

Figure 1: Thomson's model of the atom: (a) A sphere of positive charge with electrons embedded in it so that the net charge would normally be zero. The atom shown would have been phosphorus. (b) An α particle scattered by such an atom would have a scattering angle θ much smaller than 1°

The Nuclear Atom, Rutherford Scattering and its Conclusion.

Rutherford's alpha particle scattering experiments showed that the entire positive charge in atom is concentrated to very small region at centre. Rutherford arrived at a formula, describing the scattering of alpha particles by thin foils on the basis of his atomic model, that agreed with the experimental results. The derivation of this formula both illustrates the application of fundamental physical laws in a novel setting and introduces certain notions, such that of the *cross section* for an interaction, that are important in many other aspects of modern physics.

Rutherford began by assuming that the alpha particle and the nucleus it interacts with are both small enough to be considered as point masses and charges; that the electrostatic repulsive force between alpha particle and nucleus (which are both positively charged) is the only one acting; and that the nucleus is so massive compared with the alpha particle that it does not move during their interaction. Owing to the variation of the electrostatic force with $1/r^2$, where r is the instantaneous separation between alpha particle and nucleus, the alpha particle's path is a hyperbola with the nucleus at the outer focus. The *impact parameter* b is the minimum distance to which the alpha particle would approach the nucleus if there were no force between them, and the *scattering angle* θ is the angle between the asymptotic direction of approach of the alpha particle and asymptotic direction in which it recedes.

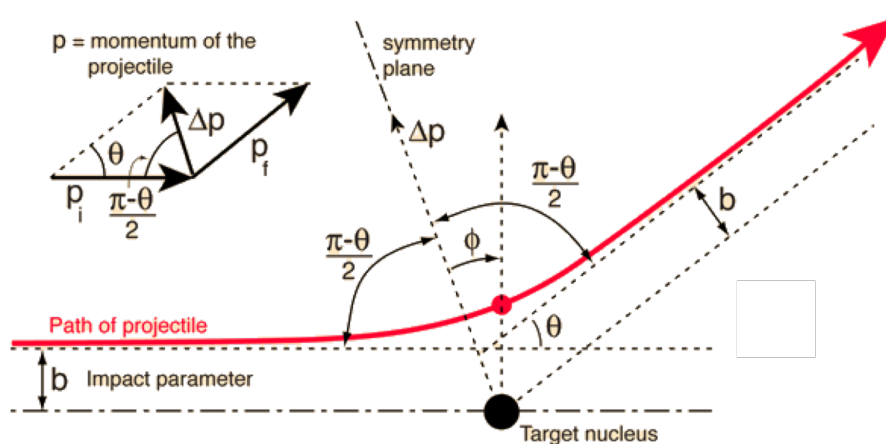


Figure 2: Geometrical relationships in Rutherford scattering

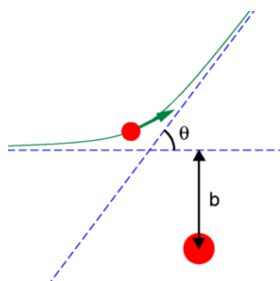


Figure 3: Impact parameter and scattering angle.

As a result of the impulse $\int F dt$ given it by the nucleus, the momentum of the alpha particle changes by Δp from the initial value p_1 to the final value p_2 .

$$\Delta \vec{p} = \vec{p}_2 - \vec{p}_1 = \int \vec{F} dt \quad (1)$$

Because the nucleus remains stationary during the passage of the alpha particle, the alpha-particle kinetic energy remains constant; hence the magnitude of its momentum also remains constant,

$$p_1 = p_2 = mv$$

Here v is the alpha-particle velocity far from the nucleus. From figure we see that, according to the law of sines,

$$\frac{\Delta p}{\sin \theta} = \frac{mv}{\sin\left(\frac{\pi-\theta}{2}\right)}$$

$$\frac{\Delta p}{2 \sin\left(\frac{\theta}{2}\right) \cos\left(\frac{\theta}{2}\right)} = \frac{mv}{\cos\left(\frac{\theta}{2}\right)}$$

$$\Delta p = 2mv \sin\left(\frac{\theta}{2}\right) \quad (2)$$

Because the impulse $\int \vec{F} dt$ is in the same direction as the momentum change Δp , its magnitude is,

$$\int F dt = \int F \cos \phi dt \quad (3)$$

where ϕ is the instantaneous angle between F and Δp along the path of the alpha particle. Inserting equation (2) and (3) in equation (1),

$$2mv \sin \frac{\theta}{2} = \int_0^\infty F \cos \phi dt$$

To change the variable on the right-hand side from t to ϕ , we note that the limits of integration will

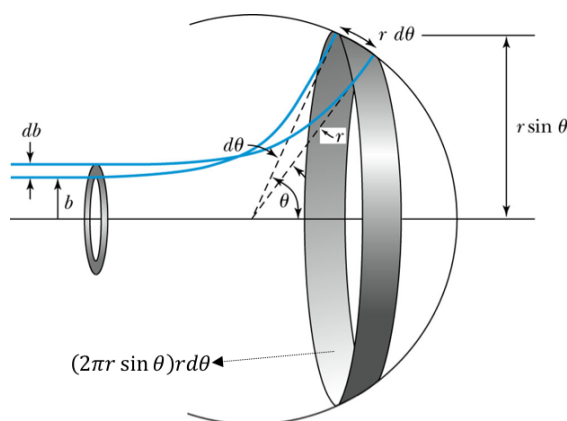


Figure 4: Geometrical relationships in Rutherford scattering

change to $-\frac{1}{2}(\pi - \theta)$ and $+\frac{1}{2}(\pi - \theta)$, corresponding to ϕ at $t = 0$ and $t = \infty$ respectively, and so,

$$2mv \sin \frac{\theta}{2} = \int_{-\frac{1}{2}(\pi-\theta)}^{+\frac{1}{2}(\pi-\theta)} F \cos \phi \frac{dt}{d\phi} d\phi \quad (4)$$

The quantity $\frac{d\phi}{dt}$ is just the angular velocity ω of the alpha particle about the nucleus.. The electrostatic force exerted by the nucleus on the alpha particle acts along the radius vector joining them, and so there is no torque on the alpha particle and its angular momentum $m\omega r^2$ is constant. Hence,

$$\begin{aligned} m\omega r^2 &= \text{constant} \\ &= mr^2 \frac{d\phi}{dt} \\ &= mvb \end{aligned}$$

from which we see that

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

Substituting this expression for $dt/d\phi$ in equation (4),

$$2mv^2b \sin \frac{\theta}{2} = \int_{-\frac{1}{2}(\pi-\theta)}^{+\frac{1}{2}(\pi-\theta)} F r^2 \cos \phi d\phi \quad (5)$$

As we recall, F is the electrostatic force exerted by the nucleus on the alpha particle. The charge on the nucleus is Ze , corresponding to the atomic number Z , and that on the alpha particle is $2e$. Therefore,

$$F = \frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{r^2}$$

and

$$\begin{aligned} \frac{4\pi\epsilon_0 mv^2b}{Ze^2} \sin \frac{\theta}{2} &= \int_{-\frac{1}{2}(\pi-\theta)}^{+\frac{1}{2}(\pi-\theta)} \cos \phi d\phi \\ &= 2 \cos \frac{\theta}{2} \end{aligned}$$

The scattering angle θ is related to the impact parameter b by the equation

$$\cot \frac{\theta}{2} = \frac{2\pi\epsilon_0 mv^2}{Ze^2} b$$

It is more convenient to specify the alpha-particle kinetic energy $T (= \frac{1}{2}mv^2)$,

$$\boxed{\cot \frac{\theta}{2} = \frac{4\pi\epsilon_0 T}{Ze^2} b} \quad (6)$$

This is the relation between scattering angle and impact parameter.

Rutherford Scattering Formula

All alpha particles approaching a target nucleus with an impact parameter from 0 to b will be scattered through an angle of θ or more. This means that an alpha particle that is initially directed anywhere within the area πb^2 around a nucleus will be scattered through θ or more; the area πb^2 is called the *cross section* for the interaction. The general symbol for cross section is σ .

$$\sigma = \pi b^2 \quad (7)$$

Now we consider a foil of thickness t that contains n atoms per unit volume. An alpha-particle beam incident upon an area A therefore encounters ntA nuclei. The aggregate cross section for scatterings of θ or more is the number of target nuclei $ntA\sigma$.

Hence the fraction f of incident alpha particles scattered by θ or more is,

$$\begin{aligned} f &= \frac{\text{alpha particles scattered by } \theta \text{ or more}}{\text{incident alpha particles}} \\ &= \frac{\text{aggregate cross section}}{\text{target area}} = \frac{ntA\sigma}{A} = nt\pi b^2 \end{aligned}$$

Substituting for b from equation (6),

$$f = \pi n t \left(\frac{Ze^2}{4\pi\epsilon_0 T} \right)^2 \cot^2 \frac{\theta}{2} \quad (8)$$

In the above calculation it was assumed that the foil is sufficiently thin so that the cross sections of adjacent nuclei do not overlap and that a scattered alpha particle receives its entire deflection from an encounter with a single nucleus.

If a total of N_i alpha particles strike the foil during the course of the experiment, the number scattered into $d\theta$ is $N_i df$.

The number $N(\theta)$ per unit area striking the screen at θ is

$$N(\theta) = \frac{N_i |df|}{ds}$$

From equation (8),

$$df = \pi n t \left(\frac{Ze^2}{4\pi\epsilon_0 T} \right)^2 \cot \frac{\theta}{2} \csc^2 \frac{\theta}{2} d\theta$$

And,

$$ds = 2\pi r \sin \theta r d\theta = 4\pi r^2 \sin \frac{\theta}{2} \cos \frac{\theta}{2}$$

Therefore,

$$N(\theta) = \frac{N_i \pi n t \left(\frac{Ze^2}{4\pi\epsilon_0 T} \right)^2 \cot \frac{\theta}{2} \csc^2 \frac{\theta}{2} d\theta}{4\pi r^2 \sin \frac{\theta}{2} \cos \frac{\theta}{2} d\theta}$$

$$N(\theta) = \frac{N_i n t Z^2 e^4}{(8\pi\epsilon_0)^2 r^2 T^2 \sin^4 \left(\frac{\theta}{2} \right)} \quad (9)$$

Equation (9) is the *Rutherford scattering formula*.

Electron Orbits

The Rutherford model of the atom, so convincingly confirmed by experiment, postulates a tiny, massive, positively charged nucleus surrounded at a relatively great distance by enough electrons to render the atom, as a whole, electrically neutral. Thomson visualized the electrons in his model atom as embedded in the positively charged matter that fills it, and thus as being unable to move. The electrons in Rutherford's model atom, however, cannot be stationary, because there is nothing that can keep them in place against the electrostatic force attracting them to the nucleus. If the electrons are in motion around the nucleus, however, dynamically stable orbits are possible.

Consider an electron of charge $-e$ moving in a circular orbit of radius r around a positively charged nucleus having charge $+e$. Then the centripetal force holding the electron in the orbit is provided by electrostatic force.

$$\frac{mv^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} \Rightarrow v = \frac{e}{\sqrt{4\pi\epsilon_0 mr}} \quad (10)$$

The total energy E of the electron in a hydrogen atom is the sum of its kinetic energy and its potential energy

$$KE(T) = \frac{1}{2}mv^2 \quad \text{and} \quad PE(V) = -\frac{e^2}{4\pi\epsilon_0 r}$$

Hence,

$$\text{Total Energy}(E) = T + V = \frac{mv^2}{2} - \frac{e^2}{4\pi\epsilon_0 r}$$

Substituting for v ,

$$E = \frac{e^2}{8\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 r} \Rightarrow \boxed{E = -\frac{e^2}{8\pi\epsilon_0 r}} \quad (11)$$

The total energy of an atomic electron is negative; this is necessary if it is to be bound to the nucleus. If E were greater than zero, the electron would have too much energy to remain in a closed orbit about the nucleus.

Experiments indicate that $13.6eV$ is required to separate a hydrogen atom into a proton and an electron; that is, its binding energy E is $-13.6eV$. Using this value of energy we can estimate orbital radius of electron in hydrogen atom.

$$r = -\frac{e^2}{8\pi\epsilon_0 E} \Rightarrow \boxed{r = 5.3 \times 10^{-11} m}$$

The atomic radius of this order of magnitude agrees with estimates made in other ways too.

Few points to be noted:

1. The above analysis is straightforward application of Newton's law of motion and Coulomb's law of electric force -both from classical physics - and is in accord with the experimental observation that atoms are stable.
2. However, it is not in accord with electromagnetic theory-another pillar of classical physics- which predicts that accelerated electric charges radiate energy in the form of electromagnetic waves.
3. An electron pursuing a curved path is accelerated and therefore should continuously lose energy, rapidly spiraling into the nucleus. Whenever they have been directly tested, the predictions of electromagnetic theory have always agreed with experiment.
4. Yet the atoms do not collapse.
5. This contradiction can mean only one thing: *The laws of physics that are valid in the macroscopic world do not hold true in the microscopic world of the atom.*

Bohr Atom

Bohr's Postulates

Postulate 1 An electron cannot revolve round the nucleus in all possible orbits as suggested by classical theory. The electron can revolve round the nucleus only in those allowed or permissible orbits for which the angular momentum of the electrons is an integral multiple of $\frac{h}{2\pi}$, where h is Planck's constant.

If m is the mass of electron and v is velocity of the electron in an orbit of radius r , then,

$$\text{Angular momentum}(L) = mvr = n \frac{h}{2\pi} = n\hbar$$

$$L = n\hbar$$

where n is an integer and can take values $n = 1, 2, 3, 4, \dots$ It is called principal quantum number. This equation is called Bohr's quantization condition.

Postulate 2 When electron revolves in permitted orbits they do not radiate energy. An atom radiates energy only when an electron jumps from a higher energy state to the lower energy state and the energy is absorbed, when it jumps from lower to higher energy orbit.

If E_{n_1} and E_{n_2} are energies associated with first and second orbits respectively, then the frequency ν of the radiation emitted is given by

$$\nu = \frac{E_{n_2} - E_{n_1}}{h}$$

This is called Bohr's frequency condition.

Bohr's Theory of Hydrogen Atom

Bohr assumed that a hydrogen atom consists of a nucleus with one unit positive charge $+e$ (i.e. a proton) and a single electron of charge $-e$, revolving around it in a circular orbit of radius r . The electrostatic force of attraction between the proton and the electron is given by

$$F = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} \quad (12)$$

If m and v are mass and velocity of the electron in the orbit, then the centripetal force required by the electron to move in circular orbit of radius r is given by

$$F = \frac{mv^2}{r} \quad (13)$$

The electrostatic force of attraction between the electron and the nucleus provides the necessary centripetal force. Therefore,

$$\frac{mv^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} \quad (14)$$

According to Bohr's first postulate,

$$mvr = n \frac{h}{2\pi}$$

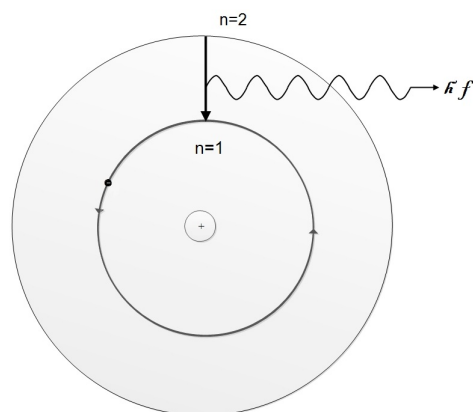


Figure 5: Bohr's atom

$$\boxed{v = \frac{nh}{2\pi r m}} \quad (15)$$

$$v^2 = \frac{n^2 h^2}{4\pi^2 r^2 m^2}$$

substituting this value of v^2 in equation (3), we get

$$\frac{m}{r} \left(\frac{n^2 h^2}{4\pi^2 r^2 m^2} \right) = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2}$$

$$r = \frac{\epsilon_0 n^2 h^2}{\pi m e^2} \quad (16)$$

Radius of the n^{th} permissible orbit for hydrogen is given by

$$\boxed{r_n = \frac{\epsilon_0 n^2 h^2}{\pi m e^2}} \quad (17)$$

As $n = 1, 2, 3, \dots$ it follows from equation (6) that the radii of the stationary orbits are proportional to n^2 .

Bohr Radius

The radius of the innermost orbit in hydrogen atom is called Bohr's radius and is denoted by a_0 .

For $n = 1$,

$$r = a_0 = \frac{\epsilon_0 h^2}{\pi m e^2}$$

Substituting the known values of ϵ_0 , h , m , and e , we get,

$$a_0 = 0.529 \text{ \AA}$$

$$r_n = 0.529 \times n^2 \text{ \AA} \quad (18)$$

$$1 \text{ \AA} = 10^{-10} m$$

Velocity of the Electron

The velocity of the electron in the n^{th} orbit, v_n is given by

$$v_n = \frac{nh}{2\pi r_n m}$$

Substituting the value of r_n from equation (6) we get,

$$v_n = \frac{nh}{2\pi m} \left(\frac{\pi m e^2}{\epsilon_0 n^2 h^2} \right)$$

$$\boxed{v_n = \frac{e^2}{2\epsilon_0 n h}} \quad (19)$$

Therefore $v_n \propto \frac{1}{n}$, the electrons closer to the nucleus move with higher velocity than lying farther.

Energy of the Electron in n^{th} orbit

As electron is revolving round the nucleus, it has kinetic energy.

$$K.E. = \frac{1}{2} m v_n^2$$

And,

$$P.E. = -\frac{1}{4\pi\epsilon_0} \frac{e \cdot e}{r_n^2}$$

Therefore, total energy of the electron in the n^{th} orbit is

$$E_n = K.E. + P.E.$$

$$E_n = \frac{1}{2}mv_n^2 - \frac{1}{4\pi\epsilon_0} \frac{e \cdot e}{r_n^2}$$

Substituting values of r_n and v_n from (6) and (8), we get,

$$E_n = -\frac{me^4}{8\epsilon_0^2 n^2 h^2} \quad (20)$$

Bohrs Interpretation of the Hydrogen Spectrum

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

$$h\nu = E_{n_2} - E_{n_1}$$

where E_{n_2} and E_{n_1} are energies of the electron in the stationary orbits then

$$E_{n_1} = -\frac{me^4}{8\epsilon_0^2 n_1^2 h^2} \quad \text{and} \quad E_{n_2} = -\frac{me^4}{8\epsilon_0^2 n_2^2 h^2}$$

therefore, the energy of photon emitted is given by

$$h\nu = \left(-\frac{me^4}{8\epsilon_0^2 n_2^2 h^2} \right) - \left(-\frac{me^4}{8\epsilon_0^2 n_1^2 h^2} \right) \Rightarrow h\nu = \frac{me^4}{8\epsilon_0^2 h^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Therefore,

$$\nu = \frac{me^4}{8\epsilon_0^2 h^3} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (21)$$

Wavenumber($\bar{\nu}$): Reciprocal of wavelength of radiation is called wavenumber. i.e. $\bar{\nu} = \frac{1}{\lambda}$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{f}{c}$$

Therefore,

$$\bar{\nu} = \frac{\nu}{c} = \frac{me^4}{8\epsilon_0^2 ch^3} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\bar{\nu} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (22)$$

where $R = \frac{me^4}{8\epsilon_0^2 ch^3}$ known as Rydberg's constant. The value of Rydberg's constant is $1.097 \times 10^7 m^{-1}$

Spectral Series of Hydrogen Atom

When an electron jumps from the higher energy state to the lower energy state, the difference of energies of two states is emitted as a radiation of definite frequency. It is called *spectral line*. The spectral lines are divided into a number of series.

1. Lyman Series The spectral lines of this series correspond to the transition of an electron from some higher energy state to the innermost orbit ($n = 1$). Therefore, for Lyman series $n_1 = 1$ and $n_2 = 2, 3, 4, 5, \dots$

2. Balmer Series The spectral lines of this series correspond to the transition of an electron from some higher energy state to the orbit having $n = 2$. Therefore, for Balmer series $n_1 = 2$ and $n_2 = 3, 4, 5, 6, \dots$

3. Paschen Series The spectral lines of this series correspond to the transition of an electron from some higher energy state to the orbit having $n = 3$. Therefore, for Paschen series $n_1 = 3$ and $n_2 = 4, 5, 6, 7, \dots$

4. Brackett Series The spectral lines of this series correspond to the transition of an electron from some higher energy state to the orbit having $n = 4$. Therefore, for Brackett series $n_1 = 4$ and $n_2 = 5, 6, 7, 8, \dots$

5. P-fund Series The spectral lines of this series correspond to the transition of an electron from some higher energy state to the orbit having $n = 5$. Therefore, for P-fund series $n_1 = 5$ and $n_2 = 6, 7, 8, \dots$

Limitations of Bohrs Theory of Hydrogen Atom

1. Elliptical orbits are possible for the electron orbits, but Bohrs theory does not tell us why only elliptical orbits are possible.
2. Bohrs theory does explain the spectra of only simple atoms like hydrogen but fails to explain the spectra of multi-electron atoms.
3. The fine structure of certain spectral lines of hydrogen could not be explained by Bohrs theory.
4. It does not explain the relative intensities of spectral lines.
5. This theory does not account for the wave nature of electrons.

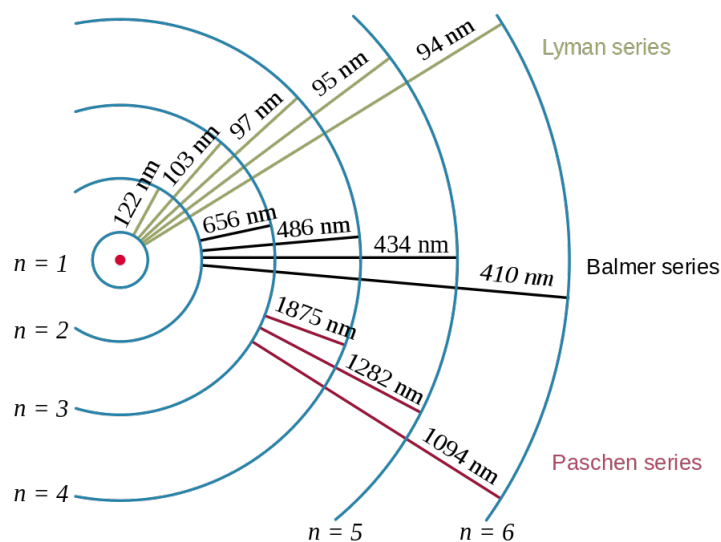


Figure 6: Spectral series of Hydrogen atom

Franck-Hertz Experiment

The existence of discrete energy levels in atoms was demonstrated directly by James Franck and Gustav Hertz in 1914.

A schematic of the experimental set-up is shown in Figure. The essential part of the apparatus consists of a tube containing vapor of the element under study. The tube contains three electrodes: a filament (F) that provides electrons when heated, a plate (P), and a grid (G). A grid is a charged screen that can attract or repel electrons but, because most of it is open space, the majority of the electrons pass through it. A variable accelerating voltage V_0 is applied between the filament and the grid. As a consequence of this potential difference, the electrons will reach the grid (in the absence of collisions) with a kinetic energy $E_k = eV_0$. After reaching the grid the majority of these electrons will go through the holes in the grid, be collected by the plate P, and contribute to the plate current i , which can be measured by the ammeter A. A small, constant retarding voltage V_r ($\approx 1V$) is applied between the plate and the grid. If $V_r > V_0$, the electrons will be turned back before they can reach the plate and they will not contribute to the current measured by A. But even if $V_r < V_0$, the electrons will not be able to reach the plate if they lose enough kinetic energy through collisions with the atoms in the tube as they travel between the filament and the grid.

In the absence of any vapor, that is, a vacuum, the $i-V_0$ characteristics are those of a typical vacuum tube. This dependence is shown by the dashed line of Figure 2. If vapor of some element is present in the tube, one observes a series of fairly sudden dips superimposed on the monotonic vacuum curve. The solid curve in Figure 2 shows this effect for the case where mercury vapor is present in the tube.

The fact that there is no drop in the current until certain voltage is reached ($V_0 = 4.9V$ in this case) indicates that the electrons do not lose energy through collisions until they have a particular value of kinetic energy ($4.9eV$ in this case).

If the gas atoms in the tube can have a continuous distribution of internal energy states, the transfer of kinetic energy from the bombarding electrons to the atoms could and should occur regardless of the energy of the electrons, that is, the drop in the current should occur for any value of V_0 . The fact that the drop occurs only when $V_0 = 4.9V$ (and therefore the E_k of the electrons is $4.9eV$) indicates that the first excited state of the gas atom used in the tube is $4.9eV$ above the ground state. As V_0 increases beyond the $4.9V$, the current begins to increase again because, although the electrons can and do collide inelastically and lose $4.9eV$ of energy, they still have enough energy remaining to overcome the small retarding voltage V_r . When $V_0 = 2 \times 4.9V$ or $3 \times 4.9V$, or so on, dips in the current occur again because now the electrons can undergo two, three, or more inelastic collisions with the gas atom; in each collision they lose $4.9eV$.

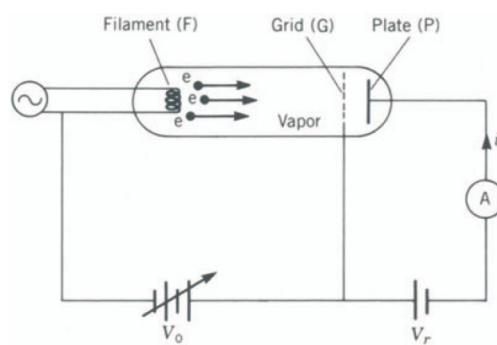


Figure 7: Schematic of the apparatus used in the Franck-Hertz experiment to show the quantization of the internal energy of atoms.

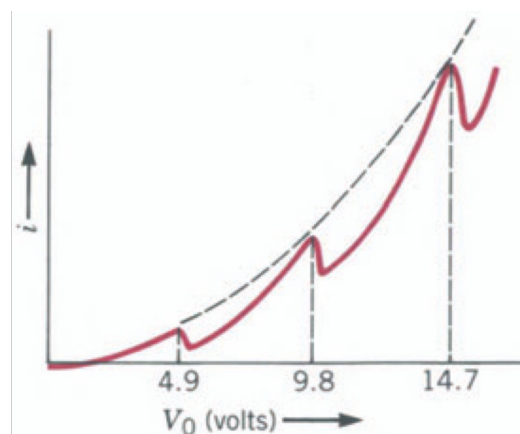


Figure 8: Dependence of the plate current i (measured by the ammeter A in the apparatus of Figure 1) on the accelerating voltage V_0 .

This interpretation is corroborated by the electromagnetic radiation emitted by Hg atoms. There should be a spectral line whose frequency is given by $h\nu = 4.9eV$ or $\lambda = 2530\text{\AA}$. Such a wavelength is found in the spectrum of Hg . An energy diagram for Hg is shown in Figure 3. The energy difference ΔE between the first excited state and the ground state is $\Delta E = 10.4eV - 5.5eV = 4.9eV$.

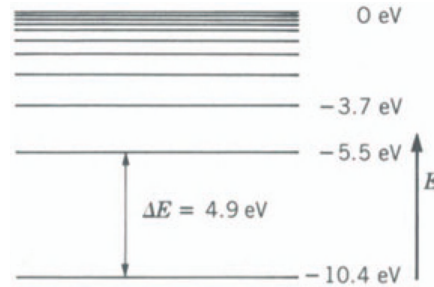


Figure 9: Atomic energy levels of a mercury atom

Bohr's Correspondence Principle

The principles of quantum physics, so different from those of classical physics in the microscopic world that lies beyond the reach of our senses. Nevertheless, the quantum physics should yield results identical with those of classical physics in the domain where experiment indicates that the classical physics is valid.

According to electromagnetic theory an electron moving in a circular orbit radiates electromagnetic waves whose frequencies are equal to its frequency of revolution and to harmonics of that frequency. In a hydrogen atom the electron's speed is

$$v = \frac{e}{\sqrt{4\pi\epsilon_0 mr}}$$

Hence the frequency of revolution f of the electron is,

$$\begin{aligned} f &= \frac{\text{electron speed}}{\text{orbit circumference}} \\ &= \frac{v}{2\pi r} \\ &= \frac{e}{2\pi\sqrt{4\pi\epsilon_0 mr^3}} \end{aligned}$$

The radius r of a stable orbit is given in terms of its quantum number n by,

$$r_n = \frac{n^2 h^2 \epsilon_0}{\pi m e^2}$$

and so the frequency of revolution is,

$$f = \frac{m e^4}{8 \epsilon_0^2 h^3} \left(\frac{2}{n^3} \right) \quad (23)$$

The energy of photon emitted when an electron jumps from n_2 orbit to n_1 orbit is given by

$$\nu = \frac{m e^4}{8 \epsilon_0^2 h^3} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

If $n_2 = n$ and $n_1 = n - 1$

$$\begin{aligned} \nu &= \frac{m e^4}{8 \epsilon_0^2 h^3} \left(\frac{1}{(n-1)^2} - \frac{1}{n^2} \right) \\ &= \frac{m e^4}{8 \epsilon_0^2 h^3} \left(\frac{n^2 - (n-1)^2}{n^2(n-1)^2} \right) = \frac{m e^4}{8 \epsilon_0^2 h^3} \left(\frac{n^2 - n^2 + 2n - 1}{n^2(n-1)^2} \right) = \frac{m e^4}{8 \epsilon_0^2 h^3} \left(\frac{2n - 1}{n^2(n-1)^2} \right) \end{aligned}$$

For very large n , $(2n - 1) \approx 2n$, and $n - 1 \approx n$. Therefore,

$$v \approx \frac{me^4}{8\epsilon_0^2 h^3} \left(\frac{2n}{n^4} \right) = \boxed{\frac{me^4}{8\epsilon_0^2 h^3} \left(\frac{2}{n^3} \right)} \quad (24)$$

Equation (24) is identical to equation (23). This shows that the quantum theory agrees with classical theory in the limit of large quantum numbers. This verifies Bohr's correspondence principle.

Sommerfeld Atomic Model

To explain the observed fine structure of spectral lines, Sommerfeld proposed an atom model. The assumption of this atomic model are:-

1. The path of electron around the nucleus of an atom is general elliptical. The circular orbit of Bohr's theory are special case of elliptical orbit.
2. While revolving in elliptical orbit there is variation of speed of electron due to which there is relativistic variation in the most of electron.

Elliptical orbit of Hydrogen atom

Consider (r, ϕ) be the instantaneous position of electron with respect to nucleus being at one of the foci of ellipse. The quantization condition associated with two coordinate r and ϕ are.

$$\oint p_\phi d\phi = n_\phi h \dots (1)$$

$$\oint p_r dr = n_r h \dots (2)$$

where,

p_ϕ = angular momentum associated with change in $\phi = mr^2 \frac{d\phi}{dt}$

n_ϕ = angular or Azimuthal quantum number

P_r = radial momentum $m \frac{dr}{dt}$

n_r = radial quantum number

The principle quantum number is related with n_ϕ and n_r as

$$n_\phi + n_r = n \dots \dots \dots (3)$$

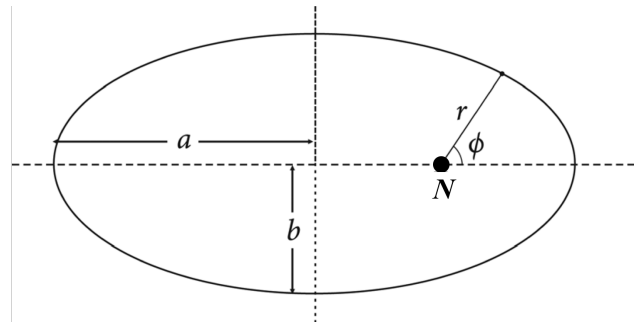


Figure 10: Elliptical Orbit of Electron

Evaluation of $\oint p_\phi d\phi = n_\phi h$

$$\oint p_\phi d\phi = n_\phi h \Rightarrow p_\phi \oint d\phi = n_\phi h \quad [\because p_\phi \text{ is constant, being angular momentum in central force }]$$

$$2\phi \cdot p_\phi = n_\phi h \Rightarrow p_\phi = \frac{n_\phi h}{2\pi} \dots \dots \dots (4)$$

Evaluation of $\oint p_r dr = n_r h$

$$\begin{aligned} p_r dr &= m \cdot \frac{dr}{dt} \cdot dr = m \frac{dr}{d\phi} \cdot \frac{d\phi}{dt} \cdot \frac{dr}{d\phi} \cdot d\phi = m \left(\frac{dr}{d\phi}\right)^2 \cdot \left(\frac{d\phi}{dt}\right) \cdot d\phi \\ &= m \left(\frac{dr}{d\phi}\right)^2 \cdot \left(\frac{p_\phi}{mr^2}\right) d\phi \\ &= \left(\frac{1}{r} \frac{dr}{d\phi}\right)^2 \cdot p_\phi d\phi \dots\dots\dots (5) \end{aligned}$$

We have from polar equation of ellipse,

$$\frac{1}{r} = \frac{1 + \epsilon \cos \phi}{a(1 - \epsilon^2)} \dots\dots\dots (6)$$

where, a = semi-major axis, ϵ = eccentricity

Taking log on both side

$$-\log r = \log(1 + \epsilon \cos \phi) - \log[a(1 - \epsilon^2)]$$

Differentiating with respect to ϕ , we get,

$$\begin{aligned} \frac{-d(\log r)}{dr} \cdot \frac{dr}{d\phi} &= \frac{d \log(1 + \epsilon \cos \phi)}{d(1 + \epsilon \cos \phi)} \cdot \frac{d(1 + \epsilon \cos \phi)}{d\phi} - 0 \\ \frac{-1}{r} \cdot \frac{dr}{d\phi} &= \frac{1}{(1 + \epsilon \cos \phi)} \cdot (0 - \epsilon \sin \phi) \\ \frac{1}{r} \frac{dr}{d\phi} &= \frac{\epsilon \sin \phi}{(1 + \epsilon \cos \phi)} \dots\dots\dots (7) \end{aligned}$$

From (5) and (7),

$$\begin{aligned} P_r dr &= \left(\frac{\epsilon \sin \phi}{1 + \epsilon \cos \phi}\right)^2 p_\phi d\phi \\ \oint p_r \cdot dr &= \int_0^{2\pi} \left(\frac{\epsilon \sin \phi}{1 + \epsilon \cos \phi}\right)^2 p_\phi d\phi \dots\dots\dots (8) \end{aligned}$$

$$\text{Let, } I = \int_0^{2\pi} \frac{\epsilon^2 \sin^2 \phi}{(1 + \epsilon \cos \phi)^2} d\phi \dots\dots\dots (9)$$

We have,

$$d[uv] = u dv + v du \Rightarrow u dv = d[uv] - v du \Rightarrow \int u \cdot dv = [uv] - \int v du \dots\dots\dots (10)$$

put,

$$\epsilon \sin \phi = u, \quad \epsilon \cos \phi d\phi = du \quad \text{and} \quad dv = \frac{\epsilon \sin \phi d\phi}{(1 + \epsilon \cos \phi)^2} \Rightarrow v = \frac{1}{1 + \epsilon \cos \phi}$$

Substituting above equation in (10)

$$\begin{aligned}
 I &= \int_0^{2\pi} \epsilon \sin \phi \cdot \frac{\epsilon \sin \phi \cdot d\phi}{(1 + \cos \phi)^2} = \left[\frac{\epsilon \sin \phi}{1 + \epsilon \cos \phi} \right]_0^{2\pi} - \int_0^{2\pi} \frac{\epsilon \cos \phi d\phi}{1 + \epsilon \cos \phi} \\
 &= - \int_0^{2\pi} \frac{\epsilon \cos \phi}{1 + \epsilon \cos \phi} \cdot d\phi \\
 &= \int_0^{2\pi} \left[\frac{-(1 + \epsilon \cos \phi)}{1 + \epsilon \cos \phi} + \frac{1}{1 + \epsilon \cos \phi} \right] d\phi = \int_0^{2\pi} \frac{1}{1 + \epsilon \cos \phi} \cdot d\phi - \int_0^{2\pi} 1 d\phi \dots \dots \dots (11)
 \end{aligned}$$

Using the value of standard integral $\int_0^{2\pi} \frac{d\phi}{1 + \epsilon \cos \phi} = \frac{2\pi}{\sqrt{1 - \epsilon^2}}$,

$$I = \frac{2\pi}{\sqrt{1 - \epsilon^2}} - [\phi]_0^{2\pi} \Rightarrow I = \frac{2\pi}{\sqrt{1 - \epsilon^2}} - 2\pi \dots \dots \dots (12)$$

Substituting equation (12) and (9) in (8)

$$\oint p_r dr = p_\phi \left(\frac{2\pi}{(1 - \epsilon^2)^{\frac{1}{2}}} - 2\pi \right) = n_r h$$

$$\oint p_r dr = \frac{n_\phi h}{2\pi} \cdot 2\pi \left(\frac{1}{(1 - \epsilon^2)^{\frac{1}{2}}} - 1 \right) = n_r h$$

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

$$\frac{n_\phi}{(1 - \epsilon^2)^{\frac{1}{2}}} = n \text{ [from eq}^n(3)]$$

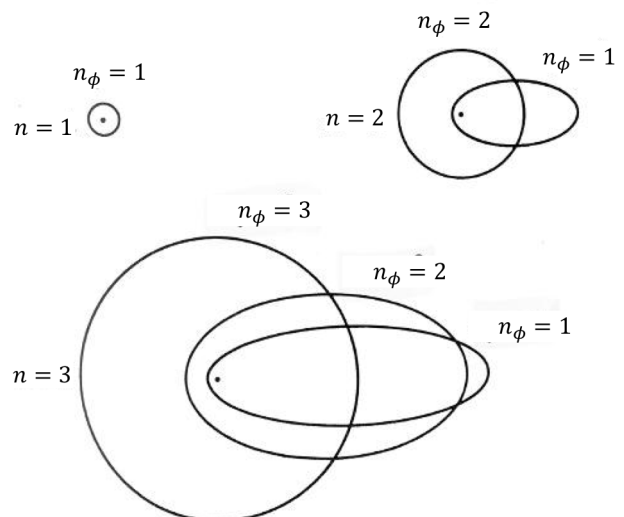
$$\frac{n_\phi}{n} = (1 - \epsilon^2)^{\frac{1}{2}} \Rightarrow \frac{n_\phi^2}{n^2} = (1 - \epsilon^2) = \frac{b^2}{a^2} \text{ [for an ellipse } b^2 = a^2(1 - \epsilon^2)]$$

$$\frac{n_\phi}{n} = \frac{b}{a} \dots \dots \dots (13)$$

Equation (13) determines the shape and number of allowed electronic orbits. The allowed elliptical orbits are those for which the ratio of major and minor axes is that of two integers.

Few points to be noted:

1. When $n_\phi = 0 \Rightarrow b = 0$, the path of electronic orbit straight line is passing through nucleus. But electron doesn't pass through nucleus ($n_\phi \neq 0$).
2. Since b and a are always positive n_ϕ can not be negative.
3. Since $b \leq a \Rightarrow n_\phi \leq n$. When $b = a \Rightarrow n_\phi = n$, the path of electronic orbit is circular. When $b < a \Rightarrow n_\phi < n$, the path of electronic orbit is elliptical.
 - (a) When $n = 1 \Rightarrow n_\phi = 1$. The orbit



- is circular $n_r = 0$. This is the case of Bohr's theory.
- (b) When $n = 2 \Rightarrow n_\phi = 2$ Two orbits are possible.
- i. $n = 2, n_\phi = 2 \Rightarrow a = b$ Orbit is circular
 - ii. $n = 2, n_\phi = 1 \Rightarrow b < a \Rightarrow b = \frac{a}{2}$
Orbit is elliptical
- (c) When $n = 3, n_\phi = 3, 2, 1$ Three possible orbits.
- i. $n = 3, n_\phi = 3 \Rightarrow b = a$ Orbit circular
 - ii. $n = 3, n_\phi = 2 \Rightarrow b = \frac{2}{3}a$ Orbit is elliptical.
 - iii. $n = 3, n_\phi = 1 \Rightarrow b = \frac{1}{3}a$ Orbit is elliptical.

Usually the allowed orbits are described by giving values of n and n_ϕ . The value of azimuthal quantum number n_ϕ is described by letters s, p, d, f , etc. 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 $n_\phi = 3$.

Total Energy

Total energy of a single electron in an orbit is given by

$$E_n = K.E. + P.E.$$

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

As we know,

$$p_r = m \frac{dr}{dt} \Rightarrow \frac{dr}{dt} = \frac{p_r}{m} \quad \text{and} \quad p_\phi = mr^2 \frac{d\phi}{dt} \Rightarrow \frac{d\phi}{dt} = \frac{p_\phi}{mr^2} \dots\dots\dots (2)$$

$$\begin{aligned}
 K.E. &= \frac{1}{2}m \left[\left(\frac{p_r}{m} \right)^2 + \left(r \frac{p_\phi}{mr^2} \right)^2 \right] \\
 &= \frac{1}{2m} \left[p_r^2 + \frac{1}{r^2} p_\phi^2 \right] \\
 &= \frac{p_\phi^2}{2mr^2} \left[r^2 \frac{p_r^2}{p_\phi^2} + 1 \right] \\
 &= \frac{p_\phi^2}{2mr^2} \left[\frac{r^2}{p_\phi^2} \left(\frac{p_\phi}{r^2} \frac{dr}{d\phi} \right)^2 + 1 \right] \\
 &= \frac{p_\phi^2}{2mr^2} \left[\left(\frac{1}{r} \frac{dr}{d\phi} \right)^2 + 1 \right] \\
 &= \frac{p_\phi^2}{2mr^2} \left[\left(\frac{\epsilon \sin \phi}{(1 + \epsilon \cos \phi)} \right)^2 + 1 \right]; \quad \left[\because \frac{1}{r} \frac{dr}{d\phi} = \frac{\epsilon \sin \phi}{(1 + \epsilon \cos \phi)} \right] \\
 &= \frac{p_\phi^2}{2m} \left(\frac{1 + \epsilon \cos \phi}{a(1 - \epsilon^2)} \right)^2 \left[\left(\frac{\epsilon \sin \phi}{(1 + \epsilon \cos \phi)} \right)^2 + 1 \right]; \quad \left[\because \frac{1}{r} = \frac{1 + \epsilon \cos \phi}{a(1 - \epsilon^2)} \right] \\
 &= \frac{p_\phi^2}{2m a^2 (1 - \epsilon^2)^2} \left[(1 + \epsilon \cos \phi)^2 \left(\frac{\epsilon \sin \phi}{(1 + \epsilon \cos \phi)} \right)^2 + (1 + \epsilon \cos \phi)^2 \right]
 \end{aligned}$$

$$\begin{aligned}
 K.E. &= \frac{p_\phi^2}{2m a^2 (1 - \epsilon^2)^2} \left[\epsilon^2 \sin^2 \phi + 1 + 2\epsilon \cos \phi + \epsilon^2 \cos^2 \phi \right] \\
 &= \frac{p_\phi^2}{2m a^2 (1 - \epsilon^2)^2} \left[1 + \epsilon^2 + 2\epsilon \cos \phi \right]
 \end{aligned}$$

$$K.E. = \frac{p_\phi^2}{2m a^2 (1 - \epsilon^2)^2} \left[1 + \epsilon^2 + 2\epsilon \cos \phi \right] \dots \dots \dots (3)$$

Similarly,

$$P.E. = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} = -\frac{1}{4\pi\epsilon_0} Ze^2 \left(\frac{1 + \epsilon \cos \phi}{a(1 - \epsilon^2)} \right) \dots \dots \dots (4)$$

Therefore,

$$E_n = K.E. + P.E. = \frac{p_\phi^2}{2m a^2(1 - \epsilon^2)^2} [1 + \epsilon^2 + 2\epsilon \cos \phi] - \frac{1}{4\pi\epsilon_0} Z e^2 \left(\frac{1 + \epsilon \cos \phi}{a(1 - \epsilon^2)} \right)$$

$$E_n = \frac{p_\phi^2}{2m a^2(1 - \epsilon^2)^2} \cdot (1 + \epsilon^2 + 2\epsilon \cos \phi) - \frac{1}{4\pi\epsilon_0} \cdot \frac{z e^2 (1 + \epsilon \cos \phi)}{a(1 - \epsilon^2)}$$

$$E_n = \left[\frac{p_\phi^2 (1 + \epsilon^2)}{2m a^2(1 - \epsilon^2)^2} - \frac{z e^2}{4\pi\epsilon_0 a(1 - \epsilon^2)} \right] + \left[\frac{p_\phi^2 \epsilon}{m a^2(1 - \epsilon^2)^2} - \frac{z e^2 \epsilon}{4\pi\epsilon_0 a(1 - \epsilon^2)} \right] \cos \phi \dots \dots \dots (5)$$

Due to presence of $\cos \phi$ in the expression of total energy, total energy becomes variable. However, according to conservation of energy total energy should be constant. Therefore, the coefficient of $\cos \phi$ must be zero.

$$\frac{p_\phi^2 \epsilon}{m a^2(1 - \epsilon^2)^2} - \frac{z e^2 \epsilon}{4\pi\epsilon_0 a(1 - \epsilon^2)} = 0 \Rightarrow \frac{\epsilon}{a(1 - \epsilon^2)} \left[\frac{p_\phi^2}{m a(1 - \epsilon^2)} - \frac{z e^2}{4\pi\epsilon_0} \right] = 0$$

$$\left[\frac{p_\phi^2}{m a(1 - \epsilon^2)} - \frac{z e^2}{4\pi\epsilon_0} \right] = 0 \Rightarrow \frac{p_\phi^2}{m a(1 - \epsilon^2)} = \frac{Z e^2}{4\pi\epsilon_0} \dots \dots \dots (6)$$

$$a = \frac{p_\phi^2 4\pi\epsilon_0}{Z e^2 m (1 - \epsilon^2)} \Rightarrow a = \frac{\left(\frac{n_\phi h}{2\pi} \right)^2 4\pi\epsilon_0}{Z e^2 m \left(\frac{n_\phi}{n} \right)^2} \left[\because \frac{n_\phi}{n} = (1 - \epsilon^2)^{\frac{1}{2}} \right]$$

$$\therefore a = \left(\frac{n^2 h^2 \epsilon_0}{\pi m Z e^2} \right) \dots \dots \dots (7)$$

Therefore,

$$E_n = \left[\frac{p_\phi^2 (1 + \epsilon^2)}{2m a^2(1 - \epsilon^2)^2} - \frac{Z e^2}{4\pi\epsilon_0 a(1 - \epsilon^2)} \right] = \frac{p_\phi^2}{m a(1 - \epsilon^2)} \frac{1 + \epsilon^2}{2a(1 - \epsilon^2)} - \frac{Z e^2}{4\pi\epsilon_0 a(1 - \epsilon^2)}$$

$$\begin{aligned}
 E_n &= \frac{Ze^2}{4\pi\epsilon_0} \frac{1 + \epsilon^2}{2a(1 - \epsilon^2)} - \frac{Ze^2}{4\pi\epsilon_0 a(1 - \epsilon^2)} \left[\because \frac{p_\phi^2}{ma(1 - \epsilon^2)} = \frac{Ze^2}{4\pi\epsilon_0} \text{ (from equation (6))} \right] \\
 &= \frac{Ze^2}{4\pi\epsilon_0 a(1 - \epsilon^2)} \left(\frac{1 + \epsilon^2}{2} - 1 \right) \\
 &= \frac{Ze^2}{4\pi\epsilon_0 a(1 - \epsilon^2)} \left(\frac{\epsilon^2 - 1}{2} \right) \\
 &= \frac{-Ze^2}{4\pi\epsilon_0 2a} = \frac{-Ze^2}{8\pi\epsilon_0} \cdot \frac{\pi m Z e^2}{n^2 h^2 \epsilon_0}
 \end{aligned}$$

$$\boxed{E_n = \frac{-me^4 Z^2}{8\epsilon_0^2 n^2 h^2}} \dots\dots\dots (8)$$

Thus, Non-relativistic Sommerfeld atomic model gives the same energy as in Bohr's theory. This means that the theory of elliptical orbits 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 to be expected because of this multiplicity of orbits.

Sommerfeld proceeded further to find the solution on the basis of variation of the mass of the electron with velocity.

Sommerfeld's relativistic correction

Sommerfeld pointed out that origin of the fine structure of the spectral lines of the hydrogen like atoms was due to the relativistic variation of the mass of the electron. It is apparent that the velocity of electron in an atom is comparable to the velocity of light and therefore, relativistic effects are significant.

According to the theory of relativity, the mass of particle m moving with a velocity v is related to its rest mass is given by

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

Applying relativistic effect in the Sommerfeld atomic model, the energy of electron is calculated to be,

$$\boxed{E_n = \frac{-me^4 Z^2}{8\epsilon_0^2 n^2 h^2} \left[1 + \frac{Z^2 \alpha^2}{n^2} \left(\frac{n}{n_\phi} - \frac{3}{4} \right) \right]} \dots\dots\dots (9)$$

Where $\alpha = \frac{e^2}{2\epsilon_0 ch} = \frac{1}{137.04}$, α is equal to the ratio of velocity of the electron in the first Bohr orbit Hydrogen to the velocity of light c . It is called fine structure constant. The first term in equation (9) is the energy of the electron in the orbit with the principal quantum number n . The second term is the Sommerfeld relativistic correction. This term shows that the energy does depend on the azimuthal quantum number n_ϕ . This results in a splitting of the energy levels of the atom.

Sommerfeld's relativistic calculation based on the Bohr model agrees with the experimental measurements of fine structure for hydrogen, but the agreement turned out to be accidental since this calculation predicts fewer lines than are seen for other atoms.