattering of alpha-particles by thin metal foils (Geiger and Marsden, 1909). Alpha-particles have a mass four times that of a hydrogen atom and carry two units of positive charge. The massive energetic α-particles from a radioactive source were allowed to strike a very thin gold foil, 0.0004 mm in thickness. The position of the particles after passing through the foil was ascertained by the flash produced on a zinc sulfide screen.

Marsden, a young scholar of Rutherford, was asked to see if any alpha-particle could be scattered through a large angle. Actually most of the alpha particles passed without any appreciable deviation. But all on a sudden, one or two particles out of thousands (approximately 1 in 20,000) returned after hitting the gold foil. To quote Rutherford:

"*It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15 inch shell at a piece of tissue paper and it came back and hit you.*"

Analysis of the results

According to Rutherford, the wide angle scattering of the alpha-particle could not occur by the additive effect of a number of small scatterings. It was due to a *single* collision. From the angle of scattering, Rutherford made an idea about the charge of the target which scattered the alpha particle. He concluded that there exists a central position in the atom; the entire mass and positive charge of the atom is concentrated therein. This was termed the *nucleus* of the atom.

As already stated, the chance of such a collision was extremely rare. But the alpha particles passed through a layer of about 1000 gold atoms. This can be easily estimated : atoms were known to have diameters in the range of 10^{-10} m; nearly 4000 such atoms would therefore, produce a thickness of the gold foil used, i.e., 0.0004 mm or 4×10^{-7} m. The rare chance of large angle scattering could, therefore, be explained by assuming the nucleus to be very small in comparison to the total size of the atom.

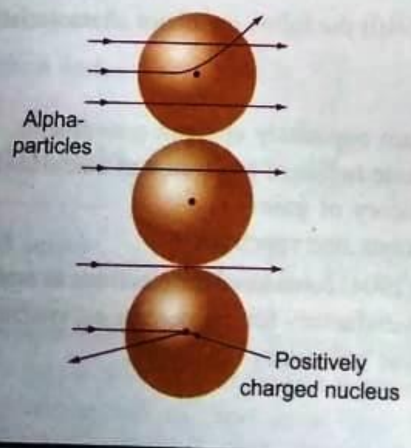

Fig.3.8: Scattering of α-particles as interpreted by Rutherford.

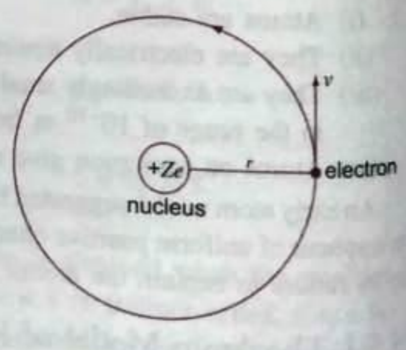

Fig.3.9: The nuclear atom of Rutherford.

Based on the experimental results, Rutherford proposed the model in 1911 and the basic feature of the model is as follows:

1) Atom consist of a central nucleus and the entire positive charge of the atom being concentrated there,

2) The dimension of the nucleus is extremely small in comparison to the size of the atom. Most part of the atom is thus vacant.

3) Electrons are present outside the nucleus and their number is equal to the nuclear positive charge to maintain the electrical neutrality of the atom.

4) The electrons revolve around the nucleus in circular orbits. The centripetal force and the electrostatic force balance each other to give a stable orbit

Drawback of Rutherford Atomic Model:

1. Instability of Atomic Nucleus and

2 No explanation of the atomic line spectra.

Details are as follows:

Drawbacks of the Rutherford's Model

i. *Instability of the Rutherhford's atom* : Though it was attempted to explain the stability of the atoms by considering two strong foundation stones of the classical physics, *i.e.* Newton's law of motion and Coulomb's law of electrostatic force, it could not be supported by the electromagnetic theory, another big foundation stone of the classical physics. According to the demand of electromagnetic theory, a revolving electron under an acceleration will radiate its energy in the form of electromagnetic radiation. Thus by losing its energy, it will gradually spiral down (Fig. 1.7.1.2) into the nucleus and the atom will get destroyed. As a matter of fact, if it occurs so, it can be shown mathematically that the revolving electron will require about one hundred-millionth of a second to get plunged into the nucleus.

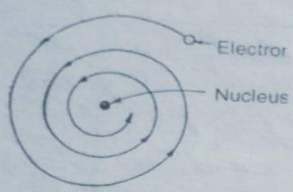

Fig. 1.7.1.2 Fate of the revolving electron in Rutherford's model.

ii. *No explanation of atomic line spectra* : From the Rutherford's model, according to the electromagnetic theory, the energy radiated in the form of electromagnetic radiation from the revolving electron should lead to a *continuous spectrum* covering all frequencies in a certain range. But experimentally, some well defined spectral lines corresponding to certain frequencies are noted instead of a continuous spectrum.

To remove the drawbacks in the Rutherford's model, combining some basic laws of Classical Physics and some principles of Quantum Theory (1900), Niels Bohr proposed in 1913 his famous atomic model. Because of this contribution, Bohr was awarded the Nobel Prize. However, it is applicable for mono electronic system.

1.8.1 Bohr's Atomic Model

Basic postulates of the model :

i. The electrons are revolving in some specified circular orbits around the nucleus where the whole positive charge is concentrated. These permitted orbits are restricted by *the quantum condition* that the angular momentum of the electron in the circular path about the nucleus must be an integral multiple of $h/2\pi$, where h is the Planck constant, *i.e.* angular momentum $= mur = n(h/2\pi)$, $n = 1, 2, 3, 4, \ldots$ where m = mass of the electron; r = radius of the orbit; and u = tangential velocity of the revolving electron.

ii. When an electron is revolving in a permitted orbit, it will neither accept nor radiate any energy. This situation is called *stationary state*. Here it is worth mentioning that this postulate ignores the demand of electromagnetic theory according to which for the revolving charged particle (*e.g.* electron), energy will be radiated in the form of electromagnetic radiation.

iii. When an electron jumps from an orbit of energy E_i to another orbit of energy E_f, a definite amount of energy in the form of radiation is emitted or absorbed depending upon whether the final state is at lower or higher energy compared to the initial one respectively. The frequency (ν) of radiation is given by $h\nu = E_f \sim E_i$.

iv. For all other considerations, the model will obey the laws of classical physics, such as : for the revolving electron in a circular orbit in a stationary state, the electrostatic Coulombic force of attraction between the nucleus and electron is balanced by the centrifugal force (mu^2/r) due to angular motion of the electron as obtained from Newton's law of motion.

Calculation of Energy as per Bohr's model:

Page. 1

Energy of an electron in a Bohr orbit:

An electron in the atom possesses (i) K.E. due to it's motion and (ii) Potential Energy owing to its attachment to the nucleus.

Total Energy (E_{Total}) = K.E. ($E_{K.E}$) + P.E. ($E_{P.E.}$)

Kinetic Energy (K.E.) = $\frac{1}{2}mv^2$ ...... (1)

In Bohr's theory, the basic of Rutherford Model is maintained. Hence the condition of equilibrium between centripetal force / centrifugal force still applies to these orbits.

So, for an $e^{\ominus}$ moving in an orbit of radius 'r' around a nucleus with Z units of positive charge, we have

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2} \quad \text{[in c.g.s unit]}$$

or, $\frac{1}{2}mv^2 = \frac{Ze^2}{2r} = E_{K.E}$ .... (2)

Again we know from Bohr's condition that

$$mvr = \frac{nh}{2\pi}$$

or, $m^2v^2r^2 = \frac{n^2h^2}{4\pi^2}$ [Squaring both side]

Now putting the value of v^2 from (2) we get

$$\overset{mr}{\cancel{m^2}\cancel{r^2}} \cdot \left[\frac{\cancel{2}Ze^2}{\cancel{2}\cancel{m}\cancel{r}}\right] = \frac{n^2h^2}{4\pi^2}$$

or, $mr \cdot Ze^2 = \frac{n^2h^2}{4\pi^2}$

or, $\boxed{r = \frac{n^2h^2}{4\pi^2 Zme^2}}$ ..... (3)

Now,

Potential Energy is calculated as work done in bringing the electron from infinity to its position in the orbit of radius = r.

Thus, $E_{P.E} = W = \int_{r=\infty}^{r=r} \frac{Ze^2}{r^2} \cdot dr$

$$\left[W = \vec{F} \cdot \vec{dr} = \underbrace{\frac{Ze^2}{r^2}}_{\text{Coulombic force}} \cdot dr \right]$$

or, $E_{P.E} = W = \int_{r=\infty}^{r=r} \frac{Ze^2}{r^2} dr$

$$= -\left[\frac{Ze^2}{r}\right]_{r=\infty}^{r=r} = -\frac{Ze^2}{r} - 0 \quad \cdots (4)$$

Now, Total Energy = E_{Total}

$$= E_{K.E} + E_{P.E}$$

$$= \frac{Ze^2}{2r} - \frac{Ze^2}{r} \quad [\text{from } (2) \text{ and } (4)]$$

$$E_{Total} = -\frac{Ze^2}{2r}$$

$$E_{Total} = -\frac{Ze^2}{2} \cdot \left[\frac{4\pi^2 Z m e^2}{n^2 h^2}\right]$$

$$\boxed{E_{Total} = -\frac{2\pi^2 Z^2 m e^4}{n^2 h^2}} \quad \cdots (5)$$

Let us consider two orbits with quantum no n_1 and n_2 in a Bohr atom type, such that $n_1 < n_2$ and their energy E_{n_1} and E_{n_2} respectively

$$E_{n_2} - E_{n_1} = h\nu = \frac{2\pi^2 z^2 me^4}{h^2 . h}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

or, $$\nu = \frac{2\pi^2 z^2 me^4}{h^2 . h}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

or, $$\bar{\nu} . c = \frac{2\pi^2 z^2 me^4}{h^2 . h}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

or, $$\boxed{\bar{\nu} = \underbrace{\frac{2\pi^2 z^2 me^4}{ch^3}}_{R_H = \text{Rydberg constant}}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]} \quad \ldots (6)$$

Ionisation Energy

$n_2 = \infty$

$$\therefore \Delta E_{Total} = \frac{2\pi^2 z^2 m e^4}{h^2}\left[\frac{1}{n_2^2} - \frac{1}{n_1^2}\right]$$

$$= -\frac{2\pi^2 z^2 m e^4}{h^2 n_1^2}$$

For H, $n_1 = 1$

Electronic Transition

According to Bohr's theory electron can jump from one selected orbit to another and difference of energy betwn the two states is emitted or absorbed according to the quantum theory of radiation.

Final position $\longrightarrow n_f$

initial " $\longrightarrow n_i$

Then.

$$\bar{\nu} = R_H\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right] \quad \text{From } (6)$$

	n_f	n_i
Lyman Series	$n_f = 1$	$n_2, n_3, n_4 \ldots\ldots$
Balmer	$n_f = 2$	3, 4, 5, 6, ...
Paschen	3	4, 5, 6, ...
Bracket	4	5, 6, 7, 8 ....
Pfund	5	6, 7, 8, ...

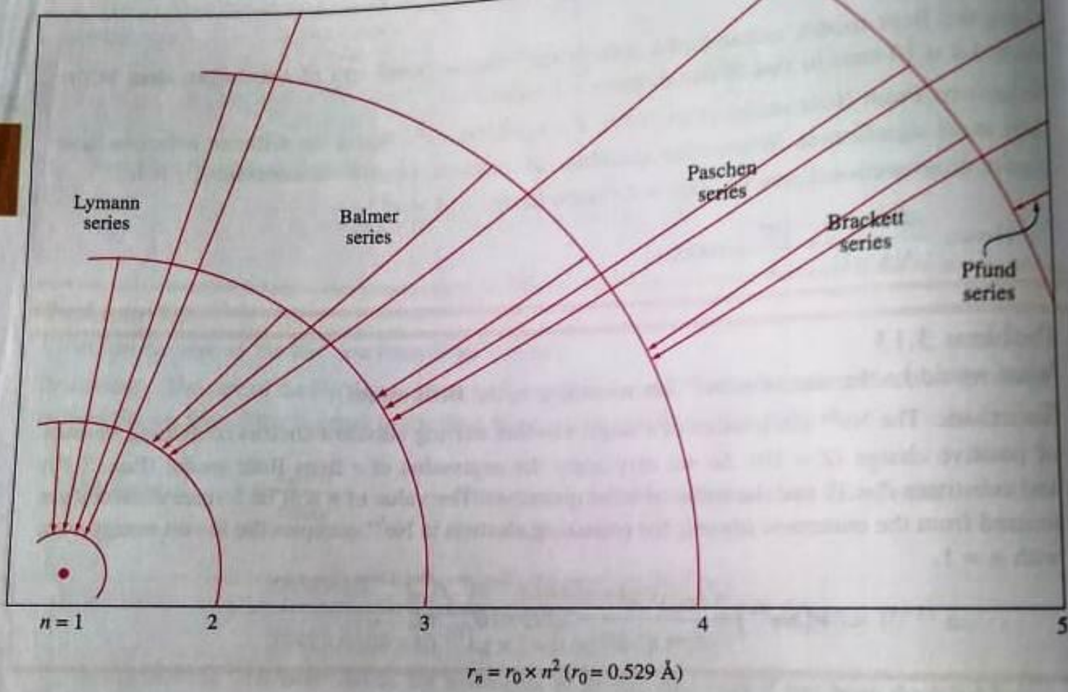

Fig.3.11: Transitions which give rise to different series in the spectrum of atomic hydrogen (schematic). One electron can undergo only one transition at any instant of time giving rise to a line of one particular frequency or wavelength. In an aggregate of atoms, different transitions occur in different atoms.

Merit and demerits of Bohr's Theory:

Merits and demerits of the Bohr atom model

Bohr's model of the atom successfully explained (i) the stability of atoms and (ii) the origin of discontinuous line spectrum by them. It also helped in understanding some related phenomena like the production of characteristic x-rays by elements. Satisfactory agreement with experimental results was observed for the Rydberg constant, excitation potential of atoms, characteristic x-rays, etc.

But the model had its own drawbacks also. Using instruments of high resolving power, several of the apparent "single" lines in the spectrum were found to consist of a number of closely spaced lines. This fine structure of the spectral lines has no explanation in Bohr's theory. Also, its agreement with experiment in the case of higher elements was far from satisfactory.

Bohr's introduction of the concept of integers (n) in selecting the stable orbits for electrons was also arbitrary, merely to fit experimental results. There was no theoretical justification for it.

Bohr discarded the classical behaviour of the electron as regards the emission of radiation. But the motion of the electron was still considered by the classical Newtonian mechanics. The position and the momentum of the electron in a Bohr orbit could be evaluated accurately at the same time. Later developments in physics showed that this is not possible for a tiny particle like the electron; there always exists some uncertainty in these quantities. Bohr's theory was thus inadequate to cope up with later developments of science.

Lecture 4

Sommerfeld's Modification:

Sommerfeld's extension of Bohr's atomic model was motivated by the quest for a theory of the Zeeman and Stark effects. The crucial idea was that a spectral line is made up of coinciding frequencies which are decomposed in an applied field. In October 1914 Johannes Stark had published the results of his experimental investigation on the splitting of spectral lines in hydrogen (Balmer lines) in electric fields, which showed that the frequency of each Balmer line becomes decomposed into a multiplet of frequencies. The number of lines in such a decomposition grows with the index of the line in the Balmer series. Sommerfeld concluded from this observation that the quantization in Bohr's model had to be altered in order to allow for such decompositions. He outlined this idea in a lecture in winter 1914/15, but did not publish it. The First World War further delayed its elaboration. When Bohr published new results in autumn 1915, Sommerfeld finally developed his theory in a provisional form in two memoirs which he presented in December 1915 and January 1916 to the Bavarian Academy of Science. In July 1916 he published the refined version in the Annalen der Physik. The focus here is on the preliminary Academy memoirs whose rudimentary form is better suited for a historical approach to Sommerfeld's atomic theory than the finished Annalen-paper. This introductory essay reconstructs the historical context (mainly based on Sommerfeld's correspondence). It will become clear that the extension of Bohr's model did not emerge in a singular stroke of genius but resulted from an evolving process.

to each Bohr orbit.

Principal aspects of Sommerfeld's treatment

In 1915 Sommerfeld proposed that the general shape of an electron's orbit was elliptical; corresponding to each principal quantum number (n), several orbits of varying ellipticity were possible. The nucleus was now situated at one of the focii of the ellipse describing the electron's orbit. When the two axes of an ellipse became equal, a circular orbit was obtained.

The position of an electron moving in an elliptical orbit is determined by two quantities (Fig. 3.14): (i) the radius-vector (OA) and (ii) the angle subtended by the radius-vector with the semi-

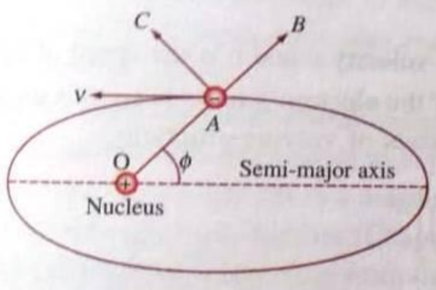

Fig.3.14: The motion of an electron along an elliptical orbit.

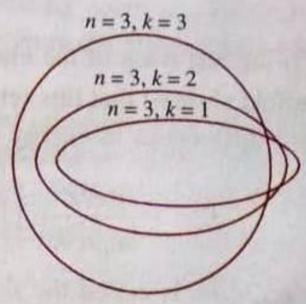

Fig.3.15: The possible elliptical orbits for $n = 3$.

major axis (ϕ). ϕ is called the *azimuthal* angle*. The velocity (v) of the electron is directed tangentially to the curve; accordingly, its momentum can be resolved into two components: (i) one component along the radius vector (AB) (ii) and the other perpendicular to it (AC). The second part now represents the angular momentum. Two quantum numbers, n_r and k were now necessary to separately quantize each resolved part of the momentum. These are (i) radial quantum number, n_r and (ii) azimuthal quantum number, k. These were related to the principal quantum number (n) and the ellipticity of the orbit by the following relations:

$$\text{(i) } n = n_r + k, \quad \text{(ii) } \frac{n}{k} = \frac{\text{length of semi-major axis }(a)}{\text{length of semi-minor axis }(b)}.$$

The ellipticity of the orbits was thus determined by the relative values of n and k. The eccentricity of the ellipse ε is expressed as

$$\frac{b}{a} = \frac{k}{n} = \sqrt{1-\varepsilon^2}.$$

For any given n, permissible values of n_r and k are:

$$n_r = n, (n-1), (n-2), \cdots, 1, 0;\ k = n, (n-1), (n-2), \cdots, 1.$$

Calculation shows that the total energy of an electron in an orbit of principal quantum number n is given by

$$E_n = -\frac{me^4Z^2}{8\varepsilon_0^2 n^2} = -\frac{me^4Z^2}{8\varepsilon_0^2 (n_r+k)^2}.$$

This implies that the energy of an electron would be same in any orbit of principal quantum number n, whatever be the ellipticity. At this point Sommerfeld considered relativistic variation of the mass of the electron during its motion in an elliptical orbit and showed that the energy of the electron will be different for different values of k.

To maintain balance with the varying electrostatic force with varying distance from the nucleus, an electron moving in an elliptical orbit has to change its velocity continuously. The velocity is greatest when the electron is closest to the nucleus; it decreases gradually as the electron moves farther. According to the theory of relativity, the mass of the electron also changes according to the relation

$$m = \frac{m_0}{\sqrt{1 - v^2/c^2}}$$

where m_0 is the rest mass of the electron, m its mass at velocity v and c is the speed of light.

Sommerfeld showed that this relativistic variation of the electron's mass is significant and causes slight differences in energy of the electron in orbits of varying ellipticity:

$$E = -\frac{\mu e^4 Z^2}{8\varepsilon_0^2 n^2 h^2}\left[1 + \frac{\alpha^2 Z^2}{n}\left(\frac{1}{k} - \frac{3}{4n}\right)\right],$$

where $\alpha = e^2/2\varepsilon_0 hc$ is called the *fine structure constant*.

*Medieval English; from Arabic *as-sumūt*, the way (*via* Latin).

Relativistic variation of the mass of the electron has a further consequence: each time the electron passes near the nucleus, the equilibrium force between the electron and the nucleus is slightly perturbed and the major axis of the ellipse shifts, i.e., undergoes *precession*. The resulting path of the electron appears like a *rosette* (Fig. 3.16).

The fine structure of the spectra was now understood by assuming transitions involving orbits of different n and k. However, experimentally it was found that only those fine-structure lines are actually observed which correspond to $\Delta k = \pm 1$. This has been used as a ***selection rule*** for transitions which are allowed: $\Delta k = \pm 1$. This puts a limit to the number of fine structure lines (Fig. 3.17).

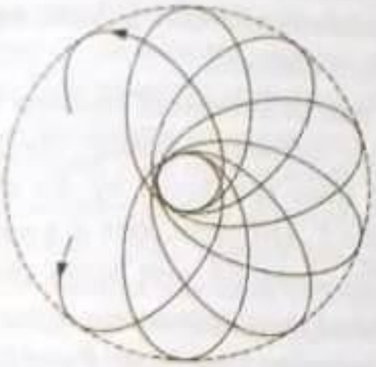

Fig.3.16: The electron's path represented by a precessional ellipse.

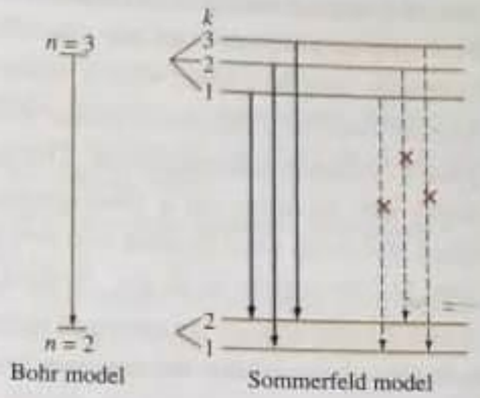

Fig.3.17: Transitions responsible for fine structure of H_α line in the Balmer series of hydrogen. Dashed lines are not allowed by the selection rules.

...are not allowed by the selection rules.

The azimuthal quantum number k has subsequently been replaced by the symbol l for certain mathematical advantages. The values of l are fixed in relation to k as $l = k - 1$. Thus for any given value of n, l may have values 0, 1, $\cdots$ to $(n - 1)$.

Sommerfeld's theory was supported by experimental data; the agreement, however, was not perfect in all cases. At the same time, the objections raised against the Bohr idea of discrete orbits by later developments in physics are equally applicable to Sommerfeld's theory. Also, the correct number of fine structure lines was not available from this theory and further quantum numbers were required for this purpose.

The existence of definite energy levels within the atom has been further confirmed from successive excitation potentials of electrons and corresponding spectral observations. The x-ray spectra of elements were also explained satisfactorily from the Bohr-Sommerfeld atom model (Section 3.5.4).

Further interpretation of atomic spectra introduced two more quantum numbers. The magnetic quantum number was introduced to explain the observed splitting of spectral lines when the source of spectra was placed in a magnetic field (*Zeeman effect*). Further details of the spectra led to the spin quantum number (Chapter 4). It was soon realized that an atomic system has its own peculiarities originating from the very microscopic nature of the system. These could be more rationally interpreted only with a new approach based on wave properties of matter.