Sommerfeld Relativistic Atom Model.

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The Sommerfeld Relativistic Atom Model :-

Bohr's simple theory of circular orbits was found inadequate to explain certain details in the spectrum of hydrogen. According to Bohr, the lines in the hydrogen spectrum should each have a well defined wavelength. Studies with high resolving power spectrographs, showed that H_α, H_β and H_γ lines in the hydrogen spectrum were not single but each line consisted of a number of lines very close to each other. For example H_α line was found by Michelson to consist of two lines with a wavelength difference of only 0.13 Å. This is known as fine structure of spectral lines. In terms of energy levels, the existence of fine structure means that instead of a single energy level corresponding to a given value of quantum number n there exist more than one energy levels close to each other. Bohr's theory could not explain this fine structure and existence of more than one energy levels corresponding to a single quantum number n, whereas the observed fine structure suggested that for any given quantum number n there might be several orbits of slightly different energies.

Sommerfeld, in 1915, extended the Bohr's atom model to include the ideas of motion of the electron in elliptical orbits and of the consequent relativistic variation of the mass of the electron. The Bohr atom thus improved upon, is known as the relativistic atom model, the main features of which are as follows :-

(i) The path of the electron around the nucleus, in general is an ellipse with the nucleus as one of the foci. The circular orbit of Bohr being only a special case.

(ii) The velocity of an electron moving in an elliptic orbit varies considerably at different points of the orbit. The velocity is greater when the electron is near the nucleus but smaller when it is far away from the nucleus. Due to the variation in velocity of the electron, its mass varies in accordance with the special theory of relativity. Sommerfeld took into account this variation of mass of the electron with velocity to explain the fine structure.

Elliptical Orbits :-

The electron is moving around and under the influence of a massive nucleus, it might describe elliptical orbits as well. Considering therefore the electron(e) moving in an elliptical orbit, its position at any instant can be fixed in terms of polar coordinates r and ϕ, where r is the radius vector, i.e. the distance of the electron from the nucleus (+E) at one of the foci of the ellipse and ϕ the vectorial angle i.e. the angle which the radius vector makes with the major axis of the ellipse. The tangential velocity v of the electron at the instant considered can be resolved into two components, one radial, i.e. along the radius vector equal to $\frac{dr}{dt}$ and the other transverse, i.e. at the right angles to the radius vector equal to $r\frac{d\phi}{dt}$. Corresponding to these two components we have a radial momentum p_r equal to $m\left(\frac{dr}{dt}\right)$ and an angular or azimuthal momentum p_ϕ equal to $mr^2\left(\frac{d\phi}{dt}\right)$, where m is the mass of the electron.

Sommerfeld assumed that, since the elliptical orbits should satisfy the quantum condition just as the circular orbits, the circle being only a special case of the ellipse, to each of these two momenta the phase integral of the quantum theory might be applied, so that

$$\oint p_r \cdot dr = n_r h \quad \text{and} \quad \oint p_\phi \cdot d\phi = n_\phi h \qquad \text{--- (1)}$$

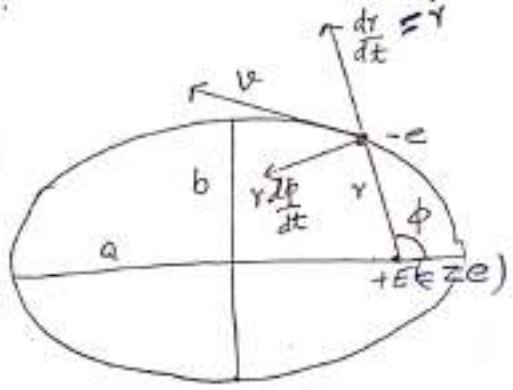

Fig :- Elliptic orbit

Thus the two new quantum numbers n_r and n_ϕ have appeared replacing the single one n of Bohr's theory. The three quantum numbers are related by the equation:

$$n = n_r + n_\phi \qquad \text{--- (2)}$$

where n is called the total quantum number and is identical with the quantum number of Bohr's circular orbit, n_r the radial quantum number and n_ϕ the angular or azimuthal quantum number.

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The total energy W of the system is partly potential and partly kinetic, the latter being further subdivided into radial and angular. Hence

$$W = \text{P.E.} + \text{radial K.E.} + \text{angular K.E} \quad \left[= \frac{1}{2}m\dot{r}^2 + \frac{1}{2}r^2 m\dot{\phi}^2 - \frac{Ze^2}{4\pi\epsilon_0 r}\right]$$

$$= -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{1}{2}m\left(\frac{dr}{dt}\right)^2 + \frac{1}{2}mr^2\left(\frac{d\phi}{dt}\right)^2 \quad ---(3)$$

From these three fundamental equations which depict the motion of the electron in the elliptical orbit satisfying the quantum conditions.

Evaluation of $\oint p_\phi d\phi$:- The angular momentum p_ϕ corresponding to the co-ordinate ϕ is the angular momentum of the electron in the elliptic orbit and is a constant according to Keplers law.

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

or $$p_\phi [\phi]_0^{2\pi} = n_\phi h$$

or $$p_\phi 2\pi = n_\phi h \quad \text{or} \quad p_\phi = n_\phi \frac{h}{2\pi} = n_\phi \hbar$$

$\dot{r} = \frac{dr}{dt} = \frac{dr}{d\phi}\cdot\frac{d\phi}{dt} = \frac{dr}{d\phi}\dot{\phi}$

$p_\phi = mr^2\dot{\phi} \Rightarrow \dot{\phi} = \frac{p_\phi}{mr^2}$

$\therefore \dot{r} = \frac{p_\phi}{mr^2}\frac{dr}{d\phi}$

Eq (3) becomes

$W = \frac{1}{2}m\frac{p_\phi^2}{m^2r^4}\left(\frac{dr}{d\phi}\right)^2 + \frac{1}{2}mr^2\left(\frac{p_\phi}{mr^2}\right)^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$

Multiply both side $\frac{2mr^2}{p_\phi^2}$ we get ↓

$\frac{2mr^2}{p_\phi^2}W = \frac{m}{2}\frac{p_\phi^2}{m^2r^4}\left(\frac{dr}{d\phi}\right)^2\frac{2mr^2}{p_\phi^2} - \frac{2mr^2}{p_\phi^2} + \frac{1}{2}\frac{p_\phi^2}{mr^2}\cdot\frac{2mr^2}{p_\phi^2} - \frac{Ze^2}{4\pi\epsilon_0 r}\frac{2mr^2}{p_\phi^2}$

$\frac{2mr^2W}{p_\phi^2} = \frac{1}{r^2}\left(\frac{dr}{d\phi}\right)^2 + 1 - \frac{2Ze^2rm}{4\pi\epsilon_0 p_\phi^2}$

$\boxed{\frac{1}{r^2}\left(\frac{dr}{d\phi}\right)^2 = \frac{2mr^2W}{p_\phi^2} - 1 + \frac{2Ze^2rm}{4\pi\epsilon_0 p_\phi^2}}$

Evaluation of $\oint p_r dr$:- This integral can be calculated by using equation of an ellipse in polar co-ordinates as

$$\frac{1}{r} = \frac{1+\epsilon\cos\phi}{a(1-\epsilon^2)} \quad ---(4)$$

where a is the semi-major axis and ϵ the eccentricity of ellipse. Differentiating both sides of above eq^n with respect to ϕ, we get

$1-\epsilon^2 = \frac{b^2}{a^2}$

$$-\frac{1}{r^2}\frac{dr}{d\phi} = -\frac{\epsilon\sin\phi}{a(1-\epsilon^2)}$$

or $$\frac{1}{r}\frac{dr}{d\phi} = \frac{r\epsilon\sin\phi}{a(1-\epsilon^2)}$$

Substituting the value of r from Eq^n (4), we have

$$\frac{1}{r}\frac{dr}{d\phi} = \frac{a(1-\epsilon^2)}{1+\epsilon\cos\phi}\cdot\frac{\epsilon\sin\phi}{a(1-\epsilon^2)} = \frac{\epsilon\sin\phi}{1+\epsilon\cos\phi} \quad ---(5)$$

$p = mv = m\frac{dr}{dt}$

Now $$p_r dr = m\frac{dr}{dt}dr = m\left(\frac{dr}{d\phi}\cdot\frac{d\phi}{dt}\right)\left(\frac{dr}{d\phi}\right)d\phi$$

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

$v = r\omega$

Also $$p_\phi = mvr = mr^2\omega = mr^2\frac{d\phi}{dt}$$

or $$m\frac{d\phi}{dt} = \frac{p_\phi}{r^2}$$

Hence [from Eq^n 1] $n_r h = \oint p_r dr = \oint\left(m\frac{d\phi}{dt}\right)\left(\frac{dr}{d\phi}\right)^2 d\phi = \oint \frac{p_\phi}{r^2}\left(\frac{dr}{d\phi}\right)^2 d\phi$

using $p_\phi = mr^2\frac{d\phi}{dt}$

$\frac{p_\phi}{r^2} = m\frac{d\phi}{dt}$

or $$= \oint p_\phi\left(\frac{1}{r}\frac{dr}{d\phi}\right)^2 d\phi$$

Now using, $\oint p_\phi d\phi = n_\phi h$ and $\boxed{\frac{1}{r}\frac{dr}{d\phi} = \frac{\epsilon\sin\phi}{1+\epsilon\cos\phi}}$ using Eq^n (5) we get ---(6a)

$$n_r h = n_\phi\frac{h}{2\pi}\oint\left(\frac{\epsilon\sin\phi}{1+\epsilon\cos\phi}\right)^2 d\phi = n_\phi\frac{h}{2\pi}\int_0^{2\pi}\frac{\epsilon^2\sin^2\phi}{(1+\epsilon\cos\phi)^2}d\phi \quad ----(6)$$

• But $\int_0^{2\pi} \frac{\epsilon^2 \sin^2\phi}{(1+\epsilon\cos\phi)^2} d\phi$ is a standard integral the value of which equal to $2\pi\left[\frac{1}{(1-\epsilon^2)^{1/2}} - 1\right]$.

$$\int uv = u\int v - \int \frac{du}{d\phi}\left(\int v\,du\right)d\phi$$

Hence the eqn (6) becomes

$$n_r h = n_\phi \frac{h}{2\pi} 2\pi\left[\frac{1}{(1-\epsilon^2)^{1/2}} - 1\right]$$

or $$n_r = n_\phi\left[\frac{1}{(1-\epsilon^2)^{1/2}} - 1\right] = \frac{n_\phi}{(1-\epsilon^2)^{1/2}} - n_\phi$$

or $$n_r + n_\phi = \frac{n_\phi}{(1-\epsilon^2)^{1/2}}$$

or $$n = \frac{n_\phi}{(1-\epsilon^2)^{1/2}} \quad \because n = n_r + n_\phi$$

or $$1-\epsilon^2 = \frac{n_\phi^2}{n^2} \qquad ----(7)$$

$u = \epsilon\sin\phi$, $v = \frac{1}{1+\epsilon\cos\phi}$

so that $dv = \frac{\epsilon\sin\phi\,d\phi}{(1+\epsilon\cos\phi)^2}$

$$n_r h = p_\phi \int_0^{2\pi} u\,dv$$

Integrating by parts

$$n_r h = p_\phi\left[uv - \int v\,du\right]$$

$$= p_\phi\left[\frac{\epsilon\sin\phi}{1+\epsilon\cos\phi}\right]_0^{2\pi} - p_\phi\int_0^{2\pi}\frac{\epsilon\cos\phi}{1+\epsilon\cos\phi}d\phi$$

For an ellipse, $1-\epsilon^2 = \frac{b^2}{a^2}$ where a and b are the semi-major and semi-minor axes respectively.

$$\therefore \frac{b^2}{a^2} = \frac{n_\phi^2}{n^2} \quad \text{or} \quad \boxed{\frac{b}{a} = \frac{n_\phi}{n}} \Rightarrow \boxed{\epsilon = \sqrt{\frac{n-n_\phi}{n}}} \quad (8)$$

→ quantum condition for elliptical orbit.

$$W = -\frac{b^2 m^2 e^4}{2a^2(4\pi\epsilon_0)^2 p_\phi^2}$$

This result indicates that out of all the classically possible ellipses, only those ellipses are allowed by the quantum condition for which the ratio of major to minor axis is the same as that of the quantum number n and n_ϕ. The value of 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. When n_ϕ is equal to n, the path becomes circular, since then b = a and the eccentricity ϵ is equal to zero. Hence for a given value of n, n_ϕ can assume only n different values, which means there can be only n elliptical orbits of different eccentricities, the orbits becoming less eccentric the higher the value of n_ϕ, until finally circular with zero eccentricity when $n_\phi = n$.

$n_r = 0, 1, 2, 3, \ldots$
$n_\phi = 1, 2, 3, 4 \ldots$
$n = 1, 2, 3, 4, \ldots$

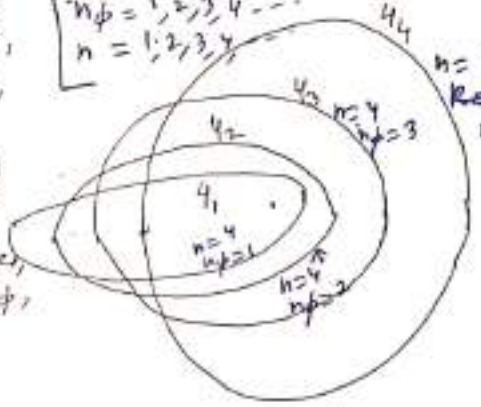


Fig :- Permitted ellipses for n = 4

For example, when n = 4, four different ellipses are permitted, usually designated by 4_1, 4_2, 4_3, 4_4, of which the last one is evidently a circle. The orbits need not be concentric it is enough that they are confocal as shown in figure, nor is it necessary that they should be in the same plane or have a common major axis.

It can be shown that the total energy thus given by in terms of quantum numbers n, n_ϕ and n_r, viz

$$W_n = -\frac{m Z^2 e^4}{h^2 8\epsilon_0^2}\left(\frac{1}{n_\phi + n_r}\right)^2 = -\frac{m Z^2 e^4}{8\epsilon_0^2 h^2 n^2} \qquad ----(9)$$

put: $E = 2e$

We find that the energy is the same for all the ellipses having the same total quantum number, i.e. elliptical orbits which have the same value for n, though of different eccentricities, have the same energy and hence are indistinguishable from this point of view, e.g., the orbits 4_4, 4_3, 4_2, 4_1 have all the same energy.

The theory of elliptical orbits, in spite of the two new quantizing conditions involved introduces no new energy levels other than those given by Bohr's theory of circular orbits. No new spectral lines, which would explain the fine structure are therefore predicted.

Sommerfeld solved the fine structure problem on the basis of variation of mass of the electron with velocity according to the theory of relativity.

$a = \frac{n^2}{Z} r_0$; r_0 is the first Bohr radius for hydrogen

$b = a(1-\epsilon^2)^{1/2}$

P T O

Relativistic Variation of electronic mass :- The velocity of the electron in a circular orbit is constant but the velocity of the electron moving in an elliptical orbit varies considerably at different parts of the orbit, being a maximum when the electron is nearest to the nucleus. The velocity is quite large, being about $\frac{1}{137}$ of the velocity of light.

Sommerfeld, modified Bohr's theory by taking into account the variation of mass of the electron with velocity. When the relativity effect is taken into account the energy of the electron is found to depend on both, the principal quantum number n and azimuthal quantum number n_ϕ. The value of energy W of the system, corrected for the relativistic variation of the mass of the electron, can be shown to be

$$E = -\frac{me^4 Z^2}{8\varepsilon_0^2 h^2 n^2} - \frac{me^4 Z^4 \alpha^2}{8\varepsilon_0^2 h^2}\left(\frac{1}{n_\phi n^3} - \frac{3}{4n^4}\right) = -\frac{me^4 Z^2}{8\varepsilon_0^2 h^2 n^2} - \frac{me^4 Z^4 \alpha^2}{8\varepsilon_0^2 h^4}\left(\frac{n}{n_\phi} - \frac{3}{4}\right) \quad -(10)$$

This expression is only approximate as it is limited to the first two terms of an expansion in series, but the other terms are unimportant.

The above relation differs from the previous relation (Eq 9) for W in that it contains an additional term representing the effect of the relativity correction, viz.,

$$-\frac{me^4}{n^3 8\varepsilon_0^2} \cdot \frac{4Z^4\alpha^2}{n^4}\left(\frac{n}{n_\phi} - \frac{3}{4}\right) \quad ---(11)$$

where $E = Ze$ and $\alpha = \frac{e^2}{2\varepsilon_0 ch} = \frac{1}{137}$ (MKS)

or $E = -Rch\frac{Z^2}{n^2} - R\alpha^2 Z^4 ch\left(\frac{n}{n_\phi} - \frac{3}{4}\right)$ where $R = \frac{me^4}{8\varepsilon_0^2 ch^3}$

α is called Sommerfeld's fine structure constant.

quantum $\alpha = 7.2972 \times 10^{-3}$

This shows that energy depends not simply on the total quantum number n, but also upon the azimuthal quantum number n_ϕ on account of the presence of the ratio $\frac{n}{n_\phi}$.

For a given total quantum number n, different energies are obtained for the different orbits corresponding to the different value of n_ϕ.

The correction term Eq (11), is a very small quantity as it involves α, whose value, readily estimated from the known values of e, c and h is found to be only $\frac{1}{137}$. α is called the fine structure constant

The relativity correction, therefore, results in splitting up a given energy level, W_n into n levels differing slightly from one another in energy. This splitting up of each energy level naturally gives rise to a fine structure of single spectral lines, on application of the usual Bohr frequency condition.

Sommerfeld Model to Explain the Fine Structure of H_α-line :- The H_α line of Balmer series of hydrogen spectrum is due to the transition from $n = 3$ to $n = 2$ state. For $n=2$ there will be 2 sub-energy levels and for $n=3$ there will be 3 sub-energy levels. They are

(a) For $n=2$, (i) $n=2$, $n_\phi=1$ (ii) $n=2$, $n_\phi=2$

(b) for $n=3$, (i) $n=3$, $n_\phi=1$ (ii) $n=3$, $n_\phi=2$ (iii) $n=3$, $n_\phi=3$

Theoretically following six transitions are possible :

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

but experimentally it has been proved that there are only 3 transition. This discrepancy was removed by using a selection rule for transition. According to this selection rule only allowed transition are for $\Delta n_\phi = \pm 1$. Thus it can be seen that only 3 possibilities are for $\Delta n_\phi = \pm 1$, but there are 5 transitions, hence, the model partially explain the existence of fine structure of lines. The forbidden lines are indicated by dotted lines and permitted lines are indicated by full lines.

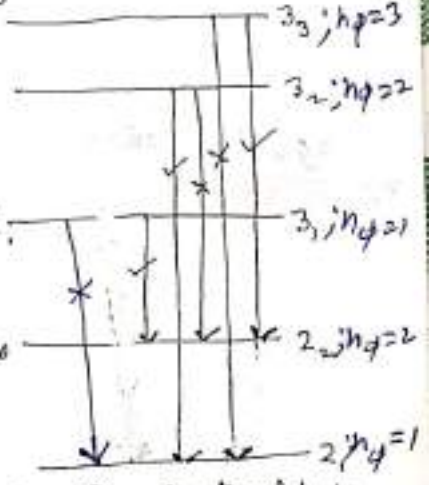


Fig :- Fine structure of H_α line

Selection rule :- $\Delta n_\phi = \pm 1$

$\times \to$ is not allowed transition

Selection rule. $\Delta n_\phi = \pm 1$

We know

$$\frac{mze^2}{4\pi\epsilon_0 p_\phi^2} = \frac{1}{a(1-\epsilon^2)}$$

$p_\phi = \frac{n_\phi h}{2\pi}$

$1-\epsilon^2 = \frac{b^2}{a^2} = \frac{n_\phi^2}{n^2}$

or $$a = \frac{4\pi\epsilon_0 p_\phi^2}{mze^2(1-\epsilon^2)} = \frac{4\pi\epsilon_0}{mze^2(1-\epsilon^2)} \cdot \frac{n_\phi^2 h^2}{4\pi^2} = \frac{\epsilon_0 n_\phi^2 h^2}{mze^2\pi} \cdot \frac{n^2}{n_\phi^2}$$

$$= \frac{\epsilon_0 h^2 n^2}{mze^2\pi}$$

$$\boxed{a = a_0 \frac{n^2}{z}} \text{ where } a_0 = \frac{\epsilon_0 h^2}{me^2\pi}$$

Radius of Bohr first orbit

Using $\frac{b}{a} = \frac{n_\phi}{n}$

or $$b = a\frac{n_\phi}{n} = \frac{a_0 n^2}{z} \cdot \frac{n_\phi}{n} = \frac{a_0 n n_\phi}{z}$$

$$\boxed{b = \frac{a_0 n n_\phi}{z}}$$

For hydrogen atom $z=1$

$$\boxed{a = a_0 n^2 \text{ and } b = a_0 n n_\phi} \quad \text{---(1)}$$

$$n = n_r + n_\phi$$

$n_\phi = 1, 2, 3.$

$n_r = 0, 1, 2$

$n = 1, 2, 3$

Using Eq^n (1) we get

Case $n=1$

$a = a_0$

$b = a_0 n_\phi \Rightarrow n_\phi = 1$ and $n_r = 0$

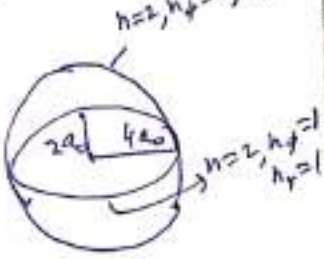
$\boxed{b = a_0}$ circle.

Case $n=2$

$n_r + n_\phi = 2$

$n=2, n_\phi = 2, n_r = 0 \Rightarrow a = 4a_0, b = 4a_0.$

$n=2, n_\phi = 1, n_r = 1 \Rightarrow a = 4a_0, b = 2a_0.$



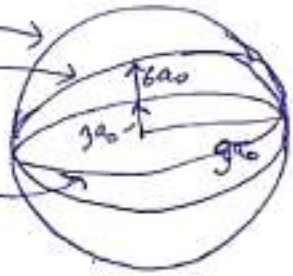
Case $n=3$

$n=3, n_r + n_\phi = 3$

$n=3, n_\phi = 3, n_r = 0 \Rightarrow a = 9a_0, b = 9a_0$

$n=3, n_\phi = 2, n_r = 1 \Rightarrow a = 9a_0, b = 6a_0$

$n=3, n_\phi = 1, n_r = 2 \Rightarrow a = 9a_0, b = 3a_0$



Improvement made by Sommerfeld's in Bohr's model :- He paths of the electron includes in elliptical orbits in addition to circular orbit and the motion of electron is treated relativistically and thus the mass of the electron varys with velocity in elliptic orbits. In this light the result of the improvement are

(1) The electron while moving in elliptical path has two components of its motion, radial and azimuthal and thus there are three quantum numbers (a) n (b) n_r and (c) n_ϕ

(2) The orbits are described in terms of a, b (semi-major axis a and semi-minor axis 'b' of the ellipse orbit) alongwith n, n_r and n_ϕ. $\frac{b}{a} = \frac{n_\phi}{n}$ $n = n_r + n_\phi$

(3) Important result is the fact that the expression for the total energy in Sommerfeld model is exactly same as the expression in Bohr's model.

(4) For a given 'n' value, suborbits possess slightly different energies due to relativistic variation of mass of the moving electron in the elliptical orbits.

Drawbacks of Sommerfeld Model :- The Bohr-Sommerfeld atom model explained many experimental observations on the atomic spectra and atomic structure but it suffered from following defects :-

(1) The theory was silent on the observed fine structure of spectral lines.

(2) The theory is valid only to single electron atom for example hydrogen etc. but the theory failed even in case of two electron system i.e. neutral helium.

(3) The theory could not explain the variation in the intensity of spectral lines because the theory did not tell the rate at which transition between allowed states of atom take place.

(4) The theory was silent regarding the distribution and arrangement of electrons inside the atom.

(5) The theory could not explain the effect of magnetic or electric field on spectral lines such as Zeeman effect, Paschen back effect, Stark effect etc.

To overcome the difficulties of these model, Gouldsmit and Uhlenbeck proposed vector atom model using spin of the electron and spatial quantization.

Q :- How many elliptical and how many circular orbits are there for n=1, n=2 and n=3 according to Sommerfeld's model of the atom.

Ans :- In the case, when n=1. As $n_r + n_\phi = 1$ and $n_\phi \neq 0$, the only value of n_ϕ can have is $n_\phi = 1$.

When $n = n_\phi = 1$; b=a and the first orbit is circle. This is shown in Fig. (a).

In the case when n=2, n_ϕ can have the value 2 or 1 so that there are two possible orbits, n=2, n_ϕ=2 and n=2, n_ϕ=1.

n=2, n_ϕ=2 orbit is a circle and n=2, n_ϕ=1 orbit is an ellipse as shown in fig (b).

In the case, when n=3, n_ϕ can have the value 3, 2 and 1 so that there are three possible orbits, n=3, n_ϕ=3; n=3, n_ϕ=2; n=3, n_ϕ=1.

for n_ϕ=3 orbit is a circle, n_ϕ=2 is an ellipse and n_ϕ=1 is also an ellipse as shown in fig (c).

The allowed orbits are indicated by assigning the values of n and n_ϕ. Thus the three orbits of n=3 are represented by symbols 3_3, 3_2 and 3_1, the subscript being the azimuthal quantum number n_ϕ.

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