2

Review of Atomic Structure

I. THE RUTHERFORD MODEL OF THE ATOM

The first exploration of the structure of the atom was made by Rutherford in 1911 making use of α-particles. He bombarded a thin gold foil with α-particles (helium nuclei, which are positively charged particles with an atomic mass number of 4) and found that very many α-particles passed through the gold foil without being deflected, but some of them were deflected through a large angle. The inference was that much of the atom has void space between them, allowing most of the α-particles to pass straight through, but with some particles being deflected owing to their passing close to, or colliding with, a central mass (nucleus) or very small dimensions. The effective diameter of the gold atom is 0.3 nm and the diameter of the nucleus is about 1/10,000 of this size.

The first postulation about electrons was that they are in orbit around the central nucleus just as planets round the sun. To incorporate these findings and the discovery of the electron, Rutherford proposed the following model of the atom:

This model postulates a tiny, massive and positively charged nucleus around which the negative electrons orbit.

In Fig. 2.1, an electron is revolving in a circular orbit of radius, r, with a constant velocity, v. The system is now subjected to two forces. Acting inwards will be electrostatic attraction given by *Coulomb's law*

$$f_e = \frac{(Ze)\,(e)}{4\pi\,\varepsilon_0 r^2}$$

Here ε_0 is the *permittivity of free space*. The other one is the *centrifugal force*, f_c acting outwards. The value of this force is

$$f_c = \frac{mv^2}{r}$$

where m is the mass of the electron and (v^2/r) is its *radial acceleration*. The condition for orbit stability is $f_c = f_e$.

Thus,
$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\,\varepsilon_0 r^2} \qquad (2.1)$$

II. CONCLUSION OF RUTHERFORD'S THEORY

The atom consists of a positively charged heavy nucleus surrounded by revolving negatively charged extremely light particles called electrons, like the planets round the sun, moving at such a speed that the mechanical centrifugal force would just balance the net excess of electrostatic attraction and in consequence stability of the atom could be secured.

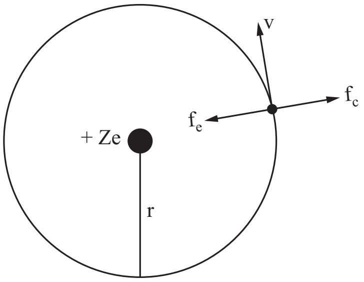

Fig. 2.1 Circular orbit of an electron in an atom

III. DRAWBACKS OF THE RUTHERFORD MODEL OF THE ATOM

A logical place for an electrical engineer or a physicist to begin his study of solid state physics is with the rudiments of quantum mechanics. Quantum mechanics was developed because classical mechanics failed to explain the behaviour of atoms. As an example, consider the hydrogen atom consisting of one electron and one proton with an attractive coulomb potential between them. Newton's laws of motion would allow the electron any value of energy in its orbit about the proton as long as the Coulomb attractive force which varies inversely as the square of the distance between the proton and electron is balanced by the outward centrifugal force of the electron. However, experiments on the hydrogen atom inform us that the electron appears to have only very specific or discrete values of energy. A further problem arises in regard to some other classical equations of physics (Maxwell's equations) which have to do with moving charges and electromagnetic fields. These equations predict that the negatively charged electron whirling around the proton would continuously radiate energy (in the form of light) and gradually be drawn into the proton as it slowed down. This is contrary to the fact that hydrogen atoms can exist in nature without continuously emitting light. After much trial and error, quantum mechanics was developed in 1926 and explained these discrepancies. Thus the laws of physics that are valid in the macroscopic world do not hold good in the case of microscopic particles such as electrons. Rutherford model also failed to explain the emission of radiations as light, X-rays, etc. from the atoms of different substances under certain conditions.

IV. BOHR MODEL OF ATOM

Hydrogen, the simplest of all elements, was investigated most extensively both experimentally and theoretically. As long ago as 1885, Balmer succeeded in obtaining a simple relationship among the wave numbers of the lines in the visible region of the hydrogen spectrum. The first quantitatively correct derivation of the Balmer formula on the basis of an atomic model was given by Bohr (1913), in his theory of the hydrogen atom. This theory has played such an important role in the development of atomic physics that, even though it has been modified and extended by the later developments in quantum mechanics, it will be worthwhile to present the original simplified theory.

In 1913, Niels Bohr proposed a model for the hydrogen atom which retained the earlier nuclear model of Rutherford but made further stipulations as to the behaviour of the electron. A dramatic explanation of the Rydberg spectral expression resulted. Many modern ideas about atomic and molecular structure stem from this model.

Bohr suggested the following postulates to explain the electron motion in an atom and the observed spectral lines:

(*i*) An electron in an atom moves in a circular orbit around the nucleus under the influence of Coulomb force of attraction between the electron and nucleus. The *Coulombian force* of attraction is balanced by *Newtonian centrifugal force*. Thus we have

$$\frac{(Ze)(e)}{4\pi\varepsilon_0 r^2} = \frac{mv^2}{r}$$

(*ii*) An electron cannot revolve round the nucleus in all possible orbits as suggested by the classical theory. It can revolve only in a few widely separated permitted orbits. While moving along these orbits round the nucleus, an electron does not radiate energy. These non-radiating orbits are called *stationary orbits*.

(*iii*) The permissible orbits of an electron revolving round a nucleus are those for which the angular momentum of the electron is an integral multiple of $h/2\pi$, where h is *Planck's constant*. Thus for any permitted orbit,

$$I\omega = n\left(\frac{h}{2\pi}\right)$$

or

$$\left(mr_n^2\right)\frac{v_n}{r_n} = n\left(\frac{h}{2\pi}\right)$$

$$mr_n v_n = n\left(\frac{h}{2\pi}\right) \tag{2.2}$$

where m and v_n are the mass and velocity of the electron, r_n the radius of the orbit and n is a positive integer, called the *quantum number*. The above equation is called *Bohr's quantum condition.*

(*iv*) An atom radiates energy only when an electron jumps from a stationary orbit of higher energy to another of lower energy. Thus if the electron jumps from an initial orbit of energy E_i to a final orbit of energy E_f $(E_i > E_f)$, the frequency υ of the radiation emitted is given by the relationship,

$$h\upsilon = E_i - E_f$$

where h is *Planck's constant.* This equation is called *Bohr's frequency condition*.

V. BOHR'S THEORY OF HYDROGEN ATOM

Let us now apply these postulates to the classical model of the atom with a nucleus of charge (Ze). From Bohr's first postulate, we have

$$\frac{mv_n^2}{r_n} = \frac{(Ze)(e)}{4\pi\varepsilon_0 r_n^2} \tag{2.3}$$

$$mr_n v_n^2 = \frac{Ze^2}{4\pi\,\varepsilon_0} \tag{2.4}$$

where $Z = 1$ for hydrogen atom.

From Bohr's third postulate, the angular momentum of the electron in a permitted orbit must be an integral multiple of $\frac{h}{2\pi}$. From equation (2.2), we have

$$mr_n v_n = n\left(\frac{h}{2\pi}\right) \tag{2.5}$$

$$v_n = n\left(\frac{h}{2\pi}\right)\left(\frac{1}{mr_n}\right) \tag{2.6}$$

Substituting this value of v_n in equation (2.4), we get

$$(mr_n)\left[\frac{nh}{2\pi\, mr_n}\right]^2 = \frac{Ze^2}{4\pi\,\varepsilon_0}$$

$$\frac{n^2h^2}{4\pi^2 mr_n} = \frac{Ze^2}{4\pi\,\varepsilon_0}$$

Thus, the radius of *n*th permissible orbit for electron in hydrogen is given by

$$\boxed{r_n = \left(\frac{n^2h^2\varepsilon_0}{\pi\, mZe^2}\right)} \tag{2.7}$$

Hence, the radii of different stationary orbits are directly proportional to the square of *n* (called *principal quantum number*). Velocity of electron in the stationary orbits can be obtained by substituting this value of r_n in equation (2.6).

$$v_n = \left(\frac{nh}{2\pi\, m}\right)\left[\frac{\pi\, mZe^2}{n^2h^2\,\varepsilon_0}\right]$$

$$\boxed{v_n = \frac{Ze^2}{2nh\,\varepsilon_0}} \tag{2.8}$$

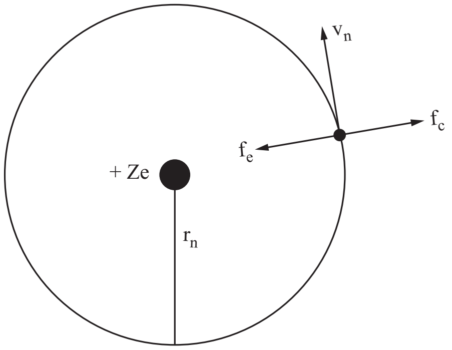

Fig. 2.2 Bohr's model of hydrogen atom

It is now clear that the velocity of the electron is inversely proportional to the principal quantum number *n*. Thus electron moves at a lower speed in higher orbits and vice versa.

The orbital frequency of an electron in the stationary orbits is calculated as follows:

$$\omega_n = \frac{2\pi}{T_n} = 2\pi f_n = \frac{v_n}{r_n}$$

Thus,

$$f_n = \left(\frac{1}{2\pi}\right)\left[\frac{Ze^2}{2nh\,\varepsilon_0}\right]\left[\frac{\pi\, mZe^2}{n^2h^2\,\varepsilon_0}\right]$$

$$\boxed{f_n = \frac{mZ^2e^4}{4\,\varepsilon_0^2 n^3h^3}} \tag{2.9}$$

i.e., $$\boxed{f_n \propto \frac{1}{n^3}}$$

VI. TOTAL ENERGY OF THE ELECTRON IN THE STATIONARY ORBITS

The electron revolving round the nucleus has both potential energy (due to its position with respect to the nucleus) and kinetic energy (due to its motion). The potential energy of the electron is considered to be zero when it is at infinite distance from the nucleus. Potential energy of an electron in an orbit is given by the work done in taking the electron from the distance r to infinity against the electrostatic attraction between the nucleus and the electron. This is obtained by integrating the electrostatic force of attraction between the nucleus and the electron from the limit ∞ to r_n.

$$\text{Thus P.E. of the electron} = -\int_{r_n}^{\infty} F(r)\, dr$$

$$\text{P.E.} = \int_{\infty}^{r_n} \frac{Ze^2 dr}{4\pi\,\varepsilon_0\, r_n^2}$$

That is, $$\text{P.E.} = -\frac{Ze^2}{4\pi\,\varepsilon_0\, r_n}$$

$$\text{Similarly K.E. of the electron} = \frac{1}{2}mv_n^2$$

Substituting the value of $\frac{1}{2}mv_n^2$ from equation (2.4), we get

$$\text{K.E.} = \frac{Ze^2}{8\pi\,\varepsilon_0\, r_n}$$

Thus, the total energy of the electron in the nth orbit is

$$E_n = \text{P.E.} + \text{K.E.}$$

$$= -\frac{Ze^2}{4\pi\,\varepsilon_0 r_n} + \frac{Ze^2}{8\pi\,\varepsilon_0 r_n} = -\frac{Ze^2}{8\pi\,\varepsilon_0 r_n}$$

Substituting the value of r_n from equation (2.7), we get

$$E_n = -\left[\frac{Ze^2}{8\pi\,\varepsilon_0}\right]\left[\frac{\pi\, mZe^2}{n^2h^2\,\varepsilon_0}\right]$$

$$\boxed{E_n = -\frac{mZ^2e^4}{8\,\varepsilon_0^2 n^2 h^2}} \tag{2.10}$$

The negative sign of the energy expression shows that the electron is bound to the nucleus and some work must be done to pull it away. It further follows from equation (2.10) that as n increases, E_n

becomes less negative and hence its algebraical value increases. The electron, therefore has minimum energy when it is in its innermost orbit, $n = 1$. The state of the atom with the electron revolving in the innermost orbit is called the ground or normal state and is obviously the most stable state of the atom.

VII. CALCULATION OF r_n AND E_n FOR HYDROGEN ATOM

$$r_n = \frac{n^2 h^2 \varepsilon_0}{\pi\, m Z e^2} \text{ with } Z = 1 \qquad \text{[Refer equation (2.7)]}$$

$$r_n = \frac{n^2 (6.626 \times 10^{-34})^2\, (8.854 \times 10^{-12})}{\pi (9.109 \times 10^{-31})\, (1.602 \times 10^{-19})^2}$$

$$r_n = (n^2)\,(0.529 \times 10^{-10}) \text{ metre} \tag{2.11}$$

Thus radius of the first orbit of hydrogen, $r_1 = 0.529 \times 10^{-10}$ m

This is called the *Bohr radius* (r_B).

Thus, $r_1 = r_B = 0.0529$ nm

$r_2 = 2^2 r_B = 4r_B, \ldots$

and $r_n = n^2 r_B$

The energy of the electron in the *n*th orbit is

$$E_n = -\frac{m Z^2 e^4}{8\, \varepsilon_0^2\, n^2 h^2} \quad \text{with } Z = 1 \qquad \text{[Refer equation (2.10)]}$$

$$\boxed{E_n = -\frac{B}{n^2}, \text{ where } B = \frac{m e^4}{8\, \varepsilon_0^2\, h^2}} \tag{2.12}$$

Thus, $$E_n = -\frac{(9.109 \times 10^{-31})\, (1.602 \times 10^{-19})^4}{n^2 \times 8\, (8.854 \times 10^{-12})^2\, (6.626 \times 10^{-34})^2}$$

$$E_n = -\frac{2.179 \times 10^{-18}}{n^2} \text{ joule}$$

$$E_n = -\frac{2.179 \times 10^{-18}}{n^2 (1.602 \times 10^{-19})} \text{ eV}$$

$$\boxed{E_n = -\frac{13.6}{n^2} \text{ eV}} \tag{2.13}$$

when $n = 1$

This corresponds to the ground state energy of the atom, and is called the *ionisation potential* of hydrogen atom. Similarly, the energy of the atom with the electron in the second orbit is

$$E_2 = -\frac{13.6}{4} = -3.4 \text{ eV}$$

and that with the electron in the third orbit

$$E_3 = -\frac{13.6}{9} = -1.511 \text{ eV and so on.}$$

VIII. BOHR'S INTERPRETATION OF HYDROGEN SPECTRUM

If an electron jumps from an outer initial orbit n_2 of higher energy to an inner final orbit n_1 of lower energy, the frequency of the radiation emitted is given by

$$h\upsilon = (E_i - E_f) = \left[-\frac{mZ^2e^4}{8\,\varepsilon_0^2\,h^2n_2^2}\right] - \left[-\frac{mZ^2e^4}{8\,\varepsilon_0^2\,h^2n_1^2}\right]$$

Hence,

$$h\upsilon = \frac{mZ^2e^4}{8\,\varepsilon_0^2\,h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\boxed{\upsilon = \frac{mZ^2e^4}{8\,\varepsilon_0^2\,h^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]} \qquad (2.14)$$

$$\upsilon = \frac{c}{\lambda} = \frac{mZ^2e^4}{8\,\varepsilon_0^2\,h^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\frac{1}{\lambda} = \frac{mZ^2e^4}{8\,\varepsilon_0^2\,ch^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

The reciprocal of the wavelength is called the *wave number*.

Thus,

$$\boxed{\bar{\upsilon} = \frac{1}{\lambda} = \frac{mZ^2e^4}{8\,\varepsilon_0^2\,ch^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]} \qquad (2.15)$$

$\dfrac{mZ^2e^4}{8\,\varepsilon_0^2\,ch^3}$ with $Z = 1$ is called *Rydberg constant* for hydrogen (R_H). Thus

$$R_H = \frac{(9.109\times10^{-31})\,(1.602\times10^{-19})^4}{8(8.854\times10^{-12})^2\,(3\times10^8)\,(6.626\times10^{-34})^3}$$

$$R_H = 1.0961 \times 10^7 \text{ m}^{-1}$$

An atom is said to be excited, if the electron is raised to an orbit of higher energy. The electron can be completely freed from the influence of the nucleus by supplying sufficient energy and the minimum energy needed for this is called *ionisation energy*.

For hydrogen

$$\boxed{\begin{aligned} E_I &= E_\infty - E_1 = \frac{me^4 Z^2}{8\,\varepsilon_0^2\, h^2}\left[\frac{1}{1} - \frac{1}{\infty}\right] \text{ with } Z = 1 \\ E_I &= 13.6 \text{ eV} \end{aligned}}$$

Thus, $E_I = 13.6$ eV (2.16)

As long as the electron remains in its orbit, no energy is radiated, but whenever an electron jumps from an outer orbit to an inner orbit, energy is emitted in the form of radiation. When the hydrogen atom is subjected to an external source to energy, the electron jumps from lower energy state to higher energy state. The atom is said to be excited. The excited state is not stable and hence the electron returns to its ground state in about 10^{-8} second. The excess of energy is now emitted in the form of radiations of different wavelengths. In a hydrogen discharge tube there are very large number of hydrogen atoms which are excited, and radiate energy. In some atoms the electrons may jump from the second orbit to the first orbit, in some others from the third to the second or first and so on. The different wavelengths due to different transitions of the electrons constitute spectral series which are characteristics of the atom emitting them.

IX. SPECTRAL SERIES OF HYDROGEN

Lyman Series

When electrons jump from second, third, etc. orbits to the first orbit, the spectral lines are in the ultraviolet region. Here, $n_1 = 1$ and $n_2 = 2, 3, 4, \ldots$

Thus,

$$\bar{\upsilon} = \frac{1}{\lambda} = R_H\left[\frac{1}{1^2} - \frac{1}{n_2^2}\right] \text{ with } n_2 = 2, 3, 4, \ldots$$

$$\bar{\upsilon}_1 = \frac{1}{\lambda_1} = R_H\left[1 - \frac{1}{4}\right] = \frac{3}{4}R_H, \text{ when } n_2 = 2$$

$$\bar{\upsilon}_2 = \frac{8}{9}R_H \text{ and } \bar{\upsilon}_3 = R_H\left(\frac{15}{16}\right) \text{ and so on.}$$

This is identified as *Lyman series*.

Balmer Series

When electrons jump from outer orbits to the second orbit ($n_1 = 2$, $n_2 = 3, 4, 5, \ldots$), we get lines of *Balmer series.*

i.e.,

$$\bar{\upsilon} = R_H\left[\frac{1}{2^2} - \frac{1}{n_2^2}\right] \text{ with } n_2 = 3, 4, 5, \ldots$$

This series is called *Balmer series* and lies in the visible region of the spectrum. The first line in the series ($n_2 = 3$) is called H_α *line*, the second line ($n_2 = 4$) is called H_β and so on.

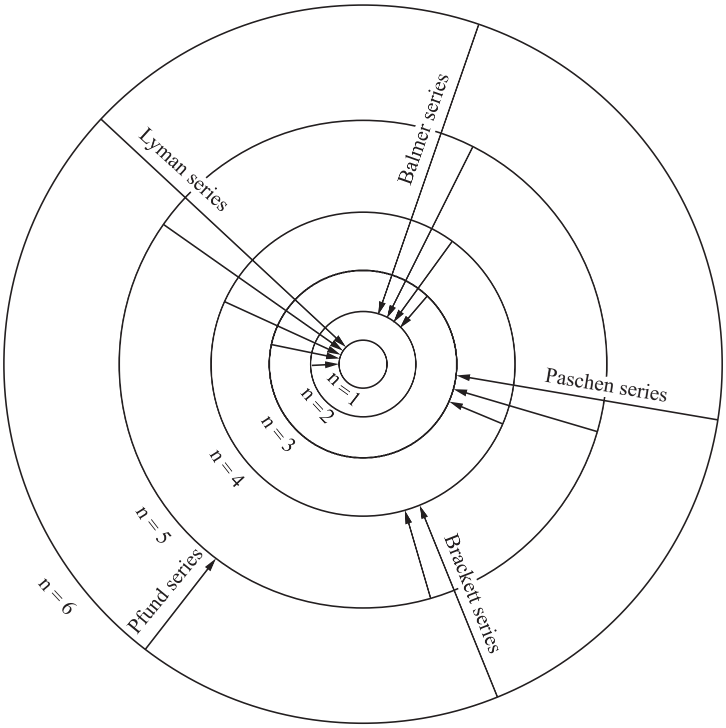

Fig. 2.3 Quantum jumps giving rise to different spectral series of hydrogen

Paschen Series

Paschen series lines in the infrared region are due to the transition of electrons from outer orbits to the third orbit.

Thus, $$\bar{\upsilon} = R_H\left[\frac{1}{3^2} - \frac{1}{n_2^2}\right] \text{ with } n_2 = 4, 5, \ldots$$

Brackett Series

If $n_1 = 4$ and $n_2 = 5, 6, 7, \ldots$, we get *Brackett series* lines.

$$\bar{\upsilon} = R_H\left[\frac{1}{4^2} - \frac{1}{n_2^2}\right] \text{ with } n_2 = 5, 6, 7, 8, \ldots$$

Pfund Series

If $n_1 = 5$ and $n_2 = 6, 7, 8, \ldots$, we get the *Pfund series* lines. For this series,

$$\bar{\upsilon} = R_H\left[\frac{1}{5^2} - \frac{1}{n_2^2}\right] \text{ with } n_2 = 6, 7, 8, \ldots$$

Brackett and Pfund series lie in the far infrared region of the hydrogen spectrum. By putting $n_2 = (n_1 + 1)$ in each one of the series, we get the longest wavelength of the series. Similarly by putting $n_2 = \infty$ in each one of the series, we get the shortest wavelength of the series (or series limit).

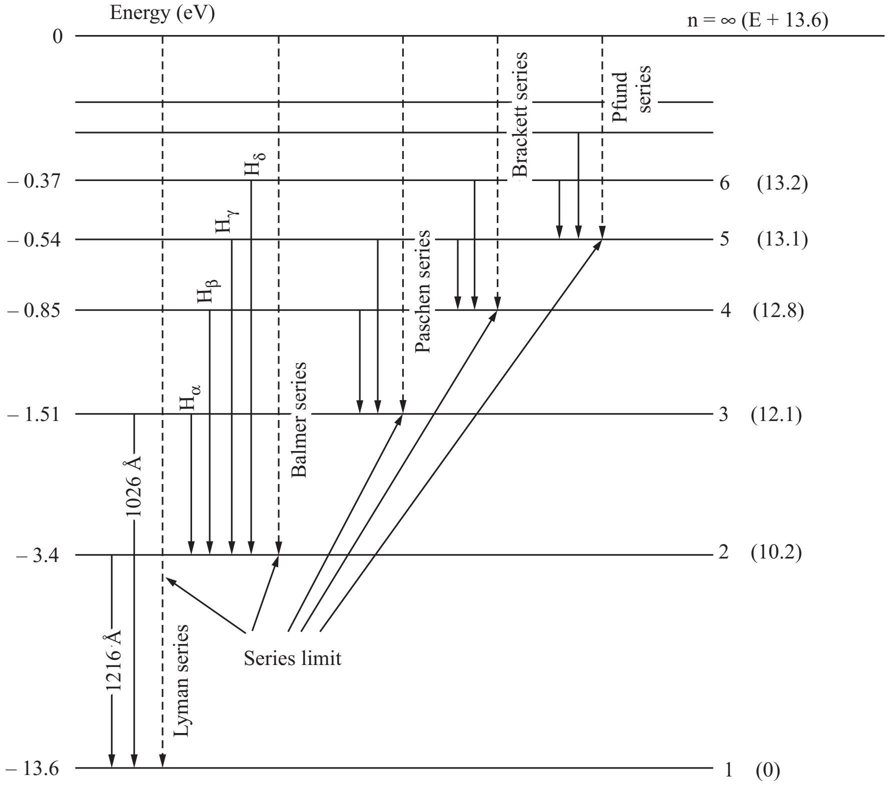

Fig. 2.4 Energy level diagram of hydrogen

X. SHORTCOMINGS OF BOHR'S THEORY

Bohr's theory, based on circular electron orbits, was able to explain successfully a number of experimentally observed facts and has correctly predicted the spectral lines of neutral hydrogen atom and singly ionised helium atom in terms of the principal quantum number *n*. However, the theory fails to explain the following facts:

(*i*) It could not account the spectra of atoms more complex than hydrogen.

(*ii*) It fails to give any information regarding the distribution and arrangement of electrons in atoms.

(*iii*) It does not explain the experimentally observed variations in intensity of the spectral lines of an element.

(*iv*) It fails to explain the transitions of electrons from one level to another, the rate at which they occur or the *selection rules* which apply to them.

(*v*) It fails to account the *fine structure* of spectral lines. Actually, it was found that when spectral lines emitted by an atom are examined, each line is composed of several lines closely packed together. Bohr's theory does not throw any light on it.

(*vi*) The theory cannot be used for the quantitative study of chemical bonding.

(*vii*) It was found that when electric or magnetic field is applied to the atom, each spectral line is splitted into several lines. The former one is called *Stark effect* while the later as *Zeeman effect*. Bohr's theory fails to explain these effects.

XI. SOMMERFELD'S RELATIVISTIC ATOM MODEL

According to Bohr, the lines of hydrogen-like spectrum should each have a well-defined wavelength. Careful spectroscopic examination showed that the H_α, H_β and H_γ lines in the hydrogen spectrum are not single. Each spectral line actually consisted of several very close lines packed together. Michelson found that under high resolution, H_α line can be resolved into two close components, with a wavelength separation of 0.013 nm. This is called the *fine structure* of the spectral lines. Bohr's theory could not explain this fine structure.

Sommerfeld succeeded partially in explaining the observed fine structure of spectral lines by introducing the following main modifications in Bohr's theory:

(*i*) Sommerfeld suggested that the path of an electron around the nucleus, in general, is an ellipse with the nucleus at one of the foci. The circular orbits of Bohr are a special case of this.

(*ii*) The velocity of the electron moving in an elliptical orbit varies considerably at different parts of the orbit. This causes relativistic variation in the mass of the moving electron. Therefore Sommerfeld took into account the relativistic variation of the mass of the electron with velocity. Hence this model of the atom is called the *relativistic atom model*.

XII. ELLIPTICAL ORBITS FOR HYDROGEN

An electron moving in the field of the nucleus describes elliptical orbits, with the nucleus at one focus. Circular orbits are only special cases of ellipses. When the electron moves along a circular orbit, the angular coordinate is sufficient to describe its motion. In an elliptical orbit, the position of the electron at any time instant is fixed by two coordinates namely the *angular coordinate* (ϕ) and the *radial coordinate* (r). Here r is the *radius vector* and ϕ is the angle which the radius vector makes with the major axis of the ellipse.

Consider an electron of mass m and linear tangential velocity v revolving in the elliptical orbit. This tangential velocity of the electron can be resolved into two components: One along the radius vector called radial velocity and the other perpendicular to the radius vector called the *transverse velocity*. Corresponding to these velocities, the electron has two momenta: One along the radius vector called *radial momentum* and the other perpendicular to the radius vector known as *azimuthal momentum* or *angular momentum*. So in the case of elliptic motion, both the angle ϕ and the radius vector r vary periodically, as shown in Fig. 2.5.

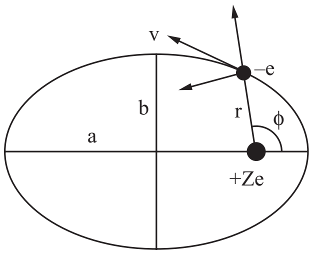

Fig. 2.5 Sommerfeld's model of the atom

Thus, the momenta associated with both these coordinates (ϕ and r) may be quantised in accordance with Bohr's quantum condition. The two quantisation conditions are

$$\boxed{\oint p_\phi \, d\phi = n_\phi h} \tag{2.17}$$

$$\boxed{\oint p_r \, dr = n_r h} \tag{2.18}$$

where n_ϕ and n_r are the two quantum numbers introduced by Sommerfeld. Since they stand for one periodic system, $n_r + n_\phi = n$. Here n_r is known as *radial quantum number,* n_ϕ as *angular* or *azimuthal quantum number* and n is known as *principal quantum number*.

Now, we have to quantise the momenta associated with both the radial and angular coordinates. The two equations are

$$\oint p_\phi \, d\phi = n_\phi h$$

and

$$\oint p_r \, dr = n_r h$$

The integrals are taken over one complete cycle of variation of the respective coordinates. Both n_ϕ and n_r are integers. Furthermore, the sum of n_r and n_ϕ is equal to the *principal quantum number* n.

The force on the electron is due to the electrostatic attraction to the nucleus and acts along the radius vector. There is no force at right angles to this radius vector, so the transverse component of the acceleration is zero throughout the atom. Hence

$$\frac{1}{r^2}\frac{d}{dt}\left[r^2\frac{d\phi}{dt}\right] \text{ is zero.}$$

Therefore $r^2\left(\frac{d\phi}{dt}\right)$ and so $mr^2\left[\frac{d\phi}{dt}\right]$ must be a constant.

Equation (2.17) can be easily evaluated. Thus,

$$p_\phi \int_0^{2\pi} d\phi = n_\phi h$$

$$p_\phi = n_\phi\left(\frac{h}{2\pi}\right) \tag{2.19}$$

This equation shows that the angular momentum of the electron is an integral multiple of $\frac{h}{2\pi}$.

It is considerably difficult to evaluate the integral in equation (2.18). However, an attempt is made here. The *polar equation* to the ellipse is

$$\frac{1}{r} = \frac{1+\varepsilon\cos\phi}{a\,(1-\varepsilon^2)} \tag{2.20}$$

where a is the *semimajor axis* and ε is the *eccentricity*. Thus differentiating this equation with respect to ϕ, we get

$$\left(\frac{1}{r^2}\right)\left(\frac{dr}{d\phi}\right) = \frac{\varepsilon\sin\phi}{a\,(1-\varepsilon^2)}$$

$$\frac{1}{r}\left(\frac{dr}{d\phi}\right) = \frac{r\,\varepsilon\sin\phi}{a\,(1-\varepsilon^2)} \tag{2.21}$$

Substituting the value of r from equation (2.20), we get

$$\frac{1}{r}\left(\frac{dr}{d\phi}\right) = \left[\frac{a\,(1-\varepsilon^2)}{(1+\varepsilon\cos\phi)}\right]\frac{\varepsilon\sin\phi}{a\,(1-\varepsilon^2)}$$

Thus, $$\frac{1}{r}\left(\frac{dr}{d\phi}\right) = \frac{\varepsilon\sin\phi}{(1+\varepsilon\cos\phi)} \tag{2.22}$$

Referring to equation (2.18),

$$\oint p_r\,dr = n_r h$$

$$\oint m\left(\frac{dr}{dt}\right)dr = n_r h$$

$$\oint m\left(\frac{dr}{d\phi}\right)\left(\frac{d\phi}{dt}\right)\frac{dr}{d\phi}\,d\phi = n_r h$$

$$\oint mr^2\,\frac{d\phi}{dt}\left[\frac{1}{r^2}\left(\frac{dr}{d\phi}\right)\left(\frac{dr}{d\phi}\right)\right]d\phi = n_r h$$

Substituting for $mr^2\,\dfrac{d\phi}{dt}$ [$= p_\phi$] and $\dfrac{1}{r}\dfrac{dr}{d\phi}$ from equation (2.22), we get

$$\oint p_\phi\left[\frac{\varepsilon\sin\phi}{(1+\varepsilon\cos\phi)}\right]^2 d\phi = n_r h$$

Referring to equation (2.19),

$$n_\phi\,\frac{h}{2\pi}\oint\left[\frac{\varepsilon\sin\phi}{(1+\varepsilon\cos\phi)}\right]^2 d\phi = n_r h$$

$$\frac{n_\phi}{2\pi}\oint\left[\frac{\varepsilon\sin\phi}{(1+\varepsilon\cos\phi)}\right]^2 d\phi = n_r \tag{2.23}$$

put $u = \varepsilon\sin\phi$ and $v = \dfrac{1}{1+\varepsilon\cos\phi}$

The above equation may now be written as

$$\frac{n_\phi}{2\pi}\oint u\,dv = \left(\frac{n_\phi}{2\pi}\right)\left[[uv]_0^{2\pi} - \int_0^{2\pi} v\,du\right]$$

$$= 0 - \left(\frac{n_\phi}{2\pi}\right)\int_0^{2\pi}\frac{(\varepsilon\cos\phi)\,d\phi}{1+\varepsilon\cos\phi} = n_r$$

$$= -\left(\frac{n_\phi}{2\pi}\right)\int_0^{2\pi}\frac{\varepsilon\cos\phi\,d\phi}{1+\varepsilon\cos\phi} = n_r$$

$$= \left(\frac{n_\phi}{2\pi}\right)\oint_0^{2\pi}\left[\frac{1}{1+\varepsilon\cos\phi} - 1\right]d\phi = n_r \tag{2.24}$$

Solution of the integral:

$$\int_0^{2\pi}\frac{d\phi}{1+\varepsilon\cos\phi}$$

Hint: Property of definite integral

$$\int_0^{2a} f(x)\,dx = 2\int_0^{a} f(x)\,dx \text{ if } f(2a-x) = f(x)$$

$$= 0 \text{ if } f(2a-x) = -f(x)$$

In the integral

$$\int_0^{2\pi}\frac{d\phi}{1+\varepsilon\cos\phi}$$

$$f(\phi) = \frac{1}{1+\varepsilon\cos\phi}$$

and $$f(2\pi-\phi) = \frac{1}{1+\varepsilon\cos(2\pi-\phi)} = \frac{1}{1+\varepsilon\cos\phi}$$

Thus $\int_0^{2\pi}\frac{d\phi}{(1+\varepsilon\cos\phi)}$ can be written as $2\int_0^{\pi}\frac{d\phi}{1+\varepsilon\cos\phi}$

The solution of this integral is obtained as follows:

Let $$t = \tan\frac{\phi}{2}$$

When $$\phi = 0,\ t = 0; \quad \text{when } \phi = \pi,\ t = \infty$$

$$dt = \left[\sec^2\frac{\phi}{2}\right]\frac{d\phi}{2}$$

$$d\phi = \frac{2\,dt}{\sec^2\frac{\phi}{2}} = \frac{2\,dt}{1+\tan^2\frac{\phi}{2}} = \frac{2\,dt}{1+t^2}$$

and $$\cos\phi = \frac{1-\tan^2\frac{\phi}{2}}{1+\tan^2\frac{\phi}{2}} = \frac{1-t^2}{1+t^2}$$

Substituting these values, the integral becomes

$$2\int_0^{\pi}\frac{d\phi}{1+\varepsilon\cos\phi} \text{ which becomes}$$

$$2\int_0^{\infty}\left(\frac{2\,dt}{1+t^2}\right)\frac{1}{1+\frac{\varepsilon(1-t^2)}{(1+t^2)}}$$

$$= 2\int_0^\infty \left(\frac{2\,dt}{1+t^2}\right)\frac{(1+t^2)}{(1+t^2+\varepsilon-\varepsilon t^2)}$$

$$= 4\int_0^\infty \frac{dt}{(1+\varepsilon)+t^2(1-\varepsilon)}$$

$$= \frac{4}{(1-\varepsilon)}\int_0^\infty \frac{dt}{t^2+\dfrac{(1+\varepsilon)}{(1-\varepsilon)}} = \frac{4}{(1-\varepsilon)}\int_0^\infty \frac{dt}{t^2+\left[\sqrt{\dfrac{1+\varepsilon}{1-\varepsilon}}\right]^2}$$

$$= \frac{4}{(1-\varepsilon)}\left[\frac{1}{\sqrt{\dfrac{1+\varepsilon}{1-\varepsilon}}}\right]\left[\tan^{-1}\frac{t}{\sqrt{\dfrac{1+\varepsilon}{1-\varepsilon}}}\right]_0^\infty = \frac{4}{\sqrt{1-\varepsilon^2}}\left[\frac{\pi}{2}\right] = \frac{2\pi}{\sqrt{1-\varepsilon^2}}$$

Thus equation (2.24) becomes

$$\frac{n_\phi}{2\pi}\left[\frac{2\pi}{\sqrt{1-\varepsilon^2}} - 2\pi\right] = n_r$$

$$n_\phi\left[\frac{1}{\sqrt{1-\varepsilon^2}} - 1\right] = n_r$$

$$\frac{1}{\sqrt{1-\varepsilon^2}} = 1 + \frac{n_r}{n_\phi} = \frac{n_\phi + n_r}{n_\phi}$$

$$\sqrt{1-\varepsilon^2} = \frac{n_\phi}{n_\phi + n_r} = \frac{n_\phi}{n}$$

$$1-\varepsilon^2 = \frac{n_\phi^2}{n^2} \tag{2.25}$$

$$\varepsilon^2 = \left[1-\frac{n_\phi^2}{n^2}\right] = \frac{(n^2-n_\phi^2)}{n^2}$$

$$\varepsilon = \left[1-\frac{n_\phi^2}{n^2}\right]^{1/2} \tag{2.26}$$

For an ellipse $(1-\varepsilon^2) = \dfrac{b^2}{a^2}$ where a and b are the *semimajor* and *semiminor* axes respectively.

Thus,

$$\boxed{\frac{b^2}{a^2} = \frac{n_\phi^2}{n^2}} \tag{2.27}$$

Equations (2.25) and (2.27) are the conditions that determine the allowed elliptical orbits. The allowed elliptical orbits are those for which the ratio of major to minor axes is that of two integers.

When $n_\phi = n$, $b = a$ and $\varepsilon = 0$, the orbit becomes circular. n_ϕ cannot be zero, since the ellipse would then degenerate into a straight line passing through the nucleus. Also n_ϕ cannot be greater than n, since b is always less than a. Hence for a given value of n, n_ϕ can assume only n different values, which means that there can be only n elliptical orbits of different eccentricities.

XIII. TOTAL ENERGY OF AN ELECTRON IN AN ELLIPTICAL ORBIT

The tangential velocity of the electron at any instant can be resolved into two components: One along the radius vector called the *radial velocity* $\left[\frac{dr}{dt}\right]$ and the other at right angle to the radius vector called the *transverse velocity* $r\left[\frac{d\phi}{dt}\right]$.

Thus, the radial momentum is $$p_r = m\,\frac{dr}{dt} \tag{2.28}$$

and the orbital angular momentum is $$p_\phi = mr^2\,\frac{d\phi}{dt} \tag{2.29}$$

The kinetic energy of the revolving electron is given by

$$\text{K.E.} = \frac{1}{2}mv^2 = \frac{1}{2}m\left[\left(\frac{dr}{dt}\right)^2 + \left(r\frac{d\phi}{dt}\right)^2\right] \tag{2.30}$$

$$\text{K.E.} = \frac{p_r^2}{2m} + \frac{p_\phi^2}{2mr^2}$$

Again $$\frac{dr}{dt} = \left(\frac{dr}{d\phi}\right)\left(\frac{d\phi}{dt}\right)$$

Thus from equation (2.29),

$$\frac{dr}{dt} = \left(\frac{dr}{d\phi}\right)\left(\frac{p_\phi}{mr^2}\right)$$

and $$p_\phi^2 = m^2r^4\left(\frac{d\phi}{dt}\right)^2$$

$$r^2\left[\frac{d\phi}{dt}\right]^2 = \frac{p_\phi^2}{m^2r^2}$$

Substituting these values in equation (2.30), we get

$$\text{K.E.} = \frac{1}{2}m\left[\frac{p_\phi^2}{m^2r^4}\left(\frac{dr}{d\phi}\right)^2 + \frac{p_\phi^2}{m^2r^2}\right]$$

$$= \frac{p_\phi^2}{2mr^2}\left[\left(\frac{1}{r}\frac{dr}{d\phi}\right)^2 + 1\right]$$

$$\text{P.E.} = -\frac{Ze^2}{4\pi\,\varepsilon_0 r}$$

Thus, the total energy of the electron

$$E_n = \frac{p_\phi^2}{2mr^2}\left[\left(\frac{1}{r}\frac{dr}{d\phi}\right)^2 + 1\right] - \frac{Ze^2}{4\pi\varepsilon_0 r} \tag{2.31}$$

or
$$\frac{p_\phi^2}{2mr^2}\left[\left(\frac{1}{r}\frac{dr}{d\phi}\right)^2 + 1\right] = E_n + \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\left[\frac{1}{r}\frac{dr}{d\phi}\right]^2 = \frac{2mr^2E_n}{p_\phi^2} + \frac{mrZe^2}{2\pi\varepsilon_0 p_\phi^2} - 1 \tag{2.32}$$

From equation (2.21),

$$\frac{1}{r^2}\left[\frac{dr}{d\phi}\right]^2 = \frac{\varepsilon^2 r^2 \sin^2\phi}{[a(1-\varepsilon^2)]^2} = \frac{\varepsilon^2 r^2(1-\cos^2\phi)}{[a(1-\varepsilon^2)]^2} \tag{2.32a}$$

$$\frac{1}{r^2}\left[\frac{dr}{d\phi}\right]^2 = \left[\frac{r}{a(1-\varepsilon^2)}\right]^2\left(\varepsilon^2 - \varepsilon^2\cos^2\phi\right) \tag{2.33}$$

The term $\left(\varepsilon^2 - \varepsilon^2\cos^2\phi\right)$ of this equation can be further simplified by referring to equation (2.20)

$$(1+\varepsilon\cos\phi) = \frac{a(1-\varepsilon^2)}{r}$$

$$\varepsilon\cos\phi = \frac{a(1-\varepsilon^2)}{r} - 1$$

$$(\varepsilon\cos\phi)^2 = \left[\frac{a(1-\varepsilon^2)}{r} - 1\right]^2$$

Substituting this in equation (2.32*a*), we get

$$\left[\frac{1}{r}\frac{dr}{d\phi}\right]^2 = \left[\frac{r}{a(1-\varepsilon^2)}\right]^2\left[\varepsilon^2 - \left\{\frac{a(1-\varepsilon^2)}{r} - 1\right\}^2\right]$$

$$= \frac{r^2}{a^2(1-\varepsilon^2)^2}\left[\varepsilon^2 - \left\{\frac{a^2(1-\varepsilon^2)^2}{r^2} + 1 - \frac{2a(1-\varepsilon^2)}{r}\right\}\right]$$

$$= \frac{r^2\varepsilon^2}{a^2(1-\varepsilon^2)^2} - 1 - \frac{r^2}{a^2(1-\varepsilon^2)^2} + \frac{2r}{a(1-\varepsilon^2)}$$

$$= \frac{r^2\varepsilon^2}{a^2(1-\varepsilon^2)^2} - \frac{r^2}{a^2(1-\varepsilon^2)^2} + \frac{2r}{a(1-\varepsilon^2)} - 1$$

$$= \frac{r^2\varepsilon^2 - r^2}{a^2(1-\varepsilon^2)^2} + \frac{2r}{a(1-\varepsilon^2)} - 1$$

$$= -\frac{r^2(1-\varepsilon^2)}{a^2(1-\varepsilon^2)^2} + \frac{2r}{a(1-\varepsilon^2)} - 1 \tag{2.34}$$

Equating the coefficients of r^2 and r in equations (2.34) and (2.32), we get

$$\frac{2mE_n}{p_\phi^2} = -\frac{1}{a^2(1-\varepsilon^2)} \tag{2.35}$$

and
$$\frac{mZe^2}{2\pi\varepsilon_0 p_\phi^2} = \frac{2}{a(1-\varepsilon^2)} \tag{2.36}$$

Thus equation (2.35) becomes

$$E_n = -\frac{p_\phi^2}{2ma^2(1-\varepsilon^2)} \tag{2.37}$$

Substituting the value of $(1-\varepsilon^2)$ from equation (2.36) in equation (2.37), we get

$$E_n = -\frac{p_\phi^2}{2ma^2}\left[\frac{amZe^2}{4\pi\varepsilon_0 p_\phi^2}\right]$$

$$E_n = -\frac{Ze^2}{8\pi a\varepsilon_0} \tag{2.38}$$

Again substituting for a from equation (2.36), we get

$$E_n = -\left(\frac{Ze^2}{8\pi\varepsilon_0}\right)\left(\frac{mZe^2}{2\pi\varepsilon_0 p_\phi^2}\right)\left(\frac{1-\varepsilon^2}{2}\right)$$

$$E_n = -\left[\frac{mZ^2e^4}{32\pi^2\varepsilon_0^2}\right]\frac{(1-\varepsilon^2)}{p_\phi^2}$$

Substituting for $(1-\varepsilon^2)$ and p_ϕ^2 from equations (2.25) and (2.19) respectively, we get

$$E_n = -\left[\frac{mZ^2e^4}{32\pi^2\varepsilon_0^2}\right]\left(\frac{n_\phi}{n}\right)^2\left(\frac{2\pi}{n_\phi h}\right)^2$$

$$\boxed{E_n = -\frac{mZ^2e^4}{8\varepsilon_0^2h^2n^2} = -\frac{mZ^2e^4}{8\varepsilon_0^2h^2}\left[\frac{1}{n_r+n_\phi}\right]^2} \tag{2.39}$$

which is identical with the expression for the energy of the electron in a circular orbit of quantum number *n*. Thus, the introduction of elliptical orbits does not result in the production of new energy terms; hence no new spectral lines are to be expected because of this multiplicity of orbits. Thus the introduction of elliptical orbits gives no new energy levels and hence no new transition. Hence Sommerfeld's attempt to explain the fine structure of spectral lines failed. But soon, on the basis of variation of mass of the electron with velocity, Sommerfeld was able to find a solution to the problem of fine structure of spectral lines. Here it is worthwhile to mention that experimental results and quantum mechanical predictions confirm that n_ϕ also assumes a value of zero. So corresponding to n, n_ϕ assumes 0, 1, 2, ..., $(n - 1)$, values, *i.e.*, a total of n possibilities. In wave mechanics azimuthal quantum number n_ϕ is denoted by l.

The magnitude of the semimajor axis a is obtained from equation (2.38) as follows:

$$E_n = -\frac{Ze^2}{8\,\pi\,\varepsilon_0 a} \quad \Rightarrow \quad a = \frac{-\,Ze^2}{8\,\pi\,\varepsilon_0 E_n}$$

Substituting for E_n from equation (2.39)

$$a = \left[\frac{Ze^2}{8\,\pi\,\varepsilon_0}\right]\left[\frac{8\,\varepsilon_0^2 h^2 n^2}{mZ^2 e^4}\right] \quad \text{or} \quad a = \frac{n^2 h^2 \varepsilon_0}{\pi m Z e^2} \quad \text{or} \quad a = \left[\frac{n^2 r_B}{Z}\right] \tag{2.40}$$

where $r_B = \dfrac{\varepsilon_0 h^2}{\pi m e^2} = 0.0529$ nm is the Bohr radius. Referring to the theory of ellipse, we write

$$(1 - \varepsilon^2) = \frac{b^2}{a^2}$$

$$b = a\sqrt{1 - \varepsilon^2}$$

$$b = a\left(\frac{n_\phi}{n}\right) \qquad \text{[Refer equation (2.27)]}$$

$$\boxed{b = \left(\frac{n^2 r_B}{Z}\right)\left(\frac{n_\phi}{n}\right)} \tag{2.41}$$

Equations (2.40) and (2.41) show that the length of the semimajor axis is determined solely by the principal quantum number n, while the length of the semiminor axis depends upon the azimuthal quantum number n_ϕ as well as n. For a given value of n, the possible values of n_ϕ are 0, 1, 2, ..., n, while the corresponding values of n_r are n, $(n - 1)$, ..., 0. When $n_\phi = 0$, the ellipse reduces to a straight line and the electron then passes through the nucleus traversing the orbit. This leads to the collapse of the atom. The value of $n_\phi = 0$ is therefore forbidden and for a given value n, n_ϕ is permitted to take only n values, 1, 2, 3, ..., n, with n_r taking the corresponding values $(n - 1)$, $(n - 2)$, ..., 0.

For the first orbit $n = 1$, since $(n_r + n_\phi) = 1$ and $n_\phi \neq 0 \Rightarrow n_\phi = 1$. Thus with $n = n_\phi$ and $n_r = 0$, the first orbit is a circle as seen from equation (2.27). All the n-orbits resulting from the n possible values of n, will have the same energy E, given by equation (2.39). With $n = 2$, n_ϕ may have the values 1 and 2, so that there are two possible orbits for $n = 2$. One is $n = 2$, and $n_\phi = 1$ (an ellipse) and the other is $n = 2$ and $n_\phi = 2$ (a circle); all these orbits have the same energy E_2 given by equation (2.39). Similarly with $n = 3$, n_ϕ will have values 1, 2 and 3, and the three possible orbits are two ellipses with ($n = 3$, $n_\phi = 1$ and $n = 3$, $n_\phi = 2$) and one circle with $n = 3$, $n_\phi = 3$; all these orbits have the same energy E_3. Usually the allowed orbits are described by giving values of n and n_ϕ. The three orbits for $n = 3$ are represented by symbols 3_3, 3_2 and 3_1, the subscript being the azimuthal quantum number (n_ϕ). In another notation used, the value of azimuthal quantum number n_ϕ is described by the letters *s, p, d, f* etc. The values of n_ϕ

corresponding to these letters are 1, 2, 3, 4, etc. respectively. In this notation, the orbit determined by $n = 3$ and $n_\phi = 1$ is represented by $3s$. Similarly $4d$ will represent the orbit $n = 4$ and $n_\phi = 3$. These orbits are represented in Fig. 2.6.

The transitions between the orbits $n = 3$ and $n = 2$ giving H_α line can now take place in six different ways. However, all these transitions have the same energy $E_3 - E_2$ and hence give rise to a single frequency for the H_α line, according to the frequency condition. No new lines, which would explain the fine structure are therefore predicted.

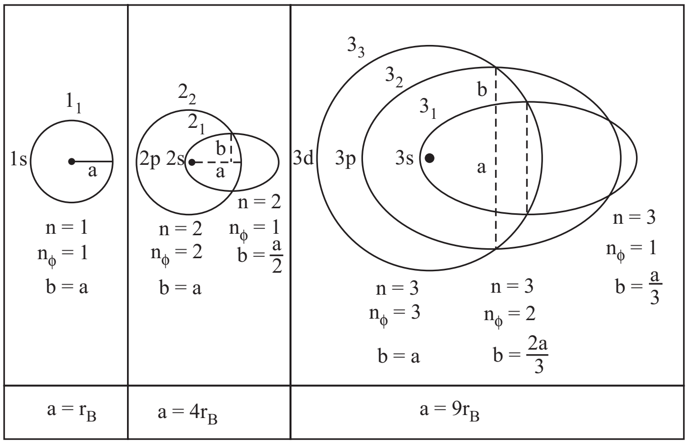

Fig. 2.6 Elliptical Bohr-Sommerfeld orbits for hydrogen

XIV. SOMMERFELD'S RELATIVISTIC CORRECTION

The velocity of an electron moving in an elliptical orbit varies from point to point in the orbit, being a maximum when the electron is nearest to the nucleus and a minimum when it is farther away from the nucleus. Furthermore, this velocity is quite large $\left(\frac{c}{137}\right)$. According to the theory of relativity, the variation of velocity means variation of mass of the electron.

Sommerfeld, including the relativistic correction in the treatment of elliptical orbits, showed that equation of the path of the electron was not simply that for an ellipse but was of the form

$$\frac{1}{r} = \frac{1 + \varepsilon \cos \psi\phi}{a(1 - \varepsilon^2)}$$

where ψ is given by

$$\psi^2 = 1 - \left[\frac{Ze^2}{4\pi\,\varepsilon_0 pc}\right]^2$$

This is the equation of an ellipse which precesses, *i.e.*, the major axis turns slowly about the focus (the nucleus) in the

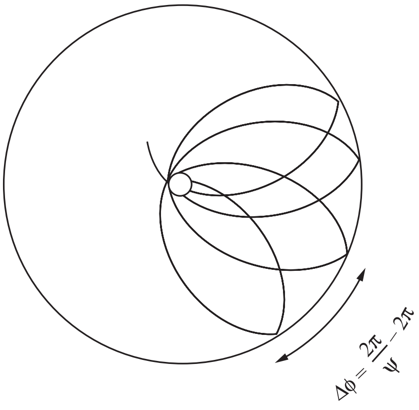

Fig. 2.7 Rosette path of the electron about the nucleus

plane of the ellipse. The path of the electron is, therefore, a *rosette*.

It can be shown that the total energy with a principal quantum number n in the relativistic theory is

$$E_n, n_\phi = -\frac{mZ^2e^4}{8\varepsilon_0^2h^2n^2} - \frac{mZ^2e^4\alpha^2}{8\varepsilon_0^2h^2}\left[\frac{n}{n_\phi} - \frac{3}{4}\right]\frac{1}{n^4} \qquad (2.42)$$

where $\alpha = \frac{e^2}{2\varepsilon_0 ch} = \frac{1}{137}$. α is a dimensionless quantity and is called the *fine structure constant.*

The first term on the right hand side is the energy of the electron in the orbit with the principal quantum number n according to Bohr's theory and the second term is Sommerfeld's relativity correction arising from the *rosette motion* of the electron orbit with principal quantum number n and azimuthal quantum number n_ϕ.The dependence of the total energy of the electron in its orbit as given by the equation (2.42) results in a splitting of energy levels in the atom. For a given value of n, there will be n components corresponding to the n permitted values of n_ϕ. Hence multiplicity of spectral lines should appear in hydrogen atom.

XV. FINE STRUCTURE OF H_α LINE

H_α *line* is due to the transition from $n = 3$ state to $n = 2$ state of hydrogen atom. For $n = 3$, there are three possible energy levels corresponding to the three values of $n_\phi = 1$, 2 and 3. Similarly, there are two possible levels for $n = 2$. Therefore, theoretically six transitions are possible:

$$3_3 \rightarrow 2_2\ ;\ 3_3 \rightarrow 2_1;\ 3_2 \rightarrow 2_2\ ;\ 3_2 \rightarrow 2_1\ ;\ 3_1 \rightarrow 2_2\ ;\ 3_1 \rightarrow 2_1$$

and these transitions are shown in Fig. 2.8. Actually, the H_α line has only three components. To make experiment and theory agree, some of the transitions have to be ruled out by some selection rule. The selection rule is that n_ϕ can change only +1 or –1 *i.e.*, $\Delta n_\phi = \pm 1$.

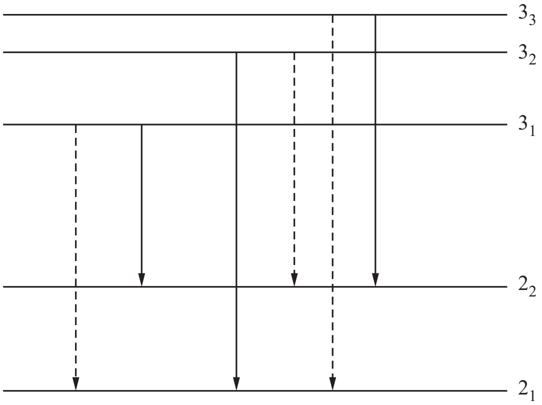

Fig. 2.8 Transitions and forbidden lines

XVI. DRAWBACKS OF BOHR-SOMMERFELD ATOM MODEL

(*i*) Bohr's theory failed to explain the fine structure of spectral lines even in the simplest hydrogen atom.

(*ii*) In the case of complex atoms, Bohr-Sommerfeld theory failed to calculate the energy of the system and frequencies of radiation emitted.

(*iii*) Sommerfeld's modification, though gave a theoretical background of the splitting of individual spectral lines of hydrogen, still it could not predict the correct number of observed fine structure lines.

(*iv*) Both the models could not explain the distribution and arrangement of electrons in atoms.

(*v*) Both the models do not throw any light on the intensities of the spectral lines.

(*vi*) Both the models could not explain anomalous *Zeeman effect* and *Stark effect.*

In order to provide a satisfactory explanation of the above, the *vector model* of the atom was formulated, this being based partly on experiments, partly on an analogy and partly on empirical methods.

XVII. VECTOR ATOM MODEL

For explaining the complex spectra of atom and their relation to atomic structure, the vector atom model was introduced. The two distinct features of the vector atom model are: (*i*) The conception of *spatial quantisation,* and (*ii*) the *spinning electron hypothesis.*

(*i*) Spatial Quantisation or Quantisation of Direction

According to Bohr's theory, the orbits are quantised in respect of their magnitude (*i.e.*, their size and shape) only. Finding this theory yet inadequate to explain further experimental observations *viz*., the *Zeeman* and *Stark effects* in which the spectral lines could be spilt up under the influence of magnetic and electric fields, the idea of orientation of the orbit in space naming it "the *space quantisation" was* introduced *i.e.*, the direction or orientation of the orbits in space also should be quantised. To specify the orientation of the electron orbit in space, we need a fixed reference axis. This reference line is chosen as the direction of an external magnetic field that is applied to the atom. The different permitted orientations of an electron orbit are determined by the fact that the projections of the *quantised orbits on the field direction must themselves be quantised. The* idea of space quantisation leads to an explanation of Zeeman effect. The Stern-Gerlach experiment provided an excellent proof of the space quantisation of atom. The quantum number associated with the space quantisation is called "*magnetic orbital quantum number"* and is represented by m_l.

(*ii*) Spinning Electron

To account for further hyperfine details in the atomic spectra of multi-electron atoms, Uhlenbeck and Goudsmit (1925) showed that the remaining difficulties could be resolved by assuming that the electrons were spinning about their own axes like a top, while traversing their orbits thus resulting in slight changes of energy. The spin of the electron is analogous to the spinning of a planet about its own axis as it moves in an elliptical orbit around the sun. In other words, the electron is endowed with a spin motion over and above the orbital motion. According to the quantum theory, the spin motion like the orbital motion, is to be quantised which will therefore introduce a new quantum number called the *magnetic spin quantum number,* denoted by m_s.

XVIII. THE CHARACTERISTIC QUANTUM NUMBERS

The state of the electron around the nucleus in terms of its location relative to the nucleus and the energy associated with it is described by a set of quantum numbers. Each electron is characterised by four important quantum numbers called the total or *principal quantum number,* the *orbital* or *azimuthal quantum number,* the *magnetic orbital quantum number* and the *magnetic spin quantum number*. The significance of these quantum numbers in terms of size, shape, orientation of orbitals in space and spin around the nucleus is now described briefly.

(*i*) The Total or Principal Quantum Number (*n*)

This is identical with the one used in Bohr-Sommerfeld's theory. It can take values 1, 2, 3, 4, ..., ∞. This specifies the major axis of the ellipse with which the energy of the electron is associated and hence pertains to the main energy level or shell. These energy levels having values of $n = 1, 2, 3, 4$, etc., as we go away from the nucleus are denoted by symbols *K, L, M, N,* etc. The energy (E) is inversely proportional to n^2. That is,

$$E_n \propto \frac{1}{n^2}$$

(*ii*) The Orbital Quantum Number (*l*)

This quantum number is an integer and for a given value of n, it can take any of the n values 0, 1, 2, 3, 4, ..., $(n - 1)$. By comparing these values with the values of the azimuthal quantum number n_ϕ of Sommerfeld's theory, it is seen that l is nothing but $(n_\phi - 1)$. l specifies the minor axis of the ellipse and is equal to $(n - 1)$ when the orbit is circular. It also divides the main shell into n slightly different energy levels of subshells so that the number of subshells in a main shell is given by its principal quantum number. Thus the shell with principal quantum number $n = 1$ or K-shell has only one subshell designated as s-subshell and in that case $l = 0$. This quantum number specifies the mechanical angular momentum of the electron and hence it is also called the *angular momentum quantum number.* The orbital angular momentum p_l associated with different orbits are

$$p_l = l\,\frac{h}{2\pi}, \quad \text{where} \quad l = 0, 1, 2, ..., \text{etc.}$$

According to quantum mechanical results, the value of orbital angular momentum p_l is not equal to $l\,\frac{h}{2\pi}$ but given by

$$p_l = \sqrt{l(l+1)}\left(\frac{h}{2\pi}\right)$$

The second principal shell or the L-shell will have two subshells having values of $l = 0$ and $l = 1$.

They are designated as s- and p-subshells. Similarly, the M principal shell has three subshells with values of $l = 0$, 1 and 2, and they are named as s-, p- and d-subshells respectively. Thus the n-subshells of the nth principal shell have the l values of 0, 1, 2, ..., $(n - 1)$. It may further be noted *that s-subshell is lower in energy than p-subshell* and the latter is lower in energy than the d-subshell and so on.

(*iii*) Magnetic Orbital Quantum Number (m_l)

This quantum number specifies the orientation of the electron in an external magnetic field; *i.e.*, this quantum number specifies the space orientation of the electron's plane elliptical orbit but has no effect on energy levels. It originated in the evidences of slight differences between almost identical energy levels obtained from the Zeeman effect; *i.e.*, the splitting of spectral lines when a light source is placed in a strong magnetic field and from the corresponding Stark effect produced by the application of an intense electric field. In these cases, the electrons because of their magnetic moments will experience torques tending to orient them so that the spin and the angular momentum vectors will take up definite positions in space with respect to the magnetic field thus introducing fresh levels. These extra subshells are denoted by the magnetic orbital quantum number m_l. For a given value of the orbital quantum number l, m_l, can take any of the $(2l + 1)$ values l, $(l - 1)$, $(l - 2)$..., 0, –1, –2, ..., $-l$. This means that m_l can assume $(2l + 1)$ values or the vector l can have $(2l + 1)$ orientations. For example, if $l = 1$, the permitted orientations of l are 3 for which m_l has the values +1, 0, –1.This is illustrated in Fig. 2.9 for $l = 3$. *The angle* θ *between l* and *B is given by l cos* $\theta = m_l$. The permitted orientations of the l vector relative to the field direction B is $(2l + 1)$. For example, if $l = 3$, the permitted orientations of l are 7, for which $m_l = 3, 2, 1, 0, -1, -2, -3$. Hence the l vector can take only the seven directions shown in Fig. 2.9. l cannot be inclined to B at any other angle. This is called *spatial quantisation*.

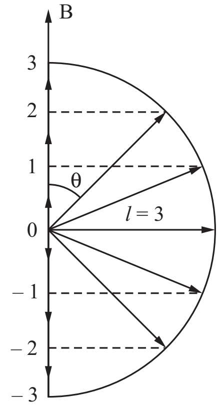

Fig. 2.9 Projection of orbital quantum vector in the direction of the magnetic field

(*iv*) The Magnetic Spin Quantum Number (m_s)

This quantum number specifies the orientation of the electron spin axis relative to the same frame of reference as used for m_l. The angular momentum can assume only two possible positions with respect to the magnetic field, clockwise or anticlockwise, that is, it may be parallel or antiparallel to it, *viz*., oppositely directed to it. Its projection along the direction of the magnetic field is denoted by m_s which is called the magnetic spin quantum number and can have only the values $+\frac{1}{2}$ or $-\frac{1}{2}$ as illustrated in Fig. 2.10, so that the difference in the spin quantum numbers for two electrons in any orbit is unity. The spin angular momentum of the electron is given by

$$p_s = s\frac{h}{2\pi},$$

where

$$s = \frac{1}{2}$$

According to wave mechanics, the spin angular momentum p_s of the electron is given by

$$p_s = \sqrt{s(s+1)}\left(\frac{h}{2\pi}\right)$$

Thus the four quantum numbers specified above define completely the state of any electron in a given atom.

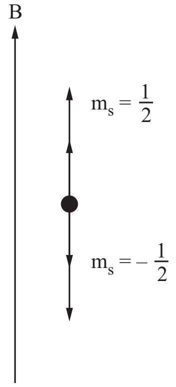

Fig. 2.10 Projection of the spin vector *s* in the direction of the magnetic field showing the two possible values of m_s

XIX. THE PAULI'S EXCLUSION PRINCIPLE

The generalised principle that governs the electronic configuration of atoms having more than one electron has been summarised in the *exclusion principle*, which was suggested by Wolfgang Pauli in 1925. According to this principle, *no two electrons in an isolated atom can exist in the same quantum state*. This principle is empirical and cannot be directly verified. But its universal acceptance rests on the fact that all the deductions which have been made from it have been either subjected to experimental verification or fit into a logical account of the theoretical physics of the structure of the atom. Pauli's principle implies that no two electrons in the same atom can have the same values of the four quantum numbers n, l, m_l, m_s. At least one quantum number must be different. To illustrate this principle, let us take the case of helium atom which has two electrons. These electrons occupy $n = 1$ orbit or K-shell. Clearly for $n = 1$, $l = 0$ and therefore, $m_l = 0$.

But m_s can have two values, namely, $+\frac{1}{2}$ and $-\frac{1}{2}$. Hence, one electron has $n = 1$, $l = 0$, $m_l = 0$, $m_s = +\frac{1}{2}$ and the other electrons has $n = 1$, $l = 0$, $m_s = -\frac{1}{2}$. Quantum representation of the electrons in the K-shell is illustrated in Fig. 2.11.

Quantum state	Electron configuration	Pictorial representation
(*a*) $n = 1, l = 0, m_l = 0, m_s = +\frac{1}{2}$	$1s^1$	$\boxed{\uparrow}$
(*b*) $n = 1, l = 0, m_l = 0, m_s = -\frac{1}{2}$	$1s^1$	$\boxed{\downarrow}$
(*c*) $n = 1, l = 0, m_l = 0, m_s = \pm\frac{1}{2}$	$1s^2$	$\boxed{\uparrow\downarrow}$

Fig. 2.11 Quantum representation of electrons in *K*-shell

XX. APPLICATION OF PAULI'S EXCLUSION PRINCIPLE

(*i*) Find the maximum number of electrons that *n* = 2 orbit can accommodate according to Pauli's exclusion principle.

For *L*-shell

$$n = 2$$
$$l = 0, 1$$
$$m_l = 0, +1, -1$$

and
$$m_s = +\frac{1}{2}, -\frac{1}{2}$$

Hence, the possible different combinations of the four quantum numbers are:

n	2	2	2	2	2	2	2	2
l	0	0	1	1	1	1	1	1
m_l	0	0	–1	–1	1	1	0	0
m_s	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$

It can now be seen that in no two vertical columns, all the four values of quantum numbers are identical. This means that the maximum number of electrons that can exist in *L*-shell is 8.

(*ii*) Maximum Number of Electrons in Orbitals or Subshells

Consider an orbit with principal quantum number n and orbital quantum number l. For finding the number of electrons in any orbital, it is clear that the values of n and l are fixed. Only the values of m_l and m_s can change. Now

$$m_l = -\,l \text{ to } +\,l \text{ including zero.}$$

Thus for a given value of l, there are $(2l + 1)$ values of m_l. Now for each value of m_l, m_s can have only two values, namely, $+\frac{1}{2}, -\frac{1}{2}$.

Hence, there can be only $2(2l + 1)$ different combinations of (n, l, m_l, m_s). Thus the maximum number of electrons in any subshell with orbital quantum number $l = 2(2l + 1)$. For example, *s*-subshell $(l = 0)$ can have a maximum of $2(2l + 1) = 2$ electrons. *p*-subshell $(l = 1)$ can have a maximum of $2(2l + 1) = 6$ electrons and so on.

(*iii*) Maximum Number of Electrons in Main Shells

The main shell consists of a number of subshells, called *orbitals*. According to Pauli's exclusion principle, the maximum number of electrons in an orbit with principal quantum number n is equal to $2n^2$. This can be proved as under:

Consider an orbit with principal quantum number n and orbital quantum number l. It has already been shown that the maximum number of electrons in an orbital is equal to $2(2l + 1)$ with $l = 0, 1, 2, ..., (n - 1)$.

Thus the total number of electrons with principal quantum number n is given by

$$\sum_{l=0}^{l=n-1} 2(2l+1)$$

$$= 2\sum_{l=0}^{l=n-1} (2l+1)$$

$$\boxed{\begin{aligned} &= 2\left[2\sum_{l=0}^{l=n-1} l + \sum_{l=0}^{l=n-1} 1\right] = \left[\frac{2n(n-1)}{2} + n\right] \\ &= 2n^2 \end{aligned}} \tag{2.42a}$$

Table 2.1 The distribution of electrons in the various states

n	*l* = 0, 1, 2, ..., (*n* – 1)	$m_l = -l$ *to* $+l$	$m_s = \pm\frac{1}{2}$	*Number of electrons in subshells*		*Number of electrons in main shells* ($2n^2$)
1	0	0	+ 1/2	2	$1s^2$	2(*K*)
1	0	0	– 1/2			
2	0	0	+ 1/2	2	$2s^2$	
2	0	0	– 1/2			
2	1	–1	+ 1/2	6	$2p^6$	8(*L*)
2	1	–1	– 1/2			
2	1	0	+ 1/2			
2	1	0	– 1/2			
2	1	1	+ 1/2			
2	1	1	– 1/2			
3	0	0	+ 1/2	2	$3s^2$	
3	0	0	– 1/2			
3	1	–1	+ 1/2	6	$3p^6$	
3	1	–1	– 1/2			
3	1	0	+ 1/2			
3	1	0	– 1/2			
3	1	1	+ 1/2			
3	1	1	– 1/2			
3	2	–2	+ 1/2	10	$3d^{10}$	18(*M*)
3	2	–2	– 1/2			
3	2	–1	+ 1/2			
3	2	–1	– 1/2			
3	2	0	+ 1/2			
3	2	0	– 1/2			
3	2	1	+ 1/2			
3	2	1	– 1/2			
3	2	2	+ 1/2			
3	2	2	– 1/2			

Hence the maximum number of electrons in an orbit is $2n^2$. This formula is applicable only to closed shells. The outermost shell cannot have more than eight electrons.

XXI. ELECTRON CONFIGURATION

The distribution of electrons in the various shells generally follows the rules given below:

(*i*) The maximum number of electrons possible in a main shell is $2n^2$ where n is the principal quantum number for the shell.
(*ii*) The outermost main shell cannot contain more than eighteen electrons.
(*iii*) The "last but one" main shell cannot contain more than eight electrons.
(*iv*) The last shell cannot contain more than two electrons and the last but one shell cannot contain more than nine electrons until the "last but two" shells has its full capacity of electrons.

Some Examples of Electron Configuration

***Hydrogen* (Z = 1)**

The hydrogen atom has only one electron occupying the *s*-subshell of the *K*-shell for which $n = 1$. This shell can have a maximum of two electrons. Since the shell is incomplete, hydrogen is chemically very active and forms new compounds on chemical reaction with suitable elements. This single electron exists either in the $m_s = +\frac{1}{2}$ state or $m_s = -\frac{1}{2}$ state. Symbolically, the electron configuration of hydrogen is represented as $1s^1$.

***Helium* (Z = 2)**

This atom has two electrons which fill the first orbit or *K*-shell. The two electrons in this shell are in the $m_s = +\frac{1}{2}$ state and $m_s = -\frac{1}{2}$ state (having opposite spins).

The shell is complete and hence helium is inert element.

The electronic configuration of helium is represented as $1s^2$. The number 4 refers to the principal quantum number 1. The symbol *s* refers to the subshell $l = 0$. The number of electrons 2 is fixed at the top of *s*.

***Carbon* (Z = 6)**

Carbon atom has 6 electrons. Two electrons fill the first main shell. The other four electrons are in the second main shell. Of these four electrons, two are in the *s*-subshell and the other two are in the *p*-subshell. The electronic configuration is represented as $1s^2\ 2s^2\ 2p^2$.

***Neon* (Z = 10)**

Two electrons fill the first main shell. Eight electrons fill the second main shell. This is another inert element.

XXII. THE PERIODIC TABLE

Mendelyeev, a Russian scientist in 1869 showed that the elements when arranged according to the magnitude of atomic weights, displayed marked periodicity in their properties. Elements were also found to exhibit periodicity in various physical properties such as atomic volume, expansion coefficient, electrical conductivity and melting point. Based on these observations, the law of periodic table states that the properties of the elements are periodic functions of their atomic weights.

Mendelyeev arranged all the elements in the order of their increasing atomic weights in horizontal rows in such a way that the elements having similar properties come directly under one another in the

Table 2.2 Electronic configuration of elements

Atomic number	*Name of element*	*Symbol*	*Atomic weight*	*Distribution of electrons within the shells*																		*Number of neutrons*
				K	***L***		***M***			***N***				***O***				***P***			***Q***	
				s	*s*	*p*	*s*	*p*	*d*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*s*	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
1	Hydrogen	H	1.008	1																		–
2	Helium	He	4.003	2																		2
3	Lithium	Li	6.939	2	1																	4
4	Beryllium	Be	9.012	2	2																	5
5	Boron	B	10.81	2	2	1																6
6	Carbon	C	12.01	2	2	2																6
7	Nitrogen	N	14.01	2	2	3																7
8	Oxygen	O	16.00	2	2	4																8
9	Fluorine	F	19.00	2	2	5																10
10	Neon	Ne	20.18	2	2	6																10
11	Sodium	Na	22.99	2	2	6	1															12
12	Magnesium	Mg	24.31	2	2	6	2															12
13	Aluminium	Al	26.98	2	2	6	2	1														14
14	Silicon	Si	28.09	2	2	6	2	2														14
15	Phosphorus	P	30.99	2	2	6	2	3														16
16	Sulphur	S	32.06	2	2	6	2	4														16
17	Chlorine	Cl	35.45	2	2	6	2	5														18
18	Argon	Ar	39.95	2	2	6	2	6														22
19	Potassium	K	39.10	2	2	6	2	6	–	1												20
20	Calcium	Ca	40.08	2	2	6	2	6	–	2												20
21	Scandium	Sc	44.96	2	2	6	2	6	1	2												24
22	Titanium	Ti	47.90	2	2	6	2	6	2	2												26
23	Vanadium	V	50.94	2	2	6	2	6	3	2												28
24	Chromium	Cr	52.00	2	2	6	2	6	5	1												28
25	Manganese	Mn	54.94	2	2	6	2	6	5	2												30

(*Contd.*)

Table 2.2 (*Contd.*)

Atomic number	*Name of element*	*Symbol*	*Atomic weight*	*Distribution of electrons within the shells*																		*Number of neutrons*
				K	***L***		***M***			***N***				***O***				***P***			***Q***	
				s	*s*	*p*	*s*	*p*	*d*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*s*	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
26	Iron	Fe	55.85	2	2	6	2	6	6	2												30
27	Cobalt	Co	58.93	2	2	6	2	6	7	2												32
28	Nickel	Ni	58.71	2	2	6	2	6	8	2												30
29	Copper	Cu	63.54	2	2	6	2	6	10	1												34
30	Zinc	Zn	65.37	2	2	6	2	6	10	2												34
31	Gallium	Ga	69.72	2	2	6	2	6	10	2	1											38
32	Germanium	Ge	75.59	2	2	6	2	6	10	2	2											42
33	Arsenic	As	74.92	2	2	6	2	6	10	2	3											42
34	Selenium	Se	78.96	2	2	6	2	6	10	2	4											46
35	Bromine	Br	79.91	2	2	6	2	6	10	2	5											44
36	Krypton	Kr	83.80	2	2	6	2	6	10	2	6											48
37	Rubidium	Rb	85.47	2	2	6	2	6	10	2	6	–	–	1								48
38	Strontium	Sr	87.62	2	2	6	2	6	10	2	6	–	–	2								50
39	Yttrium	Y	88.91	2	2	6	2	6	10	2	6	1	–	2								50
40	Zirconium	Zr	91.22	2	2	6	2	6	10	2	6	2	–	2								50
41	Niobium	Nb	92.91	2	2	6	2	6	10	2	6	4	–	1								52
42	Molybdenum	Mo	95.94	2	2	6	2	6	10	2	6	5	–	1								56
43	Technetium	Tc*	(99)	2	2	6	2	6	10	2	6	6	–	1								(54)
44	Ruthenium	Ru	101.1	2	2	6	2	6	10	2	6	7	–	1								58
45	Rhodium	Rh	102.9	2	2	6	2	6	10	2	6	8	–	1								58
46	Palladium	Pd	106.4	2	2	6	2	6	10	2	6	10	–	–								60
47	Silver	Ag	107.9	2	2	6	2	6	10	2	6	10	–	1								60
48	Cadmium	Cd	112.4	2	2	6	2	6	10	2	6	10	–	2								66
49	Indium	In	114.8	2	2	6	2	6	10	2	6	10	–	2	1							64
50	Tin	Sn	118.7	2	2	6	2	6	10	2	6	10	–	2	2							70

(*Contd.*)

Table 2.2 (*Contd.*)

Atomic number	*Name of element*	*Symbol*	*Atomic weight*	*Distribution of electrons within the shells*																		*Number of neutrons*
				K	***L***		***M***			***N***				***O***				***P***			***Q***	
				s	*s*	*p*	*s*	*p*	*d*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*s*	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
51	Antimony	Sb	121.8	2	2	6	2	6	10	2	6	10	–	2	3							70
52	Tellurium	Te	127.6	2	2	6	2	6	10	2	6	10	–	2	4							78
53	Iodine	I	126.9	2	2	6	2	6	10	2	6	10	–	2	5							74
54	Xenon	Xe	131.3	2	2	6	2	6	10	2	6	10	–	2	6							78
55	Caesium	Cs	132.9	2	2	6	2	6	10	2	6	10	–	2	6	–	–	1				78
56	Barium	Ba	137.3	2	2	6	2	6	10	2	6	10	–	2	6	–	–	2				82
57	Lanthanum	La	138.9	2	2	6	2	6	10	2	6	10	–	2	6	1	–	2				82
58	Cerium	Ce	140.1	2	2	6	2	6	10	2	6	10	2	2	6	–	–	2				82
59	Praseodymium	Pr	140.9	2	2	6	2	6	10	2	6	10	3	2	6	–	–	2				82
60	Neodymium	Nd	144.2	2	2	6	2	6	10	2	6	10	4	2	6	–	–	2				82
61	Promethium	Pm*	(145)	2	2	6	2	6	10	2	6	10	5	2	6	–	–	2				(84)
62	Samarium	Sm	150.4	2	2	6	2	6	10	2	6	10	6	2	6	–	–	2				90
63	Europium	Eu	152.0	2	2	6	2	6	10	2	6	10	7	2	6	–	–	2				90
64	Gadolinium	Gd	157.3	2	2	6	2	6	10	2	6	10	7	2	6	1	–	2				94
65	Terbium	Tb	158.9	2	2	6	2	6	10	2	6	10	9	2	6	–	–	2				94
66	Dysprosium	Dy	162.5	2	2	6	2	6	10	2	6	10	10	2	6	–	–	2				98
67	Holmium	Ho	164.9	2	2	6	2	6	10	2	6	10	11	2	6	–	–	2				98
68	Erbium	Er	167.3	2	2	6	2	6	10	2	6	10	12	2	6	–	–	2				98
69	Thulium	Tm	168.9	2	2	6	2	6	10	2	6	10	13	2	6	–	–	2				100
70	Yetterbium	Yb	173.0	2	2	6	2	6	10	2	6	10	14	2	6	–	–	2				104
71	Lutetium	Lu	175.0	2	2	6	2	6	10	2	6	10	14	2	6	1	–	2				104
72	Hafnium	Hf	178.5	2	2	6	2	6	10	2	6	10	14	2	6	2	–	2				108
73	Tantalum	Ta	180.9	2	2	6	2	6	10	2	6	10	14	2	6	3	–	2				108
74	Tungsten	W	183.9	2	2	6	2	6	10	2	6	10	14	2	6	4	–	2				110
75	Rhenium	Re	186.2	2	2	6	2	6	10	2	6	10	14	2	6	5	–	2				110

(*Contd.*)

Table 2.2 (*Contd.*)

Atomic number	*Name of element*	*Symbol*	*Atomic weight*	*Distribution of electrons within the shells*																		*Number of neutrons*
				K	***L***		***M***			***N***				***O***				***P***			***Q***	
				s	*s*	*p*	*s*	*p*	*d*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*s*	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
76	Osmium	Os	190.2	2	2	6	2	6	10	2	6	10	14	2	6	6	–	2				116
77	Iridium	Ir	192.2	2	2	6	2	6	10	2	6	10	14	2	6	9	–	–				116
78	Platinum	Pt	195.1	2	2	6	2	6	10	2	6	10	14	2	6	9	–	1				116
79	Gold	Au	197.0	2	2	6	2	6	10	2	6	10	14	2	6	10	–	1				118
80	Mercury	Hg	200.6	2	2	6	2	6	10	2	6	10	14	2	6	10	–	2				122
81	Thallium	Tl	204.4	2	2	6	2	6	10	2	6	10	14	2	6	10	–	2	1			124
82	Lead	Pb	207.2	2	2	6	2	6	10	2	6	10	14	2	6	10	–	2	2			126
83	Bismuth	Bi	209.0	2	2	6	2	6	10	2	6	10	14	2	6	10	–	2	3			126
84	Polonium	Po*	(209)	2	2	6	2	6	10	2	6	10	14	2	6	10	–	2	4			(125)
85	Astatine	At*	(210)	2	2	6	2	6	10	2	6	10	14	2	6	10	–	2	5			(125)
86	Radon	Rn*	(222)	2	2	6	2	6	10	2	6	10	14	2	6	10	–	2	6	–		(136)
87	Francium	Fr*	(223)	2	2	6	2	6	10	2	6	10	14	2	6	10	–	2	6	–	1	(136)
88	Radium	Ra*	(226)	2	2	6	2	6	10	2	6	10	14	2	6	10	–	2	6	–	2	(138)
89	Actinium	Ac*	(227)	2	2	6	2	6	10	2	6	10	14	2	6	10	–	2	6	1	2	(138)
90	Thorium	Th*	232	2	2	6	2	6	10	2	6	10	14	2	6	10	–	2	6	2	2	142
91	Protactinium	Pa*	(231)	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1	2	(140)
92	Uranium	U*	238	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2	146
93	Neptunium	Np*	(237)	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2	(144)
94	Plutonium	Pu*	(244)	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6	–	2	(150)
95	Americium	Am*	(243)	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	–	2	(148)
96	Curium	Cm*	(247)	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2	(151)
97	Berkelium	Bk*	(247)	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1	2	(150)
98	Californium	Cf*	(251)	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6	–	2	(153)
99	Einsteinium	Es*	(254)	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6	–	2	(155)
100	Fermium	Fm*	(253)	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6	–	2	(153)

(*Contd.*)

Table 2.2 (*Contd.*)

Atomic number	*Name of element*	*Symbol*	*Atomic weight*	*Distribution of electrons within the shells*																		*Number of neutrons*
				K	***L***		***M***			***N***				***O***				***P***			***Q***	
				s	*s*	*p*	*s*	*p*	*d*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*s*	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
101	Mendelevium	Md*	(256)	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6	–	2	(155)
102	Nobelium	No*	(253)	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	–	2	(151)
103	Lawtentium	Lr*	(257)	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	1	2	(154)
104	Kurchatovium	Ku		2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	2	2	
105	Hahnium	Ha		2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	3	2	

Note: 1. Elements marked *are unstable.

2. The elements whose atomic weights are given in parenthesis do not occur in nature, but have been prepared artificially in nuclear reactions.
3. The number of neutrons in these cases is calculated for the most commonly found isotope.

Table 2.3 Periodic Table

Period	Group I	II											III	IV	V	VI	VII	VIII
1	1 H 1.00797																	2 He 4.0026
2	3 Li 6.939	4 Be 9.0122											5 B 10.811	6 C 12.0112	7 N 14.0067	8 O 15.9994	9 F 19.9984	10 Ne 20.179
3	11 Na 22.989	12 Mg 24.305											13 Al 26.9815	14 Si 28.096	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
4	19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.992	34 Se 78.96	35 Br 79.909	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30
6	55 Cs 132.905	56 Ba 137.34	57–71 *	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.05	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.98	84 Po (210)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89–103 **															
	*Rare Earths		57 La 138.91	58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97	
	**Actinides		89 Ac (227)	90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (252)	99 Es (254)	100 Fm (253)	101 Md (257)	102 No (255)	103 Lr (256)	

same vertical columns or groups. In this table, there were seven horizontal rows (or periods) and eight vertical columns (or groups). Though the Mendelyeev's periodic table was of great significance in the study of elements, yet it could not explain the position of *isotopes* (elements having same atomic number but having different atomic weights are called *isotopes).* In certain cases, it was found that the elements with higher atomic weight came first and elements with lower atomic weight came later. As a result of this, it was felt that the atomic weight cannot be taken as the basis for the classifications of elements.

Modern Periodic Table

In 1913, Mosely suggested that the properties of elements are periodic functions of their atomic numbers and not atomic weights. We know that, no two elements can have the same atomic number, and hence atomic number is more a fundamental property than the atomic weight. Mosely proposed a periodic table in which the elements are arranged in the order of their increasing atomic numbers.

The periodic table proposed by Mosely was later modified by Bohr which is now popularly known as Modern periodic table. In this table, elements are arranged in the order of their increasing atomic number. There is a marked periodicity in properties. Each vertical column within this table is numbered from one to eight and is called a group, while each of the seven horizontal rows is known as a period. The periodic table can be conveniently divided into four distinct zones as shown in Fig. 2.12.

1. Non-metals
2. Light metals
3. Transition metals
4. Soft metals.

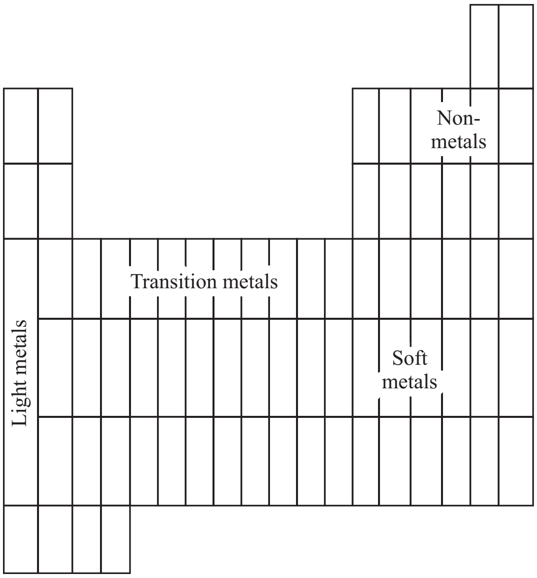

Fig. 2.12 Zones within the periodic table

The non-metals are the extreme right-hand groups of the elements in the table and include the inert gases (He, Ne, Ar, etc.). Silicon, arsenic and tellurium belong to the subgroup known as the half metals since they exhibit some of the properties of metals and some of the properties of non-metals. The light metals occupy the two groups on the extreme left of the table and are characterised by low densities, low melting points, high reactivity in chemical reactions and a tendency to form ionic compounds. This zone is made up of alkali metals and the alkaline earths having valencies of +1 and +2 respectively.

The transition metals occupy the central position of the table and possess the three general characteristics that distinguish them as a group. They are all high melting point materials, usually form coloured compounds and most of the traditional engineering metals come from this zone of the table, and they all possess relatively high densities.

The soft metals fall between the transition metals and the non-metals, and the properties of some of them grade out into those of these two classes of metals. Generally speaking, the metals of this zone are comparatively soft and unreactive and possess low melting point.

The properties of elements change in a systematic way through a period. From left to right in the periodic table, and from bottom to top, the elements become more electronegative. This means that their electron affinity increases. Inversely, from right to left and from top to bottom of the periodic table the elements become more electropositive. The *electron affinity* is defined as the energy that is given out when an electron is added to an atom to form a negative ion. On the other hand, the energy necessary to remove the most loosely bound electron from an atom is called the *ionisation potential*. In general, the ionisation potential increases on going from left to right in the table.

The first element in the table is hydrogen, which has one electron. According to the rules, this electron normally occupies one of the two $1s$ states, since these have the lowest energy. The helium atom ($Z = 2$) has two electrons, both contained in the $1s$ state, which can accommodate two electrons provided they have opposite spins. The first main shell ($n = 1$) is now full, and therefore the third electron forming lithium ($Z = 3$) must go into the lowest subshell of the second shell; *i.e.,* the $2s$ level. Thus, with the lithium a new shell begins to form and a new row of periodic table commences. The elements in this row add their electrons to the second shell until it is completely filled at neon. The order of filling may be completely understood by examining Table 2.2. It is also found that when a new shell begins to form in the structure of the atom, the element in question commences a new row in the periodic table.

An important effect occurs in the elements immediately following argon. To complete the third shell, 10 more electrons are required to occupy the $3d$ states. For these elements, however, $4s$ energy level is slightly lower than the $3d$, and so fourth shell begins to form before the third shell is filled. Thus a new period commences with an alkali metal, potassium, and an alkaline earth metal, calcium. In the following series of elements, extending to copper, the $3d$ states become increasingly occupied. Hence, there is a large group in this period with only one or two electrons in the outermost shell. All these elements are metals, and those in which the third shell is expanding from 8 to 18 electrons are known as transition metals.

The same sort of behaviour is found in the subsequent rows of the periodic table. The $5s$ states are occupied before the $4d$ and $6s$ states before the $5d$. As a result, two additional groups of transition metals are obtained. In the final long period, the situation is completed by the fact that during filling of the $5d$ states in the last group of transition metals, the $4f$ states begin to be occupied. This results in a group of elements known as the *rare earths*.

XXIII. WAVE MECHANICAL CONCEPT OF THE ATOM

There have been important developments since the Bohr-Sommerfeld theory. These developments have proposed treatments entirely foreign to the Bohr-Sommerfeld picture and these have led to even more satisfactory results from an analytical point of view. The modifications were started when de Broglie proposed that particles, such as electrons, possessed many properties of waves. He concluded theoretically that a particle of mass m now moving with a velocity v would behave as a wave having a wavelength

$$\lambda = \frac{h}{mv}$$

This wave mechanical treatment of the atom illuminates many of the odd *ad hoc* assumptions made in the previous sections. Instead of assuming the electron to be moving in a fixed stationary orbit it was imagined to generate a series of waves as it revolved round the nucleus in any permissible orbit.

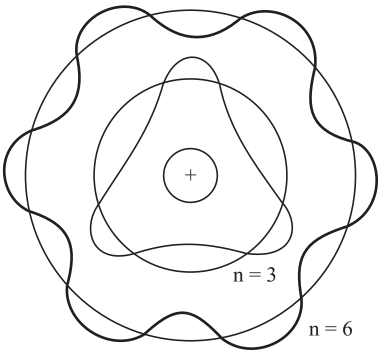

Fig. 2.13 de Broglie's stationary wave quantised orbits

In order that the waves should not cancel each other by interference in any permissible orbit, the electron must move in such a manner as to produce a standing wave in the orbit. This will happen only if the electron wavefront fills the circumference as in Fig. 2.13 where there are an integral number of wavelengths. Thus the circumference must contain an integral number of waves.

Thus $2\pi r = n\lambda$, where r is the radius of the permitted orbit and n an integer. Substituting $\frac{h}{mv}$ for λ, we get

$$\boxed{\begin{aligned} 2\pi r &= n\frac{h}{mv} \\ mvr &= n\frac{h}{2\pi} \end{aligned}} \tag{2.43}$$

But mvr is the angular momentum of the electron regarded as a particle. Thus we see that, the wave mechanical picture leads to Bohr's postulate regarding the quantisation of orbits—that the only permitted orbits are those angular momenta which are equal to an integral multiple of $\frac{h}{2\pi}$.

OBJECTIVE QUESTIONS

1. If f_1 and f_2 are the frequencies of the electron in the first and second orbits of hydrogen atom respectively, then (f_1/f_2) is

(*a*) 8 (*b*) 2

(*c*) 4 (*d*) 1

2. The total energy of the electron in the nth orbit of hydrogen atom is

(*a*) $\frac{e^2}{4\pi\,\varepsilon_0 r_n}$ (*b*) $-\frac{e^2}{4\pi\,\varepsilon_0 r^2 n}$

(*c*) $\frac{e^2}{8\pi\,\varepsilon_0 r_n}$ (*d*) $-\frac{e^2}{8\pi\,\varepsilon_0 r_n}$

3. The kinetic energy of an electron in an atom is

(*a*) half of its potential energy
(*b*) twice of its potential energy
(*c*) equal to its potential energy
(*d*) thrice of its potential energy

4. If the radius of the first orbit in hydrogen atom is 0.05 nm, the radius of the first orbit in helium atom is

(*a*) 0.025 nm
(*b*) 0.05 nm
(*c*) 1 nm
(*d*) none of these

5. The numerical value of the radius of the first orbit of hydrogen is

(*a*) 0.529 nm
(*b*) 0.0529 Å
(*c*) 5.29 Å
(*d*) 0.0529 nm

6. The total energy of the electron in hydrogen atom is

(*a*) $-(13.6/n)$ eV
(*b*) $(13.6/n)$ eV
(*c*) $-(13.6/n^2)$ eV
(*d*) $(13.6/n^2)$ eV

7. The ratio of frequencies of the first line of the Lyman series and the first line of Balmer series is

(*a*) 27/5
(*b*) 27/8
(*c*) 8/27
(*d*) 4/27

8. When an electron jumps from the fourth orbit to the second orbit, one gets

(*a*) the first line of Pfund series
(*b*) second line of Lyman series
(*c*) second line of Paschen series
(*d*) second line of Balmer series

9. The ionisation energy of hydrogen atom is

(*a*) 0.52 eV
(*b*) 13.6 eV
(*c*) –13.6 eV
(*d*) – 0.52 eV

10. When an electron in an atom shifts from an excited state to a lower state, a quantum of energy is always radiated:

(*a*) Yes
(*b*) No

11. The third subshell of an atom can have a maximum of

(*a*) 2 electrons
(*b*) 14 electrons
(*c*) 10 electrons
(*d*) 6 electrons

12. The range of frequencies of the lines of visible region in hydrogen spectrum is

(*a*) 6000×10^{14} s^{1}
(*b*) 600×10^{14} s^{1}
(*c*) 60×10^{14} s^{-1}
(*d*) 6×10^{14} s^{-1}

13. If v is the velocity of the electron in a stationary orbit of radius r, the orbital frequency of the electron is

(*a*) $v/2\pi r$
(*b*) v/r
(*c*) $v/\pi r$
(*d*) $2\pi r/v$

14. The root mean square velocity $\bar{c}$ of helium atom at T degree kelvin satisfies the relation

(*a*) $\bar{c} \propto \sqrt{T}$
(*b*) $\bar{c} \propto 1/\sqrt{T}$
(*c*) $\bar{c} \propto T$
(*d*) $\bar{c} \propto 1/T$

15. The Rydberg constant for hydrogen is

(*a*) $1.0961 \times 10^{-7}\ m^{-1}$
(*b*) 1.0961×10^{6} m
(*c*) $1.0961 \times 10^{7}\ m^{-1}$
(*d*) $1.0961 \times 10^{-6}\ m^{-1}$

16. The expression for the total energy with the principal quantum number n in the relativistic model of the atom is

(*a*) $-E_n\left\{1+\frac{\alpha^2}{n^2}\left(\frac{n}{n_\phi}-\frac{3}{4}\right)\right\}$

(*b*) $E_n\left\{1+\frac{\alpha^2}{n^2}\left(\frac{n}{n_\phi}-\frac{3}{4}\right)\right\}$

(*c*) $E_n\left\{1+\frac{\alpha^2}{n^2}\left(\frac{n_\phi}{n}-\frac{3}{4}\right)\right\}$

(*d*) $-E_n\left\{1-\frac{\alpha^2}{n^2}\left(\frac{n_\phi}{n}-\frac{3}{4}\right)\right\}$

where $\alpha = e^2/2\,\varepsilon_0 ch$

17. The maximum number of electrons in a subshell with orbital quantum number l is

(*a*) $(2l + 1)$

(*b*) $(2l - 1)$

(*c*) $2(2l + 1)$

(*d*) $2(2l - 1)$

18. The electronic configuration of the element iron is

(*a*) $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^8\, 4s^0$

(*b*) $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^7\, 4s^1$

(*c*) $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^7\, 4s^0$

(*d*) $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^6\, 4s^2$

19. The shortest wavelength of Balmer series in hydrogen spectrum is given by the equation

(*a*) $1/\lambda = R_H\,(1/4 - 1/9)$

(*b*) $1/\lambda = R_H\,(1/2 - 1/\infty)$

(*c*) $1/\lambda = R_H\,(1 - 1/\infty)$

(*d*) $1/\lambda = R_H\,(1/4 - 1/\infty)$

where R_H is the Rydberg constant for hydrogen.

20. Which of the following transition is ruled out?

(*a*) $3_1 \rightarrow 2_1$

(*b*) $3_1 \rightarrow 2_2$

(*c*) $3_2 \rightarrow 2_1$

(*d*) $3_2 \rightarrow 2_2$

21. One Bohr magneton is approximately

(*a*) 10^{23} Am^2

(*b*) 10^{-23} Am^2

(*c*) 10^{10} Am^2

(*d*) 10^{-10} Am^2

22. If M_A and ρ are the atomic weight and density of a metal respectively and N_A is the Avogadro's number, then the number of atoms present in unit volume is calculated using the relation

(*a*) $M_A/N_A\rho$

(*b*) $N_A\rho/M_A$

(*c*) $M_A\rho/N_A$

(*d*) $N_A/M_A\rho$

23. The longest wavelength of the Lyman series in hydrogen spectrum is obtained using the relation

(*a*) $1/\lambda = R_H\,(1/1^2 - 1/2^2)$

(*b*) $1/\lambda = R_H\,(1/1^2 - 1/\infty)$

(*c*) $1/\lambda = R_H\,(1/2^2 - 1/\infty)$

(*d*) $1/\lambda = R_H\,(1/1^2 - 1/3^2)$

where R_H is Rydberg constant for hydrogen.

24. The magnetic moment associated with the first orbit in hydrogen atom is given by

(*a*) $h/4\pi me$

(*b*) $4\pi m/he$

(*c*) $eh/4\pi m$

(*d*) $ehm/4\pi$

25. The length of the semimajor axis of an electron in an elliptical orbit is determined

(*a*) solely by the principal quantum number (*b*) solely by the azimuthal quantum number

(*c*) both by principal quantum number and azimuthal quantum number

26. When the azimuthal quantum number n_ϕ is zero

(*a*) the ellipse reduces to a straight line (*b*) the ellipse reduces into a circle

(*c*) none of these

27. If n_ϕ and n for an electron in an elliptical orbit are 1 and 2 respectively, then the ratio of semimajor axis and semiminor axis is

(*a*) 2 (*b*) 0.5

(*c*) 1 (*d*) 2

28. 4 electron volt is

(*a*) 2×10^{-19} joule (*b*) 6.4×10^{-19} joule

(*c*) 3.2×10^{-19} joule (*d*) 6.4×10^{19} joule

29. If the principal quantum number and the azimuthal quantum number in the relativistic model of the atom are 3 and 1 respectively, then the magnitude of the semiminor axis b in terms of the semimajor axis a is given by

(*a*) $b = a/3$ (*b*) $b = 2a/3$

(*c*) $b = a/2$ (*d*) $b = a$

SHORT QUESTIONS

1. Discuss the drawbacks of Rutherford's classical theory of the atom.
2. Give the important features of Bohr's model of atomic structure.
3. Give the postulates of Bohr to explain the structure of atom.
4. What are the various quantum numbers used to describe the electronic energy levels in an atom?
5. What do the symbols *s*, *p*, *d*, *f* stand for?
6. Show that the circumference of an electron orbit in a hydrogen atom is an integral multiple of the de Broglie wavelength of the electron in orbit.
7. Find the energy required to remove the electron from the normal hydrogen atom.
8. How do you explain the origin of spectral lines in hydrogen?
9. How is the fine structure of spectral lines accounted?
10. Compute the limit of the Balmer series in hydrogen spectrum.
11. Give the expression for Rydberg constant for hydrogen. How does this constant differ for singly ionised helium?
12. Outline the nature of the relativistic hydrogen orbit.
13. Explain the fine structure of H_α line of the Balmer series.

14. Calculate the time taken by the electron to traverse the first Bohr's orbit in hydrogen spectrum.

15. What is the frequency of radiation when the electron jumps from the third orbit to the second?

16. The energy of the electron in the permitted orbits of hydrogen atom is given by the equation – (B/n^2) with $B = 2.179 \times 10^{-18}$ joule. Give the significance of the negative sign.

17. The first member of Balmer series of hydrogen has a wavelength 656.3 nm. Calculate the wavelength of the second member.

18. What are the salient features of Bohr-Sommerfeld atom model?

19. Write down Sommerfeld's expression for the energy of the electron applying relativistic correction. Discuss the significance of this expression with that of Bohr.

20. Explain spatial quantisation and spinning of electron.

21. Discuss briefly vector atom model.

22. What do you understand by ionisation energy? On what factors does it depend?

23. Explain Pauli's exclusion principle as applied to electrons in atoms.

24. Give the electronic configuration of the elements sodium and copper.

25. Explain why *neon* is an inert gas.

26. Discuss briefly the wave mechanical concept of the atom.

REVIEW QUESTIONS

1. Give an account of Rutherford's model of the atom. What are the major deficiencies in Rutherford's nuclear model? How are they overcome by Bohr?

2. Derive the mathematical expression for energy of the electron in hydrogen atom. Give the interpretation of the negative sign.

3. Discuss Bohr's theory of hydrogen atom and derive an expression for the radius of the first Bohr orbit for the normal hydrogen atom.

4. State Bohr's fundamental postulates to explain the structure of hydrogen atom. Obtain the general expression for the radii of the Bohr's orbits and orbital frequencies of the electrons occupying them.

5. Give an account of Bohr's theory of hydrogen spectra and obtain expressions for the spectral series of hydrogen.

6. Discuss the postulates of Bohr's theory of hydrogen atom and derive an expression for the wave number of Balmer lines of hydrogen spectrum.

7. Outline Bohr's theory of hydrogen atom and show how it accounts for the observed spectrum of hydrogen.

8. Based on Bohr's assumptions obtain the expression for the orbital energy of an electron in the hydrogen atom. Also account for the different series of spectral lines of the hydrogen atom.

9. Obtain a general expression for the radii of the Bohr orbits and for the orbital frequencies. Explain H-spectrum on the basis of Bohr's theory.

10. Describe Bohr's atom model. Assuming that the nucleus is infinitely heavy and the electron has mass m and charge e, find out the energy of the electrons moving in the nth orbit. Calculate the ionisation potential of hydrogen atom.

11. Describe the Bohr's theory of hydrogen atom. How is it successful in explaining the spectrum of hydrogen atom?

12. What is meant by a spectral series? Give the formula and show how the spectral series of hydrogen arise. Illustrate with energy level diagrams.

13. Give the theory of the elliptical orbits relating to the hydrogen atom. Explain the fine structure of the H_α line of the Balmer series.

14. Outline the nature of the relativistic hydrogen orbit. Explain the fine structure of the H_α line due to relativity correction.

15. Give an account of Bohr-Sommerfeld model of elliptical electron orbits of hydrogen atom. How does it account for the fine structure of hydrogen atom?

16. What do you mean by fine structure of spectral lines? Give an account of Bohr-Sommerfeld atom model. Explain how could it explain the observed spectral lines.

17. Explain spatial quantisation and spinning of electrons. State and explain the significance of the four quantum numbers. How are they inter-related?

18. Discuss briefly vector atom model. State Pauli's exclusion principle and explain how it helped in fixing up the electronic configuration of the elements in the periodic table.

19. What are the four quantum numbers assigned to an electron in an atom? What are the significances of these quantum numbers?

20. State Pauli's exclusion principle. Explain the structure of the periodic table on the basis of Pauli's exclusion principle.

21. How are electrons distributed in the various subshells for $n = 3$? Give the quantum numbers for the electrons in the first subshell.

22. What is Pauli's exclusion principle? How does this principle help in the interpretation of the periodic system of the elements?

23. Write a detailed note on vector atom model. State and explain Pauli's exclusion principle.

24. Discuss the applications of Pauli's exclusion principle. Write a short note on the general usefulness of the periodic table in reference to atomic structure.

25. What do you understand by ionisation energy? On what factors does it depend? Why would more energy he required in the removal of an electron from the *K*-shell than an *L*-shell?

26. Explain Pauli's exclusion principle as applied to electrons in atoms. Describe how this principle assists in the interpretation of the periodic system of the elements.

27. Prove that if n be the principle quantum number of a shell, it can accommodate $2n^2$ electrons. Indicate the possible (n, l, m_l, m_s) values of electrons in the first three shells of an atom. The symbols have their usual significance.

28. Explain the quantum numbers associated with vector model of the atom. State and explain Pauli's exclusion principle. Give with examples the arrangements of electrons in an atom.

29. Give the electronic configuration of the following elements:

(*a*) Sodium (11)
(*b*) Chlorine (17)
(*c*) Copper (29)
(*d*) Germanium (32)

30. State Pauli's exclusion principle and explain how it helped in fixing up the electronic configuration of the elements in the periodic table.

Give the electronic configuration of the elements with atomic numbers (*a*) 11 and (*b*) 26.

31. Explain the various quantum numbers that are used to specify an electron in an atom. Hence discuss the periodic classification of elements.

32. State and explain the Pauli's exclusion principle. Give the theory of elliptical orbits relating to the hydrogen atom. Explain the fine structure of H_α line of the Balmer series.

33. Describe Bohr atom. What are the various quantum numbers by which an electron in an atom is designated?

Explain why neon is an inert gas.

34. What are the various quantum numbers associated with an electron in an atom? State Pauli's exclusion principle and explain how it is helpful in obtaining the arrangement of electrons in the ground state of an atom. Give the arrangement of electrons in the ground state of neon atom.

35. Describe the vector model of the atom and explain different quantum numbers associated with it. Write down the electronic configuration of copper (29) employing modern symbolism and explain.

36. Show that the circumference of an electron orbit in a hydrogen atom is an integral multiple of the de Broglie wavelengths of the electron in the orbit.

PROBLEMS

1. Calculate for the hydrogen atom (*i*) velocity of the electron in the ground state, (*ii*) radius of the orbit of the electron in the ground state, (*iii*) time taken for the electron to traverse the first Bohr orbit.

2. At what speed must the electron revolve round the nucleus of the hydrogen in its ground state in order that it may not be pulled into the nucleus by electrostatic attraction (Given: Radius of first Bohr orbit is 0.052 nm).

3. Electrons of energies 10.2 eV and 12.09 eV can cause radiation to be emitted from hydrogen atoms. Calculate in each case, the principal quantum number of the orbit to which an electron in the hydrogen atom is raised and the wavelength of the radiation emitted if it drops back to the ground state.

4. The critical potential of hydrogen is 13.05 eV. Calculate the wavelength of the radiations emitted by hydrogen atom bombarded by an electron of corresponding energy.

5. Show that for large values of principal quantum number, the frequency of an electron rotating in adjacent energy levels of hydrogen atom and the radiated frequencies for a transition between these levels, all approach the same value.

6. How many revolutions does an electron in the $n = 2$ state of a hydrogen atom make before dropping to the $n = 1$ state? (The average life time of an excited state is about 10^{-8} s).

7. A single electron revolves around a stationary nucleus of charge $+Ze$. It requires 47.2 eV to excite the electron from the second Bohr orbit to the third Bohr orbit. Calculate (*i*) the value of Z, (*ii*) the energy required to excite the electron form third to fourth Bohr orbit, (*iii*) the wavelength of the electromagnetic radiation required to remove the electron from the first Bohr orbit to infinity, (*iv*) the radius of the first Bohr orbit, (*v*) the kinetic energy, potential energy and the angular momentum of the electron in the first Bohr orbit.

8. Calculate the frequency of radiation, and also the wave number, when an electron jumps from the third orbit to the second orbit of hydrogen atom.
9. The first member of the Balmer series of hydrogen has a wavelength 655.3 nm. Calculate the wavelength of its second member.
10. Calculate the ionisation potential of hydrogen from the first principle.
11. Calculate the shortest wavelength of the Balmer series (limit of Balmer series) and the largest wavelength of Lyman series.
12. Neglecting reduced mass correction, show that (*i*) the short wavelength limit of the Lyman series ($n = 1$) of hydrogen is the same as that of Balmer series ($n = 2$) of ionised helium and (*ii*) that the wavelength of the first line of this helium series is 1.35 times the wavelength of the first line of the Lyman series.
13. The lowest two excited states of hydrogen atom are 10.2 and 12.0 eV above the ground state; calculate the wavelength of radiation that could be produced by transition between these states and the ground state.
14. Calculate the magnetic moment associated with the first orbit of Bohr in the case of hydrogen.
15. Give the electronic configurations of H, Li, C and Si.
16. The atomic weights and densities of aluminium and copper are 26.98 and 63.54, and 2700 kg/m^3 and 8960 kg/m^3 respectively. Calculate the number of atoms present in unit volume of aluminium and copper.
17. Calculate the magnetic moment due to orbital motion of the electron.
18. Energy in a Bohr orbit is given by $-\dfrac{B}{n^2}$ where $B = 2.179 \times 10^{-18}$ J.

    Calculate the frequency of radiation and also the wave number, when the electron jumps from the third orbit to the second.
19. Give a quick estimation of the binding energies of the hydrogen atom from de Broglie's hypothesis.
20. How much energy is required to raise the hydrogen atom from the ground state $n = 1$ to the first excited state $n = 2$? What is the wavelength of the line emitted if the atom returned to the ground state from the excited state?