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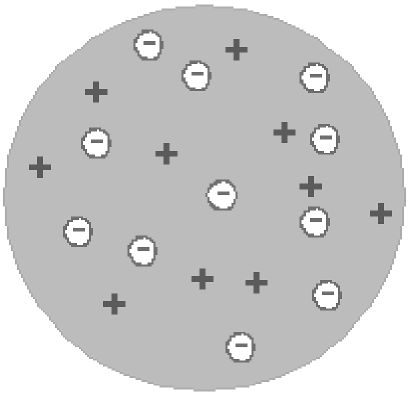
ATOMIC STRUCTURE

Thompson model

The Thompson model was the first attempt to describe how an atom looked like. It was more of a guess work based on the behavior of atoms with the outside world. During the flow of electric current, it was the electrons which flowed from the negative to the positive terminal because of the difference in potential at the two ends of the cell or source. Since they had to be free, they should be loosely attached to the main body of the atom. But everything negative should have equal positive charged particle also. So the positives should also be there, but since they are not free, they should form the main core of the atom, fully and strongly attached.



This gave an idea that an atom looked like a mass of pudding with some plums attached to them, ready to break off whenever needed. So the whole model depicting such atom has been named Plum Pudding Model. Such an atom would look like as in the figure.

Rutherford's α–scattering experiment

The Thompson's model was just a feeble attempt at depicting how an atom looked like. It did not have any strong proof. It had its base on the electric behavior of negative charged particles outside the atom, as in electric current.

The first scientific method in this direction was devised by Rutherford, the method often called as Rutherford's α-scattering experiment. The process consisting of a source of α particles, a thin foil of gold to strike the α particles and a spherical or cylindrical screen.

The source of α particles is a radioactive substance which releases a constant stream of particles throughout the course of experiment. A thin gold foil is placed in front of the source through which the α particles have to be pierced. Such foil is often see-through because of their extreme thinness. α particles have a very short range in air, so the foil should be placed very near the source. When the α – particles shoot the foil, they got through and reach the screen placed around. The screen has fluorescent substances coated from the inside. These substances release visible wavelengths of light whenever they are struck by some energetic radiations.

During the experiment, there were several observations on the fluorescent screen which made Rutherford make several conclusions about atoms.

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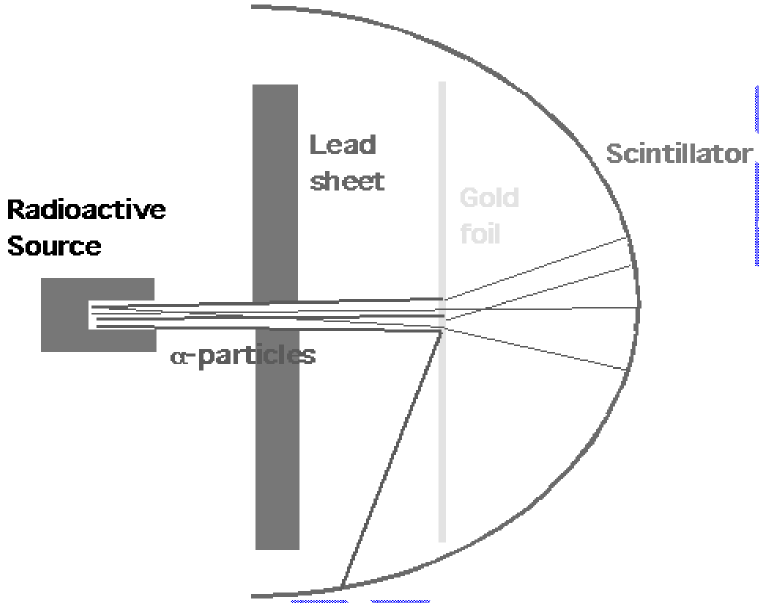
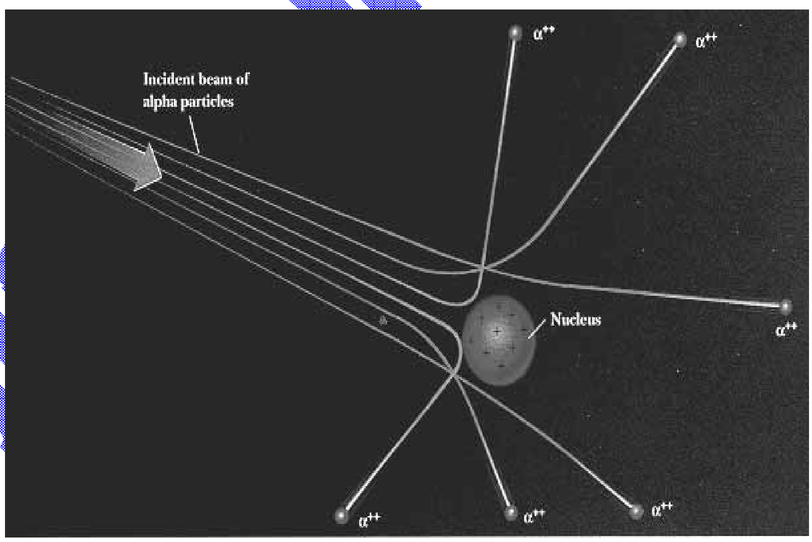
Observations and conclusions

1. Almost all of the flashes were direct, which meant most of the α – particles passed through without suffering even the slightest of deviations. Such event is possible only if the atoms are mostly empty within. This was most contrary to Thompson's idea that they were made of positive masses with negative charged particles at various points.





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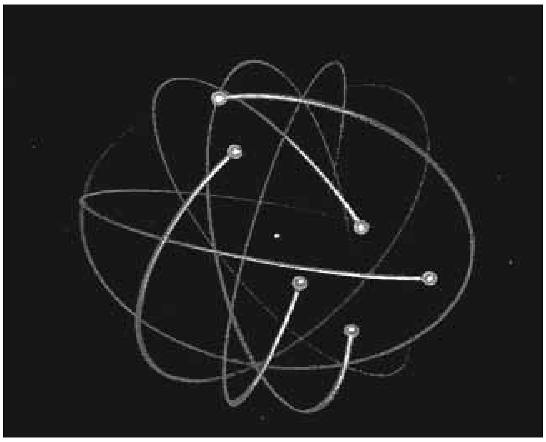

Drawback of Rutherford's Model

1. Rutherford's suggested that the electron of the atom move around the nucleus in circular orbit and all the electrons revolve in the periphery of atoms. For small number of electrons, this might be possible but not when there are a lot of electrons because they may eject out of the atom on account of mutual repulsive force between them.

2. Rutherford's suggested that the path of electrons around the atom is a circle but an electron moving in a circle is always undergoing a change of velocity which according to William Hertz should release energy. As they go on releasing energy, they suffer loss in the total energy content, subsequently becoming unable to resist the attraction thrust on to them by the nucleus. So they should follow a path spiraling inwards and collapse into the nucleus. But this has never occurred in nature, the concept of Rutherford that electrons move in a circle, or even the idea that electrons follow a curve; fell into confusion.

3. When atoms release energy most of them do so in distinct frequencies. However according to Rutherford's model, frequencies can very much according to the speed of the electrons. The release of only particular frequencies by a particular element could not explained by Rutherford's model of atom.

Bohr's model of atom

In order to explain the deficiencies of Rutherford's model, Bohr gave his own theory and model of atom very much similar to the solar system. According to him

1. Though electrons belong to the some atom, they can never have same energy because it is the rule of nature that when some input is given to something the portion they receive is the never the same.

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2. Since their energies are different the space they need should also be different (because more energy means more disturbance and so more space, less energy means less disturbance in the electrons and less space). So electrons with less energy will be revolving round the atom by staying much nearer the nucleus. Similarly the electrons with high energy should be revolving at a greater distance from the nucleus. This means the distance of electrons from the nucleus will be varying very much. The path taken by the electrons in revolving round the nucleus are called shells or orbits (much like in solar system).

3. Since electrons of different energies are in different orbits, electrons with similar energy should be staying in same orbit. However these electrons repel each other. So the number of electrons that can be accommodated in a particular orbit is also different. Smaller orbits can house less number of electrons whereas larger orbits would be able to accommodate more. The number of electrons, that can be accumulated in the orbit depends on the size of the orbit and is given by the relation $\mathbf{N = 2n^2}$, where n = order of orbits.

4. The orbits near the nucleus have electrons of less energy whereas the farther orbits have electrons with more energy. It means if energy is supplied to the inner electron, they cannot be accommodated in that orbit and they need a larger space. So they will jump to the outer orbit. However due to the vacant space created there, and due to the immense attraction of the nucleus, some outer electrons are squeezed into the vacant space. During this process that electrons will release some energy. The frequency, wavelength and the energy itself depends on the original orbit and the final orbit.

   If E_{n2} be the energy of the electrons in the outer orbit & E_{n1} be the energy in inner orbit then, energy released (E) = $E_{n2} - E_{n1} = h\nu = h\frac{c}{\lambda}$.

Determination of radius and energy

To determine the radius of the first orbit of hydrogen atom, let an electron belonging to it be moving with a velocity 'v' around the nucleus .According to Bohr, electrons move in a circular orbit therefore the electrons should be feeling a centripetal force F_c given by

$$F_c = \frac{mv^2}{r} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ (i)$$, m = mass, r = radius of the orbit.

This force is provided by the electrostatic attraction between proton and electron i.e. it is this force F_e which created F_c. Therefore their numerical values should be equal.

i.e. $F_c = F_e$

or, $\frac{mv^2}{r} = \frac{ke^2}{r^2} \qquad [\because F_e = \frac{q_1q_2}{d^2}]$

or, $mv^2 = \frac{ke^2}{r} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (ii)$

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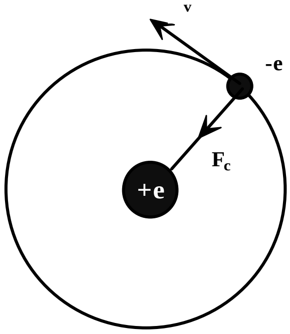

Demonstration of an electron revolving around
the nucleus of hydrogen atom

Bohr found that for an electron of first orbit, the angular momentum (mvr_1) was equal to $\frac{h}{2\pi}$, for 2nd orbit, it, i.e. mvr_2 was equal to $2\frac{h}{2\pi}$ and so on,

$$\text{Overall,} \quad mvr = n\frac{h}{2\pi} \quad \ldots\ldots\ldots\ldots\ (iii)$$

$$v = \frac{nh}{2\pi mr} \quad \ldots\ldots\ldots\ldots\ (iv)$$

Using this value in eq^n. (ii) gives,

$$m\left(\frac{nh}{2\pi mr}\right)^2 = \frac{ke^2}{r}$$

$$\therefore \quad r = \frac{n^2h^2}{4\pi^2e^2km} \quad \ldots\ldots\ (v)$$

This gives the value of the radii of the orbit of different orders.

For the 1st orbit, $n = 1$, so $r_1 = \frac{h^2}{4\pi^2e^2km} = 5.28\times10^{-11}$ m $= 0.528$ Å,

For the 2nd orbit, $n = 2$, so $r_2 = \frac{2^2h^2}{4\pi^2e^2km} = 2.11\times10^{-10}$ m $= 2.11$ Å,

For the 3rd orbit, $n = 3$, so $r_3 = \frac{3^2h^2}{4\pi^2e^2km} = 4.75\times10^{-10}$ m $= 4.75$ Å.

The separate calculation of these values show that the ratio of the radii of the first orbit to the second orbit to the third orbit and so on is given by

$r_1:r_2:r_3:r_4\ldots\ldots\ldots = 1:4:9:16\ldots\ldots$

The atom of hydrogen along with its 1st, 2nd and 3rd orbit would tentatively look like

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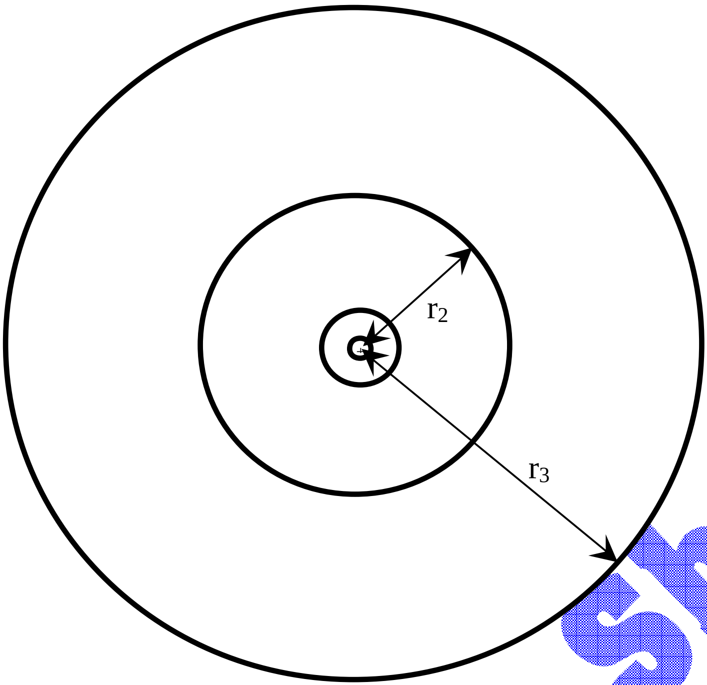

To calculate the overall energy of an electron, the kinetic and potential energies of that electron should be evaluated separately and added.

Let, E_k and E_p be the respective energies.

The relation for kinetic energy is $E_k = \frac{1}{2}mv^2$

Using the value of mv^2 from (ii) gives $E_k = \frac{1}{2}\frac{ke^2}{r} = \frac{ke^2}{2r}$

The potential energy is given by,

$$E_p = \frac{k(e)(-e)}{r} = -\frac{ke^2}{r}$$

$$\therefore E_n = E_k + E_p = \frac{ke^2}{2r} + \left(-\frac{ke^2}{r}\right) = \frac{ke^2}{2r} - \frac{ke^2}{r} = -\frac{ke^2}{2r}$$

$$= -\frac{ke^2}{2\left(\frac{n^2h^2}{4\pi^2e^2km}\right)}$$

$$E_n = -\frac{2\pi^2e^4k^2m}{n^2h^2} \;\ldots\ldots\;\ldots\ldots. \text{(vi)}$$

It means the energy of an electron in a certain orbit depends on the order of the orbit. The –ve sign denotes the attractive nature of this particular energy.

According to Bohr, when electrons jump from higher orbit to lower orbit they emit energy. The value of the emitted energy should be mathematically equal to the

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difference between value of energy at the higher orbit and lower orbit. Therefore let, E_{n1} and E_{n2} the energies of the electron at lower and higher orbits respectively.

Therefore $E_{n1} = -\frac{2\pi^2 e^4 k^2 m}{n_1^2 h^2}$ & $E_{n2} = -\frac{2\pi^2 e^4 k^2 m}{n_2^2 h^2}$

$\therefore$ Energy liberated when descending from orbit n_2 to n_1 is given by

$$E_{n21} = E_{n2} - E_{n1}$$
$$= -\frac{2\pi^2 e^4 k^2 m}{h^2}\left[\frac{1}{n_2^2} - \frac{1}{n_1^2}\right]$$
$$= \frac{2\pi^2 e^4 k^2 m}{h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(vii)}$$

The equation proves that the liberated energy depends only on the order of the orbits from where the electrons took off and where it landed. So if electrons jump from the 2nd orbit to the 1st, the expression for energy becomes

$$E_{n21} = \frac{2\pi^2 e^4 k^2 m}{h^2}\left[1 - \frac{1}{2^2}\right]$$

Similarly if they jump from the 3rd to the 1st, the expression becomes

$$E_{n31} = \frac{2\pi^2 e^4 k^2 m}{h^2}\left[1 - \frac{1}{3^2}\right]$$

And from the 3rd to the 2nd, the expression becomes

$$E_{n32} = \frac{2\pi^2 e^4 k^2 m}{h^2}\left[\frac{1}{2^2} - \frac{1}{3^2}\right]$$

Therefore overall, if the larger orbit is numbered n_l and the smaller orbit is numbered n_s, the whole expression becomes

$$E_{nls} = \frac{2\pi^2 e^4 k^2 m}{h^2}\left[\frac{1}{n_s^2} - \frac{1}{n_l^2}\right] \ldots\ldots\ldots\ldots\ldots \quad \text{(viii)}$$

However if electrons stay in the some orbit, n_l and n_s would be the same. So energy liberated would be zero. (Try yourself)

Determination of a frequency

The relationship relating energy with frequency is

$$E = h\nu$$

Or, $E_{nls} = h\nu_{nls}$

Or, $\frac{2\pi^2 e^4 k^2 m}{h^2}\left[\frac{1}{n_s^2} - \frac{1}{n_l^2}\right] = h\nu_{nls}$

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$$\text{Or, } \nu_{nls} = \frac{2\pi^2 e^4 k^2 m}{h^3}\left[\frac{1}{n_s^2} - \frac{1}{n_l^2}\right] \ldots\ldots\ldots\ldots\ldots \text{ (ix)}$$

Expression for wavelength

The relation between frequencies and wavelength is given by

$$\nu = \frac{c}{\lambda}\text{, where 'c' is the velocity of energy radiations in vacuum.}$$

$$\text{Or, } \nu_{nls} = \frac{c}{\lambda_{nls}}$$

$$\text{Or, } \frac{2\pi^2 e^4 k^2 m}{h^3}\left[\frac{1}{n_s^2} - \frac{1}{n_l^2}\right] = \frac{c}{\lambda_{nls}}$$

$$\text{Or, } \frac{1}{\lambda_{nls}} = \frac{2\pi^2 e^4 k^2 m}{h^3 c}\left[\frac{1}{n_s^2} - \frac{1}{n_l^2}\right] \ldots\ldots\ldots\ldots\ldots\ldots \text{ (x)}$$

Rydberg's constant

In the above expression, the term $\frac{2\pi^2 e^4 k^2 m}{h^3 c}$ is a constant quantity and was first formulated by Paul Rydberg. So it is called as Rydberg's constant in his honor and is denoted by 'R'. Its value is equal to 1.11×10^7/m. So the above expression is also written in simple form as

$$\frac{1}{\lambda_{nls}} = R\left[\frac{1}{n_s^2} - \frac{1}{n_l^2}\right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{ (xi)}$$

Radiation series from atoms

When electrons jump from higher to lower orbit, the amount of energy depends on the initial and final orbit. When these energies were studied by devices, they shared common properties depending on which orbit they are landing on and have been named according to their properties and other discoveries.

1. Lyman Series:

These are the radiation emitted when electron from any outer orbit drop into the first orbit. They are highly energetic and so are characterized by their extreme penetrating power. For e.g. uv rays and x-rays. Their wavelength can be calculated from eqn (x) by using $n_s = 1$ i.e.

$$\frac{1}{\lambda_{Lyman}} = \frac{2\pi^2 e^4 k^2 m}{h^3 c}\left[1 - \frac{1}{n_l^2}\right] = R\left[1 - \frac{1}{n_l^2}\right]$$

2. Balmer Series:

These are the radiations emitted when electrons from any outer orbit drop into the second orbit. They are characterized by human ability to perceive them through visual organs. For e.g. blue, violet, red radiations (VIBGYOR), their wavelength can be calculated from eqn (x) by using $n_S = 2$ i.e.

$$\frac{1}{\lambda_{Balmer}} = \frac{2\pi^2 e^4 k^2 m}{h^3 c}\left[\frac{1}{2^2} - \frac{1}{n_l^2}\right] = R\left[\frac{1}{2^2} - \frac{1}{n_l^2}\right]$$

3. Paschen Series:

These are the radiations emitted when electrons from any outer orbit drop into the third orbit. Their group falls under the infra red category and their wavelength can be calculated from eqn (x) by using $n_S = 3$ i.e.

$$\frac{1}{\lambda_{Paschen}} = \frac{2\pi^2 e^4 k^2 m}{h^3 c}\left[\frac{1}{3^2} - \frac{1}{n_l^2}\right] = R\left[\frac{1}{3^2} - \frac{1}{n_l^2}\right]$$

4. Brackett Series:

These are the radiations emitted when electrons from any outer orbit drop into the fourth orbit. Their group falls under the infra red category and their wavelength can be calculated from eqn (x) by using $n_S = 4$ i.e.

$$\frac{1}{\lambda_{Brackett}} = \frac{2\pi^2 e^4 k^2 m}{h^3 c}\left[\frac{1}{4^2} - \frac{1}{n_l^2}\right] = R\left[\frac{1}{4^2} - \frac{1}{n_l^2}\right]$$

5. Pfund Series:

These are the radiations emitted when electrons from any outer orbit drop into the fifth orbit. Their group falls under the infra red category and their wavelength can be calculated from eqn (x) by using $n_S = 5$ i.e.

$$\frac{1}{\lambda_{Pfund}} = \frac{2\pi^2 e^4 k^2 m}{h^3 c}\left[\frac{1}{5^2} - \frac{1}{n_l^2}\right] = R\left[\frac{1}{5^2} - \frac{1}{n_l^2}\right]$$

In addition, there are many types of radiations according to electron comes from other orbits to 6th, 7th, etc. orbits. Being numerous, they have not been named.

DEBROGLIE WAVE:

The electrons of atoms are in constant wave like and zigzag motion due to its interaction with different outside factors. These patterns were first of all discovered by de-Broglie and so electrons are said to move in the form of "de-Broglie waves". If they are waves they have to show the characteristics of waves for e.g. particular wavelengths.

These waves are not random and are also not located in random directions. They have a certain location and span (range). The de-Broglie wavelength can be found by the relation for the energy of the electron, once as a particle and once as a wave, which are respectively given by

$$E = mc^2 \;\&\; E = h\nu = \frac{hc}{\lambda}$$

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Or, $mc^2 = \frac{hc}{\lambda}$

Or, $mc = \frac{h}{\lambda}$

Or, $\lambda = \frac{h}{mc}$

The denominator in the right side term is the product of mass and velocity. So it is equal to the momentum of the electron, denoted by 'p'. So,

Or, $\lambda = \frac{h}{p}$

The expression gives an idea that if the momentum of a body is high, the wavelength of the body would be very small, whereas of the momentum is less, it would be higher. This determines whether a certain body can be seen in wave-like form or not. For electrons, momentum is very less, so wavelength is appreciably larger and conspicuous. For normal bodies seen around humans, momentum is high, so wavelength is so small that they can not be observed. This phenomenon is made more elaborate by Heisenberg's uncertainty principle.