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Paper II

The Structure of Atom

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The first real foundation of the modern conception of the atom was laid by Faraday who discovered that in electrolysis each atom, irrespective of the nature of the element, gave up or received a fixed quantity of positive or negative charge equal in magnitude to 1.59×10^{-19} coulomb. A more definite idea of the intrinsic nature of the atom came into existence with J.J. Thomson's discovery of the electron and his measurement of its mass and charge, that led to the result of the electrical nature of matter, according to which the following two facts were clearly established: (i) electrons enter into the constitution of all atoms, (ii) Since the atom as a whole is electrically neutral the quantity of positive and negative charges in it must be the same.

Thomson's model of the atom :- J.J. Thomson in 1898 proposed that atom may be considered as positively charged sphere in which the electrons were scattered about. The diameter of the sphere was supposed to be of the order of 10^{-9} cms, the magnitude found for the atom.

Using the phenomenon of X-ray scattering, he was able to determine the number of electrons in an atom as follows: when a beam of X-rays passes through matter, it should be scattered, the scattering coefficient σ, according to the classical theory, being given by $\sigma = \frac{8\pi}{3} \frac{e^2}{mc^4} n$, where e and m are the charge and mass of the electron, n the number of electrons per unit volume and c the velocity of light. Now σ can be experimentally determined, so that n can be estimated from the above relation. From the value of n thus obtained, the number of electrons per atom can be readily computed. He found that this number was proportional to the atomic weight of the element, increasing from one in the case of hydrogen upto 92 in the case of uranium.

The second point, regarding the arrangement of the electrons and the positive charges in the atom, was not so easy to solve. In an atom he argued that the atom as a whole being stable, the electrons must be held by the positive charge by electrostatic forces. These electrons he further argued are so positioned inside the positive sphere that their mutual repulsions are exactly balanced by the forces of attraction towards the centre of the sphere. In the case of hydrogen atom with only one electron, he argued that the electron must be situated at the centre of the positive sphere while in the case of helium atom the two electrons must be situated at the opposite sides of the centre at distances equal to half of the radius of the positive sphere. In the case of atoms having three electrons, he placed these electrons at three vertices of a symmetrically placed equilateral triangle with sides equal to the radius of the sphere. And in the similar manner he gave the arrangement of electrons in atoms having as large as one hundred electrons.

With this model he explain the observed spectra of elements. He argued that the electron being a charged particle, ~~would~~ if it vibrated about its position of equilibrium, it should radiate energy according to the electromagnetic theory and the frequency of the emitted spectral line should be the same as that of the electron. According to this viewpoint hydrogen atom ~~to~~ should give only one line whereabouts of 1400Å, while in actual practice hydrogen spectrum consists of a number of series each having many lines. Thus, Thomson's model was defective somewhere.

P.T.O.

Rutherford's Nuclear Atom model :- The nuclear atom model resulted from the Rutherford and his collaborators on the scattering of α-particles by thin sheets of matter. The scattering of α-particles by matter is evidently caused by the Coulombian repulsive forces that come into play between the α-particles and the positive charges of the atoms in the scattering material. The electrons of the scatterer on account of their extremely small mass as compared with that of the α-particles will not effect to any appreciable extent the α-particles during their passage through the scatterer. Hence the deflection of an α-particle from its original path when it comes out of the scatterer is due to a great number of small deflections produced by the action of the positive charges of a large number of atoms. This is called multiple or Compound scattering.

Experiments on the scattering of α-particles by thin foils of matter showed that although most of the α-particles suffered only a small deflection due to multiple scattering, yet there were a certain number that were scattered through much larger angles. For instance, it was found that 1 in 8000 alpha particles was deflected through more than 90° by a thin film of platinum. This experimental findings could not be accounted for on the basis of the Thomson atom model. If the Thomson's model is correct, the α-particles passing through thin metal foil should be expected to experience only weak electric forces. They should be able to pass with their initial momenta through the foil with at most only slight deviation from their original paths. When an α-particle enters the positive sphere, the charge in the shell outside the path of the α-particle will exert no deflecting force on it. Hence, the farther the path of the α-particle from the centre of the atom, the greater will be the deflecting force. As the α-particle approaches the centre of the sphere, the shell of ineffective charge increases with the result that the force of repulsion becomes less and less. This means that there would be only a small deflection due to a single encounter. Calculating the probable angle of scattering of α-particles as a function of the atomic charges, it is found that

$$N_\phi = N_0 e^{-(\phi/\phi_m)^2}$$

where N_ϕ is the number of particles scattered at an angle ϕ, N_0 is the total number of incident particles and ϕ_m is the most probable angle of scattering.

It is evident from this relation that the probability of large angle scattering is necessarily very small, since as ϕ increases N_ϕ will decrease very rapidly. For instance, when $\phi = 30°$, the probability is of the order of 10^{-13}. Hence, Thomson's picture of the atom was quite unable to account for the experimentally observed large angle scattering.

Rutherford therefore proposed, in 1911, a new type of atom model, capable of giving to an α-particle a large deflection due to a single encounter, it is necessary to assume that these particles experience a much larger repulsive force at certain point in their fall through the atom, than permitted by Thomson's model with uniform distribution of positive charge. This is possible only if it is assumed that the positive charges in the atom are concentrated in a very small region at the centre instead of being uniformly distributed in accordance with the Thomson's model. This central region where the entire positive charge and the mass (because the electrons were known to have negligibly small mass) of the atom is concentrated was named as the nucleus. The electrons were consequently assumed to be situated outside of the nucleus and rotating about it. The electrons must keep on rotating about the nucleus, because an attractive force existed between the positively charged nucleus and the negatively charged electrons, if the electrons were not moving, they would fall into the nucleus. The Rutherford's model is sketched in figure.

Considering an atom as largely empty space, it can be easily seen by α-particles must pass through the atom, undeflected. However when any α-particle approaches the nucleus of an atom, it experiences an intense repulsive force and is likely to be scattered through a large angle. The electrons in the atom, being very light, do not disturb the motion of α-particles to any appreciable extent.

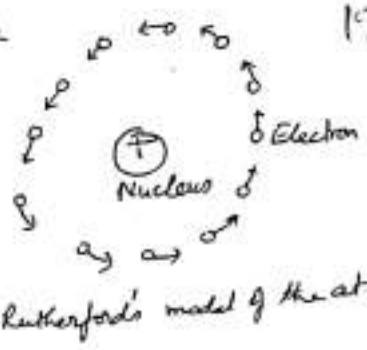


Fig:- Rutherford's model of the atom.

Further tests with different target foils showed that the deflection of α-particles by the atomic nucleus depends upon the magnitude of nuclear charge. Thus, a comparison of the scattering by different foils provided a method of estimating the nuclear charge of the atoms composing them. The nuclear charge in all the atoms of one element was found to have a unique value, increasing from element to element in the periodic table. It always turned out to be a multiple of $+e$. The number of unit positive charges in the nucleus is known as atomic number of the element. It is now well-known that nuclear charge is due to protons in the nucleus each with a $+e$ charge.

Theory of Rutherford's α-particle scattering:- Rutherford made the following assumption for arriving at a relation describing the scattering of α-particles by thin metal foils, on the basis of his atomic model.

(1) The problem is treated from the classical point of view, i.e. the scattering is regarded as due to elastic impact of two particles, the α-particle and the nucleus, their wave aspect being neglected.

(2) The nucleus and the α-particle are considered as point charges, i.e. mass centres of Coulombian force; thus the dimensions of the interacting particles are not taken into account.

(3) The nucleus is considered to be so heavy that its motion during the impact may be disregarded.

The scattering of α-particle by nucleus is treated here as due to elastic impact of two particles i.e an α-particle, initially moving along PO, approach a nucleus, stationary at N. The electrostatic force of repulsion between the two which varies as $\frac{1}{r^2}$ where r is instantaneous distance between the α-particle and the nucleus, would increase enormously as the α-particle gets closer to the nucleus. It can be shown by considering the motion under central forces, that the path of α-particle will change from straight line to a hyperbola PAP' with the nucleus N at the outer focus. The angle between asymptotic direction PO in which the α-particle approaches the nucleus and the asymptotic direction OP' in which it recedes, is the scattering angle θ.

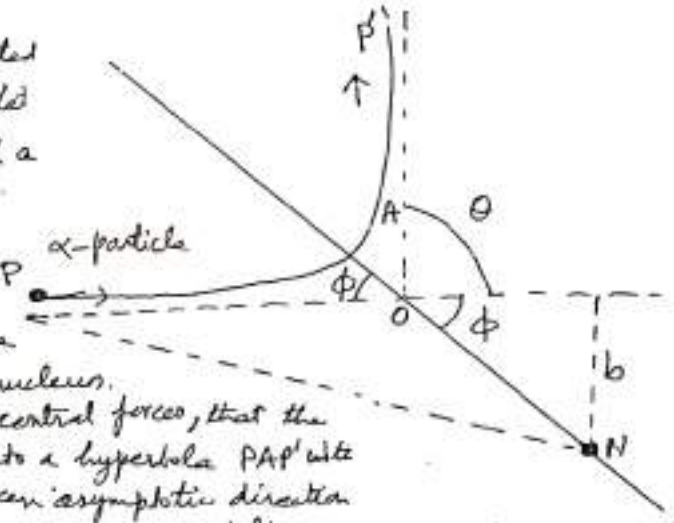


Fig:- Rutherford's scattering

Let b be the perpendicular distance from N to PO: it is the minimum distance to which the α-particle would approach the nucleus in the absence of any force between them and is known as impact parameter. Let m be the mass and v_0 be the initial velocity of the α-particle. If z is the atomic number of the element which is being used as scatterer of α-particle then the charge on the nucleus would be Ze.

For finding the relation between b and θ, consider the case of a central impact i.e. when α-particle is directed straight towards the nucleus N so that b=0. The α-particle would be [illegible] due to the repulsion between the two

and would be forced to retrace its path, in which case the scattering angle θ is equal to 180°. This distance d can be determined by using the principle of conservation of energy. The electrostatic potential due to nucleus, at a distance d is given by $\frac{Ze}{4\pi\epsilon_0 d}$, where ϵ_0 is the permittivity of free space and is equal to $10^{-7}/4\pi c^2$ farad/m. which acts on the α-particle of charge $2e$. Hence, the potential energy of the α-particle when it is a distance d from the nucleus is $\frac{Ze}{4\pi\epsilon_0 d} 2e = \frac{2Ze^2}{4\pi\epsilon_0 d}$.

As at this distance d the α-particle is momentarily stopped before it starts its back journey, its initial kinetic energy there is completely converted into potential energy. Therefore neglecting the very small amount of energy of α-particle lost in its interaction with the peripheral electrons, we have

$$\frac{2Ze^2}{4\pi\epsilon_0 d} = \frac{1}{2} m v_0^2$$

or $$d = \frac{4Ze^2}{4\pi\epsilon_0 m v_0^2} \qquad ---(1)$$

In practice it is not possible to direct the α-particle exactly towards the nucleus. We will therefore have to consider the case when $b \neq 0$ and the α-particle will be scattered through an angle θ which is less than 180° and travel along the hyperbolic path PAP'.

Let v be the velocity of α-particle at the vertex A. Applying the principles of conservation of energy and momentum we get

$$\frac{1}{2} m v_0^2 = \frac{1}{2} m v^2 + \frac{2Ze^2}{4\pi\epsilon_0 NA} \qquad ---(2)$$

$$m v_0 b = m v . NA \qquad ---(3)$$

Substituting the value of $2e^2$ from Eq(1), the Eq(2) becomes

$$\frac{1}{2} m v_0^2 = \frac{1}{2} m v^2 + \frac{m v_0^2 d}{2NA}$$

$$\therefore \quad v^2 = v_0^2 \left(1 - \frac{d}{NA}\right)$$

or $$\frac{v^2}{v_0^2} = \left(1 - \frac{d}{NA}\right)$$

From Eq(3) $$b^2 = \frac{v^2}{v_0^2} (NA)^2$$

$$\therefore \quad b^2 = (NA)^2 \left(1 - \frac{d}{NA}\right) = NA(NA - d) \qquad ---(4)$$

Using the properties of hyperbola, namely the eccentricity, $\epsilon = \frac{1}{\cos\phi}$, where $\phi = \frac{1}{2}(\pi - \theta)$ and $NO = \epsilon . OA$, we have

$$NA = NO + OA = NO\left(1 + \frac{1}{\epsilon}\right) = NO(1 + \cos\phi)$$

As $$NO = \frac{b}{\sin\phi}$$

$$\therefore \quad NA = \frac{b}{\sin\phi}(1 + \cos\phi) = b\left(\frac{1 + 2\cos^2\frac{\phi}{2} - 1}{2\sin\frac{\phi}{2}\cos\frac{\phi}{2}}\right) = \frac{b\cos\frac{\phi}{2}}{\sin\phi/2} = b\cot\frac{\phi}{2}$$

Putting this in Eq(4), we get: $$b^2 = b\cos\frac{\phi}{2}\left(b\cot\frac{\phi}{2} - d\right)$$

$$\therefore \quad d = b\,\frac{\cot^2\frac{\phi}{2} - 1}{\cot\phi/2} = 2b\cot\phi = 2b\cot\left(\frac{\pi - \theta}{2}\right) = 2b\tan\frac{\theta}{2}$$

Substituting the value of d from Eq(1), we get

$$\tan\frac{\theta}{2} = \frac{d}{2b} = \frac{Ze^2}{2\pi\epsilon_0 b m v_0^2} \qquad ---(5)$$

This expression shows that with fixed value of Z, m and v_0 the scattering angle θ increases from 0 to 180° as the impact parameter b decreases from relatively high values to the limiting value zero. From this it is concluded that if b is large and the α-particle passes far away from the nucleus, the scattering angle is very small. In the limiting case when the α-particle is directed straight towards the nucleus ($b=0$), $\theta = 180°$ and the α-particle will retrace its path after approaching the nucleus upto a distance d. The scattering of α-particles for different values of b is shown in above figure. It is clear from Eq(5) that all the α-particles approaching a target nucleus with an impact parameter from 0 to b will be scattered through an angle θ or more. This means that an α-particle initially directed anywhere within the area πb^2 around the nucleus, will be scattered through an angle θ or more. The area πb^2 is accordingly called the cross section for interaction and is generally denoted by σ.

It may be pointed out here that the incident α-particle does not necessarily pass within a distance b of the nucleus, because it is actually scattered before it reaches the immediate vicinity of the nucleus. Let us now deal with the case realised in actual experiment where a narrow beam of α-particles is directed normally towards the target foil. Let the thickness of the foil be t and suppose that it contains n atoms per unit volume.

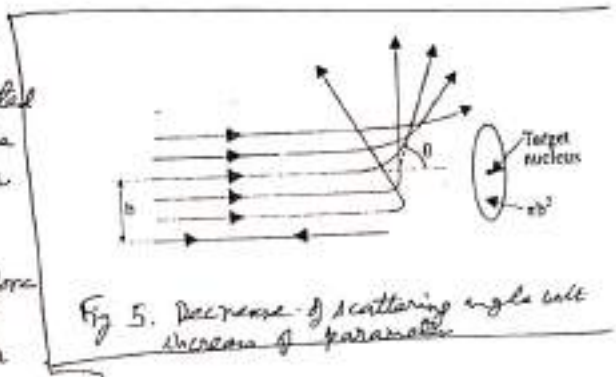


Fig 5. Decrease of scattering angle with increase of parameter

The number of target nuclei per unit area will therefore be nt and an α-particle beam incident upon an area A will encounter ntA nuclei. Since the cross-section per nucleus for the α-particle to be scattered through θ or more is σ the aggregate cross-section for scattering θ or more by ntA nuclei would be $ntA\sigma$. Hence, the fraction f of the incident α-particles scattered through θ or more is given by

$$f = \frac{\text{α-particles scattered through } \theta \text{ or more}}{\text{incident α-particle}}$$

$$= \frac{\text{Aggregate cross-section}}{\text{target area}} = \frac{ntA\sigma}{A} = nt\sigma$$

$$= nt\pi b^2 \quad \text{Fig : α-particles scattered between } \theta \text{ and } \theta + d\theta.$$

Putting the value of b from Eq(5), we get

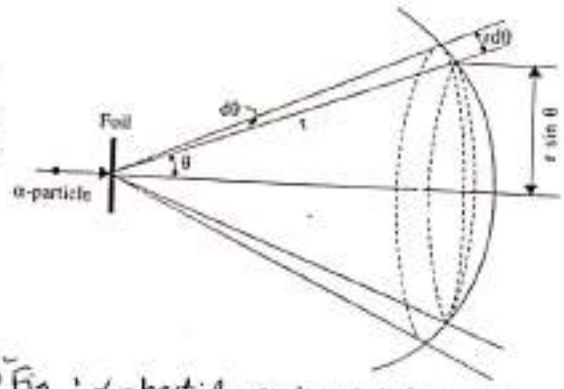
$$f = nt\pi \left(\frac{ze^2}{4\pi\varepsilon_0 mv_0^2}\right)^2 \cot^2\frac{\theta}{2} \quad ---(6)$$

This relation is based on the assumption that the foil is sufficiently thin so that there is no overlapping of the cross-section of adjacent nuclei and a scattered α-particle receives its deflection from a single encounter with a nucleus.

Now the detector used in each experiment measures the α-particles scattered between θ and $\theta + d\theta$ as shown in figure ⑥. The number of such α-particles can be obtained by differentiating Eq⑥ with respect to θ.

$$df = -nt\pi \left(\frac{ze^2}{2\pi\varepsilon_0 mv_0^2}\right)^2 \cot\frac{\theta}{2}\operatorname{cosec}^2\frac{\theta}{2}\,d\theta \quad ---(7)$$

This represents the fraction of incident α-particles scattered between θ and $\theta + d\theta$, the negative sign indicates that the fraction decreases with increasing θ.



As we have seen earlier, in the scattering experiment a fluorescent screen is placed behind the foil, say, at a distance r and the α-particles scattered between θ and $\theta+d\theta$ strike a zone of sphere of radius r whose width is $r\,d\theta$ and radius $r\sin\theta$. The area of the screen therefore struck by these particles is given by

$$dS = \text{circumference} \times \text{width} = 2\pi r\sin\theta \times r\,d\theta = 4\pi r^2 \sin\frac{\theta}{2}\cos\frac{\theta}{2}\,d\theta$$

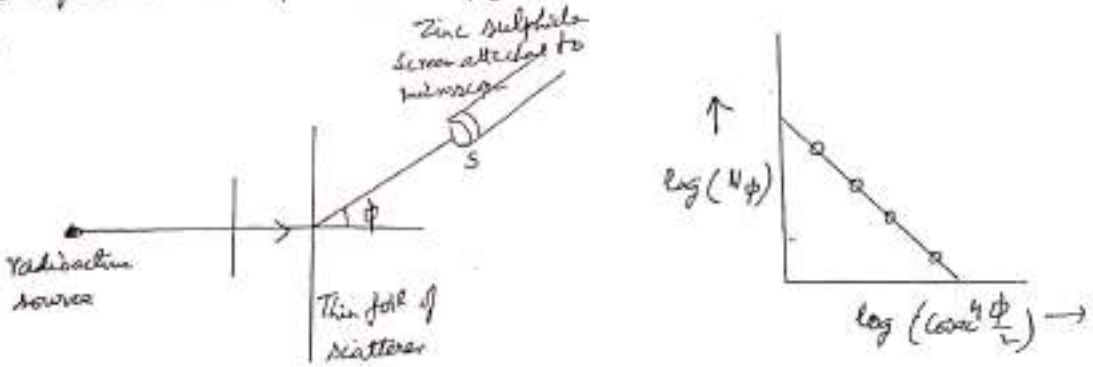
Now, let N_t be the total number of α-particles that strike the foil during the course of experiment. The number of α-particles scattered into an angle $d\theta$ at θ would then be $N_t f$. The number $N(\theta)$, which is the quantity actually measured in the experiment is given by

$$N(\theta) = \frac{N_t |df|}{dS} = \frac{N_t n\pi t \left(\frac{ze^2}{4\pi\varepsilon_0 mv_0^2}\right)^2 \cot\frac{\theta}{2}\operatorname{cosec}^2\frac{\theta}{2}\,d\theta}{4\pi r^2 \sin\frac{\theta}{2}\cos\frac{\theta}{2}\,d\theta}$$

$$= \frac{z^2 e^4 N_t n}{64\pi^2 \varepsilon_0^2 m^2 v_0^4 r^4 \sin^4\frac{\theta}{2}} \quad \text{---(B)}$$

The eq (B) represents the Rutherford scattering formula and indicates that the number of α-particles per unit area reaching the screen distant r from the foil is directly proportional to the thickness of the foil, the number of the foil atoms per unit volume n and the square of the atomic number Z and is inversely proportional to $\sin^4\frac{\theta}{2}$. As these theoretical conclusions were found to be in agreement with the measurement of Geiger and Marsden, Rutherford was led to conclude that his nuclear atom model was correct. The credit of the discovery of nucleus thus goes to Rutherford.

Experimental Verification of Rutherford theory :- Geiger and Marsden tested the theory and found an agreement of theory with experiments. Their ~~sets~~ schematic experimental set-up is shown in figure.



Source and screen were fixed and screen and microscope rotated, varying the angle of deflection. The number of α^{++} particles reaching unit area of screen in a related time are counted by scintillations. The ϕ only was varied and following graph was yielded. The linear dependence of N_ϕ with ϕ as suggested by theory was obtained. Other suggestions of theory were also verified by Geiger and Marsden experiment.

Drawbacks of the Rutherford nuclear atom :- Rutherford's atom model, though unanimously accepted, was not free from limitations, the chief of which arose from considerations of the stability of the atom as a whole. For, it became obvious that in the nuclear atom equilibrium could not be secured by the operation of electrostatic forces alone between the positively charged nucleus and the negative electrons outside the nucleus. For instance, considering the case of an atom with two electrons, the nuclear charge +2e. If the electrons are symmetrically placed at a distance r from the nucleus, the force of attraction between the nucleus and each of the electrons is $2e^2/r^2$, while the force of repulsion between the electrons is $\frac{e^2}{4r^2}$. Since the force of attraction is eight times greater than that of [illegible] the condition [illegible] electron will fall into the nucleus, thus destroying

In order to overcome this difficulty, Rutherford suggested that the electrons might be assumed to revolve round the nucleus, like the planets round the sun at such a speed that the mechanical centrifugal force would just balance the ~~rest~~ net excess of electrostatic attraction and in consequence stability could be secured. But such an assumption brought, another very serious difficulty from the point of view of the electromagnetic theory; according to which, a revolving electron should radiate energy continuously. Now this energy can only come from the atomic system, which will therefore steadily lose energy. As a result the electron will approach the nucleus by a spiral path, giving out a radiation of constantly increasing frequency and finally fall into the nucleus. Thus the orbital motion of the electrons destroys the very purpose for which it was postulated, viz, the stability of the atom. Further emission of radiation of ~~and~~ constantly increasing frequency has no experimental basis, since atoms are actually found to emit discrete spectral lines of definite frequency. One is therefore forced to conclude that either the Rutherford atom model with revolving electrons is defective or the classical electromagnetic theory fails in the present case. The dilemma was solved by Niels Bohr, who admitting the failure of the classical theory, applied with remarkable success the quantum theory to the Rutherford nuclear atom with revolving electrons. This leads us to the consideration of the Bohr atom model.

Q:- If a 5MeV, α-particle approaches a gold nucleus with an impact parameter of 2.6×10^{-11} Cm, through what angle will it be scattered. Given that for gold $Z=79$.

Ans:- The scattering angle θ is given by

$$\tan\frac{\theta}{2} = \frac{Ze^2}{2\pi\varepsilon_0 bmv_0^2} = \frac{Ze^2}{4\pi\varepsilon_0 bT}$$

where $T = K.E. = \frac{1}{2}mv_0^2$

It is given that $T = 5MeV = 5\times10^6\ eV = 5\times10^6\times1.6\times10^{-19}\ Joule = 8\times10^{-13}\ joule$

$$\therefore \tan\frac{\theta}{2} = \frac{Ze^2}{4\pi\varepsilon_0 bT} = \frac{79\times1.6\times10^{-19}\times1.6\times10^{-19}}{\frac{v_0^2}{c^2}\times2.6\times10^{-13}\times8\times10^{-13}} = 0.86750$$

$$\therefore \frac{\theta}{2} = 5^\circ \text{ or } \theta = 10^\circ$$

Q:- If we assume that charge $+Ze$ of a nucleus is spread over a sphere of radius R, then that the fastest α-particles (charge $2e$, mass $4m_p$) which can suffer 180° scattering will have speed v given by $v = \left(\frac{e^2Z}{m_pR}\right)^{\frac{1}{2}}$ with gold $Z=79$, 180° scattering is observed with α-particles of v upto 1.6×10^9 cm/sec. Deduce the upper limit for the radius of the nucleus.

Ans:- The nucleus being spherical the charge $+Ze$ may be considered to be concentrated at its centre. An α-particle will have its smallest distance of closest approach d from the centre of the nucleus when its impact parameter $b=0$ corresponding to a head-on approach resulting in a 180° scattering. Now the distance of closest approach for even the fastest α-particle [illegible] both fastest α-particle $d=R$

At the instant of closest approach, the α-particle momentarily stops at the distance R from the centre of the nucleus and its kinetic energy is entirely converted into potential energy. Therefore at that instant.

$$\frac{2Ze^2}{R} = \frac{1}{2}mv^2 = \frac{1}{2}4m_p v^2 \qquad \text{(C.G.S. system)}$$

$$v = \left(\frac{2Ze^2}{m_p R}\right)^{\frac{1}{2}}$$

From this the upper limit for the radius of the sphere is

$$R = \frac{2Ze^2}{m_p v^2}$$

Putting the given values of Z, v and $e = 4.8 \times 10^{-10}$ e.s.u, $m_p = 1.67 \times 10^{-24}$ gm,

$$R = \frac{79 \times 4.8 \times 10^{-10} \times 4.8 \times 10^{-10}}{1.67 \times 10^{-24} \times 1.6 \times 10^{9} \times 1.6 \times 10^{9}}$$

$$= 4.26 \times 10^{-12} \text{ cm}$$

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 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 right angle 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.

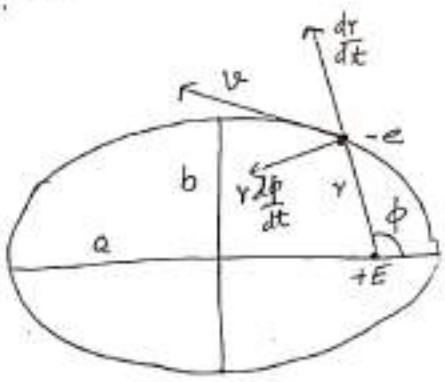


Fig :- Elliptic orbit

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

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

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.

P.T.O.

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

W = P.E. + radial K.E. + angular K.E

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

From these three fundamental equations which define 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 Kepler's law.

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

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

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

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

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

where a is the semi-major axis and e the eccentricity of ellipse.

Differentiating both sides of above eqn with respect to ϕ, we get

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

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

Substituting the value of r from Eqn (4), we have

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

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

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

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

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

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

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

using Eqn (5)

Now using, $\oint p_\phi d\phi = n_\phi h$ and $\frac{1}{r}\frac{dr}{d\phi} = \frac{e\sin\phi}{1+e\cos\phi}$ we get

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

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 $2\pi\left[\frac{1}{(1-\epsilon^2)^{1/2}} - 1\right]$.

Hence the eq^n(6) becomes

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

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

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

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

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

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, else 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 $n_\phi = n$. 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.

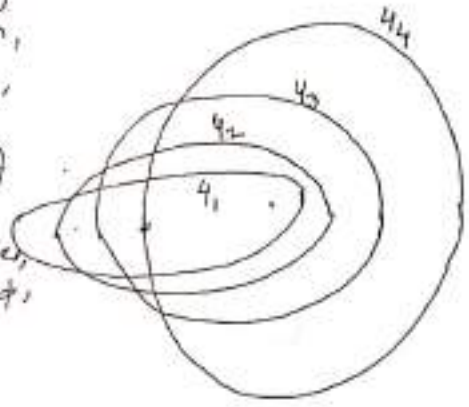


Fig :- Permitted ellipses for n=4

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

$$W = -\frac{2\pi^2 m E^2 e^2}{h^2}\left(\frac{1}{n_\phi + n_r}\right)^2 = -\frac{2\pi^2 m E^2 e^2}{h^2 n^2} \quad ---(9)$$

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 quantising 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.

PTO

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 his 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 ~~is energy~~ W of the system, corrected for the relativistic variation of the mass of the electron, can be shown to be

$$W = E_n = -\frac{2\pi^2 m E^2 e^2}{h^2}\left[\frac{1}{n^2} + \frac{4\pi^2 E^2 e^2}{c^2 h^2}\left(\frac{n}{n_\phi} - \frac{3}{4}\right)\frac{1}{n^4} + \cdots\right] \quad \text{---(10)}$$

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.,

$$-\frac{2\pi^2 m e^4}{h^2}\cdot\frac{Z^4\alpha^2}{n^4}\left(\frac{n}{n_\phi} - \frac{3}{4}\right) \quad \text{---(11)}$$

where $E = Ze$ and $\alpha = \frac{2\pi e^2}{ch}$

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 values of n_ϕ.

The correction term Eq(11), is a very small quantity as it involves α^2, whose value, readily estimated from the known values of e, c and h is found to be only 5.3×10^{-5}. α is called the fine structure constant and is equal to 7.29×10^{-3}.

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 5 transition. This discrepancy was removed by using a selection rule for transition. According to this selection rule only allowed transitions 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 explains the existence of fine structure of lines. The forbidden lines are indicated by dotted lines and permitted lines are indicated by full lines.

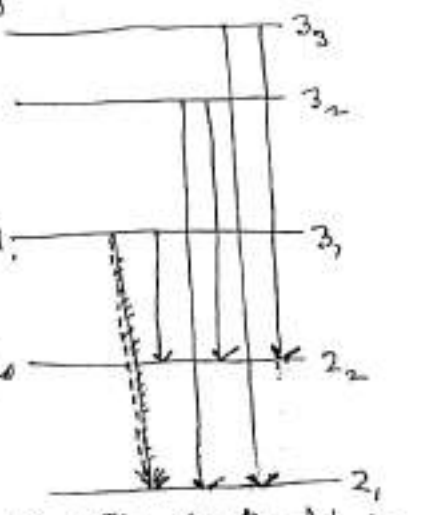


Fig :- Fine structure of H_α line

Improvement made by Sommerfeld's in Bohr's model :- The paths of the electron includes 2D' elliptical orbits in addition to circular one 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 mass 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 transitions 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, Goudsmit 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.

P.T.O.