Atomic Models

The purpose of this chapter is to build a simplest atomic model that will help us to understand the structure of atom. This is attained by referring to some basic experimental facts that have been gathered since 1900's (e.g. Rutherford scattering experiment, atomic spectral lines etc.) For this we need to explore the wave nature of electron.

Basic properties of atoms

1) Atoms are of microscopic size, ~ 10^{-10} m. Visible light is not enough to resolve (see) the detail structure of an atom as its size is only of the order of 100 nm.

2) Atoms are stable. The force (EM force) that hold an atom together is attractive.

3) Atoms contain negatively charges (e.g. as seen in Compton and photoelectric effect), electrons, but are electrically neutral. An atom with Z electrons must also contain a net positive charge of $+Ze$.

4) Atoms emit and absorb EM radiation (because of this, EM wave is usually used to probe the structure of an atom).

Emission spectral lines

A single atom or molecule which rarely interacts with other molecules (such as a gas in a tube with very diluted concentration) emit radiation characteristic of the particular atom/molecule species.

This happen when the atoms/molecules are ``excited'' e.g. by heating or passing electric current through it

The emitted radiation displays characteristic discrete sets of spectrum which contains certain specific wavelengths only. The spectral lines are analysed with ***spectrometer***, which give important physical information of the atom/molecules by analysing the wavelengths composition and pattern of these lines.

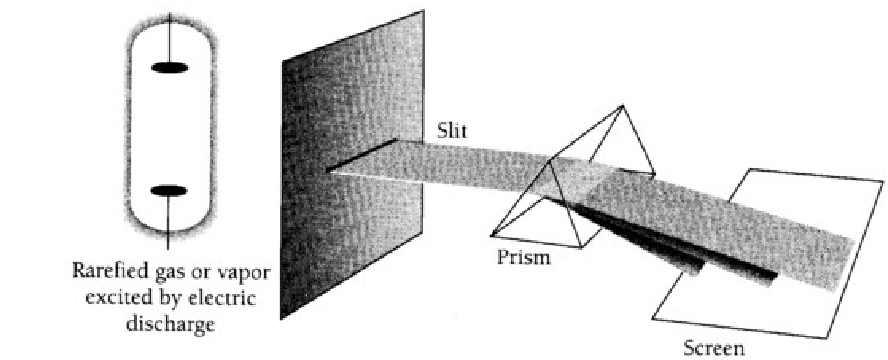


Figure 4.7 An idealized spectrometer.

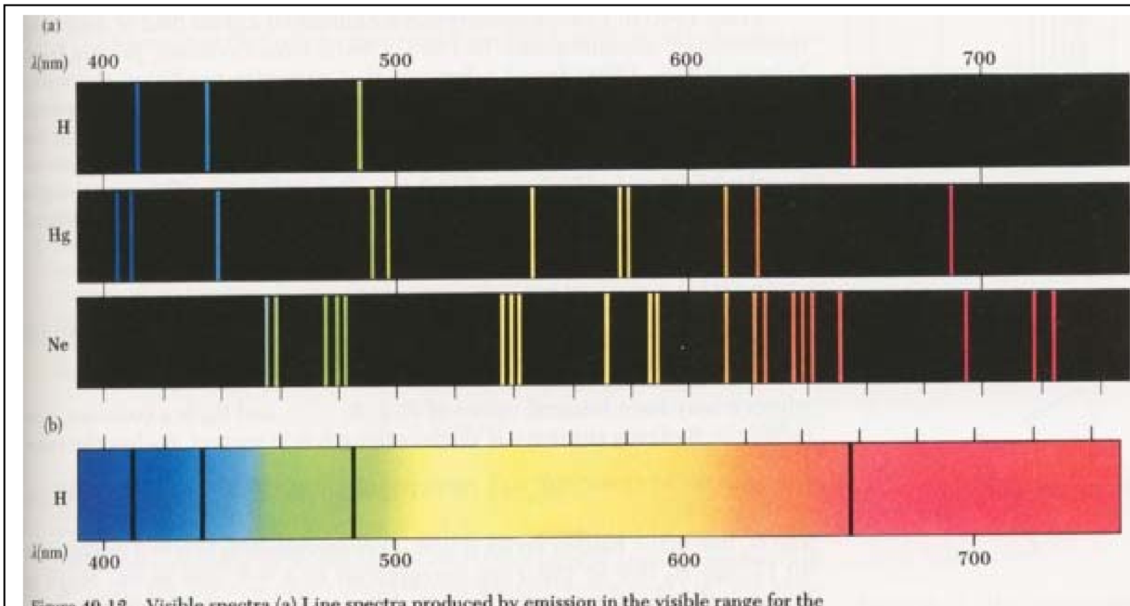
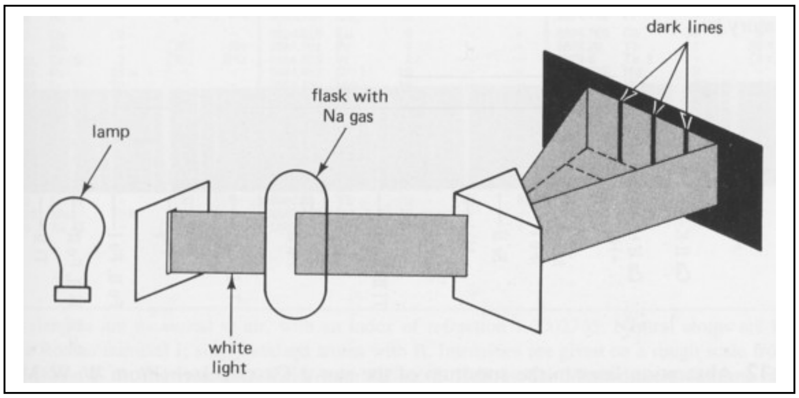


Figure 40.12 Visible spectra (a) Line spectra produced by emission in the visible range for the elements hydrogen, helium, and neon. (b) The absorption spectrum for hydrogen. The dark absorption lines occur at the same wavelengths as the emission lines for hydrogen shown in (a). (Whitten, K.W., K.D. Gailey, and R.E. Davis, *General Chemistry*, 3rd ed., Saunders College Publishing, 1987).

We also have absorption spectral line, in which white light is passed through a gas. The absorption line spectrum consists of a bright background crossed by dark lines that correspond to the

absorbed wavelengths by the gas atom/molecules.



Experimental arrangement for the observation of the absorptions lines of a gas

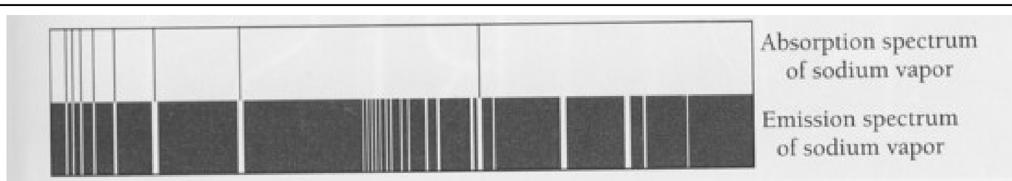
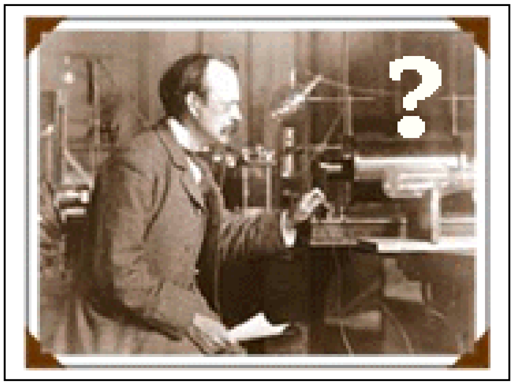


Figure 4.9 The dark lines in the absorption spectrum of an element correspond to bright lines in its emission spectrum.

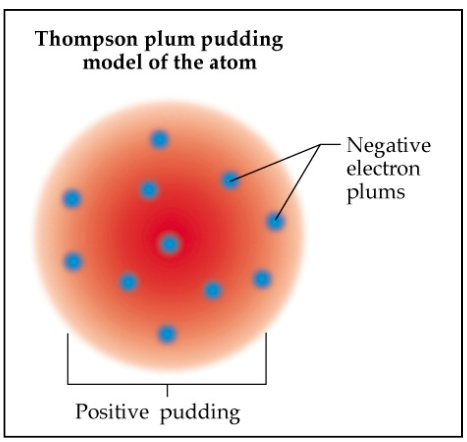
The absorption line spectra of a given gas correspond to many but NOT ALL of the wavelengths seen in the emission spectral. (This feature has to be explained in terms 'selection rule' that is due to conservation of angular momentum in quantum mechanical description of atoms).

The Thompson model – Plum-pudding model



Sir J. J. Thompson (1856-1940) is the Cavandish professor in Cambridge who discovered electron in cathode rays. He was awarded Nobel prize in 1906 for his research on the conduction of electricity by bases at low pressure.

In his model of atom: an atom consisting of *Z* electrons embedded in a cloud of positive charges that exactly neutralise that of the electrons'. The positive cloud is heavy and comprising most of the atom's mass.
Inside a stable atom, the electrons sit at their respective equilibrium position where the attraction of the positive cloud on the electrons balances the electron's mutual repulsion.



The electron at the EQ position shall vibrate like an simple harmonic oscillator with a frequency

$$\nu = \left(\frac{1}{2\pi}\right)\sqrt{\frac{k}{m}},$$

(TF)

where $k = \frac{Ze^2}{4\pi\varepsilon_o R^3}$.

Failure of the plum-pudding model

From classical EM theory, oscillating charge radiates EM

1) radiation with frequency identical to the oscillation frequency. Hence light emitted from the atom in the plum-pudding model is predicted to have exactly one unique frequency as given by Eq. (TF). This prediction has been falsified because observationally, light spectra from all atoms (such as the simplest atom, hydrogen,) have sets of discrete spectral lines correspond to many different frequencies (already discussed earlier).

2) The plum-pudding model predicts that when an alpha particle (with kinetic energy of the order of a few MeV, which is considered quite energetic at atomic scale) is scattered by the atom, deviates from its impacting trajectory by a very tiny angle only (^{4}He nucleus, which has mass >> m_e so that the interaction btw the alpha particle and the electrons in neglected, according to Newton's third law)

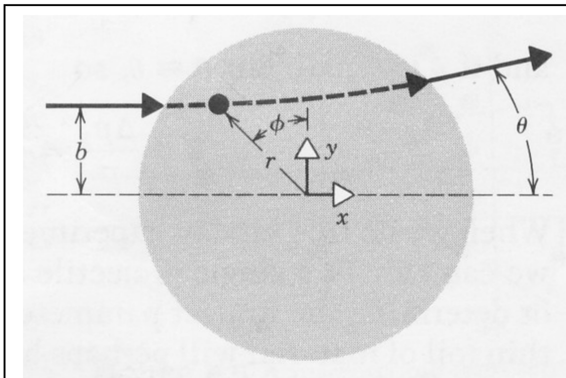


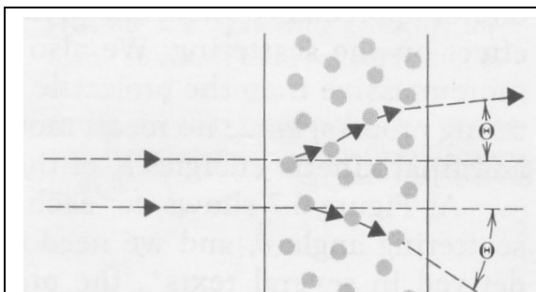
FIGURE 6.2 A positively charged alpha particle is deflected by an angle θ as it passes through a Thomson-model atom. The coordinates r and ϕ locate the alpha particle while it is inside the atom.

$$\theta_{ave} = \frac{\pi}{4}\left(\frac{kR^2}{K}\right) \sim 10^{-4}$$ rad; where

$$k = \frac{Ze^2}{4\pi\varepsilon_o R^3},$$

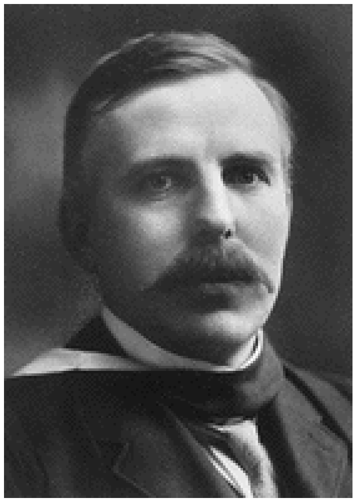
for Z = 79, R = 0.1 nm, K = 5 MeV

Experiment measures the statistically averaged angle $\Theta = \sqrt{N}\theta_{ave}$ in which a collection of projectile is scattered off by N atoms inside the bulk target (a thin sheet of gold foil) before they are detected by detector.



Theoretically, one expects $\Theta = \sqrt{N}\theta_{ave} \sim 1^{\circ}$, but Rutherford saw some electrons being bounced back at $\Theta =\sim 180^{\circ}$. He said this is like firing “a 15-inch shell at a piece of a tissue paper and it came back and hit you”

Rutherford nuclear atom



British physicist Ernest Rutherford, winner of the 1908 Nobel Prize in chemistry, pioneered the field of nuclear physics with his research and development of the nuclear theory of atomic structure. Rutherford stated that an atom consists largely of empty space, with an electrically positive nucleus in the center and electrically negative electrons orbiting the nucleus. By bombarding nitrogen gas with *alpha particles* (nuclear particles emitted through radioactivity), Rutherford engineered the transformation of an atom of nitrogen into both an atom of oxygen and an atom of hydrogen. This experiment was an early stimulus to the development of nuclear energy, a form of energy in which nuclear transformation and disintegration release extraordinary power.

The large deflection of alpha particle as seen in the scattering experiment with a thin gold foil must be produced by a close encounter between the alpha particle and a very small but massive kernel inside the atom (c.f. a diffused distribution of the positive charge as assumed in plum-pudding model cannot do the job)

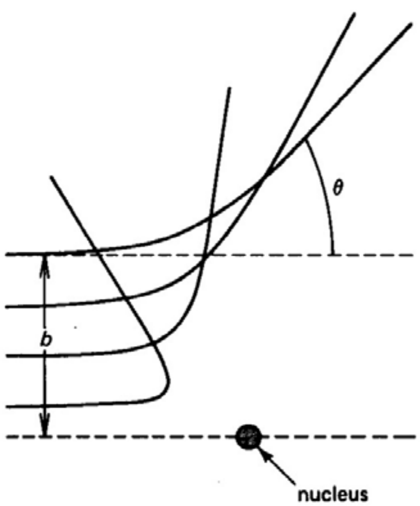


Fig. 4.16 Hyperbolic trajectories of several alpha particles deflected by the nucleus. The distance *b* is the impact parameter of one of these alpha particles.

In the scattering, the alpha particle sees only the massive core but not the electrons due to the high energy of the projectile, as well as the tiny mass of the electrons

This is the so-called **Rutherford model** (or the planetary model) in which an atom consists of a very small nucleus of charge $+Ze$ containing almost all of the mass of the atom; this nucleus is surrounded by a swarm of Z electrons.

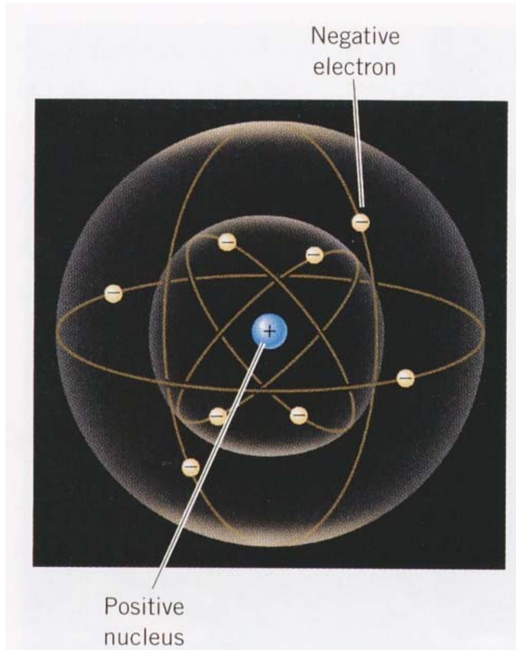


Figure 30.1 In the nuclear atom a small positively charged nucleus is surrounded at relatively large distances by a number of electrons.

Rutherford calculated the fraction of the alpha particles in the incident beam should be deflected through what angle, and he found (using standard classical mechanics):

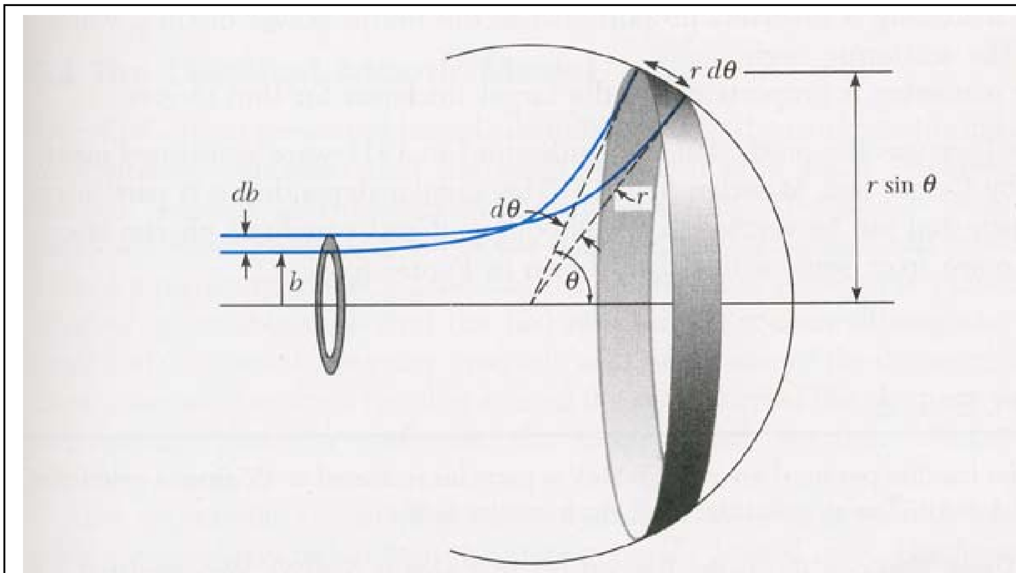


FIGURE 5.12 Particles over the range of impact parameters from b to $b + db$ scatter into the angular range θ to $\theta + d\theta$ (with db positive, $d\theta$ will be negative)

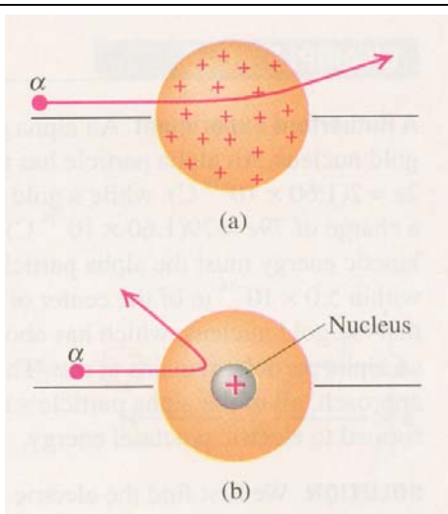
$$\theta = 2\cot^{-1}\left(\frac{4\pi\varepsilon_0 K b}{Ze^2}\right)$$

(RSA)

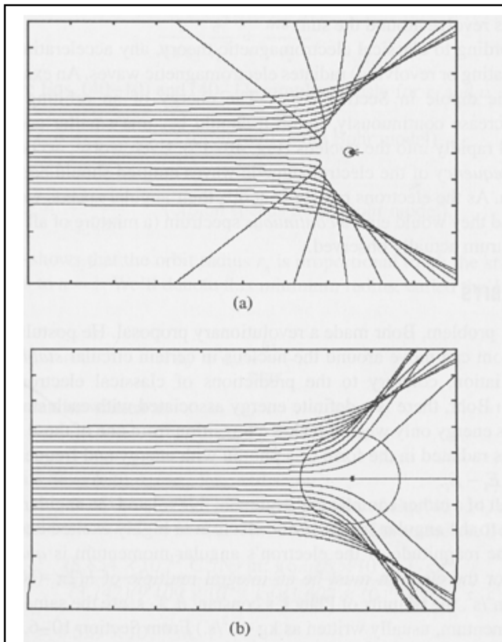
where *b*, the **IMPACT PARAMETER**, is the perpendicular distance between the nucleus and the original (undeflected) line of motion.

Note the two limits: for *b* very far away from the nucleus, no deflection should occur, ie. as $b \to \infty$, we have $\theta \to 0$. On the other hand, as the projectile nearly hit the nucleus in an head-on manner, we expect the projectile to bounce at large angle of totally reversed in direction, ie. $b \to \infty$, we have $\theta \to 180^\circ$.

In order to suffer a large deflection, the alpha particle must strike an atom with a very small impact parameter, 10^{-13} m or less – the size of the nucleus. At an impact parameter of the order 10^{-13} m deviation from Rutherford scattering as predicted by Eq.(RSA)begins to show up due to the onset of extra interaction other than the EM interaction – the nuclear forces.



40–13 (a) Thomson's model of the atom: An alpha particle is scattered through only a small angle. (b) Rutherford's model of the atom: An alpha particle can be scattered through a large angle by the dense, positively charged nucleus (not drawn to scale).



40–14 Computer simulation of scattering of 5.0-MeV alpha particles from a gold nucleus. (a) A gold nucleus with radius 7.0×10^{-15} m (its actual size); (b) a nucleus with ten times the radius of that in (a) shows *no* large-angle scattering.

Example

(a) What impact parameter will give a deflection of 1^0 for an alpha particle of 7.7 MeV incident on a gold nucleus?
(b) What impact parameter will give a deflection of 30^0?
(c) Compare the probabilities for the deflection by angles in excess of 1^0 with that of 30^0

ANS

(a) $b = \frac{Ze^2}{4\pi\varepsilon_0 K}\cot^{-1}\left(\frac{\theta}{2}\right)$ = 1.7 $\times 10^{-12}$ m (for θ = 1°)

(b) $b = \frac{Ze^2}{4\pi\varepsilon_0 K}\cot^{-1}\left(\frac{\theta}{2}\right)$ = 5.5 $\times 10^{-12}$ m (for θ = 30°)

(c) For the particles to be deflected by more than θ the projectile has to lie within the corresponding ``target area'' of πb^2. The target area corresponds to a given deflection is called the **cross section** for that deflection, σ.

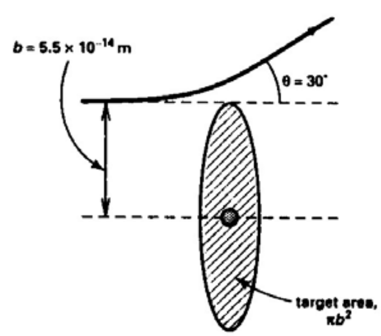


Fig. 4.17 Imaginary target area within which the alpha particle must be aimed to suffer a deflection in excess of the specified value.

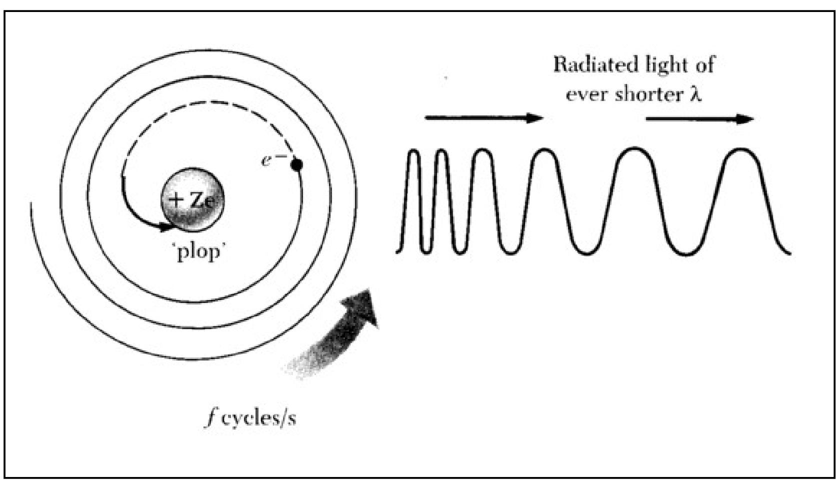
Hence the ratio of the probabilities for the deflection by angles in excess of 1^0 to that of 30^0 is

$$\frac{\text{probability for}\,\theta > 1^{\circ}}{\text{probability for}\,\theta > 30^{\circ}} = \frac{\pi\left(b = 1.7\times10^{-12}\right)^2}{\pi\left(b = 5.5\times10^{-14}\right)^2} = 940$$

Questions: The alpha particle with energy ~ MeV is treated as a point particle rather than as wave: how to verify this?

Infrared catastrophe

According to classical EM, the Rutherford model for atom (a classical model) has a fatal flaw: it predicts the collapse of the atom within 10^{-10} s. A accelerated electron will radiate EM radiation, hence causing the orbiting electron to loss energy and consequently spiral inward and impact on the nucleus. The Rutherford model also cannot explain the pattern of discrete spectral lines as the radiation predicted by Rutherford model is a continuous burst.



Bohr's postulate

Niels Bohr (1885 to 1962) is best known for the investigations of atomic structure and also for work on radiation, which won him the 1922 Nobel Prize for physics

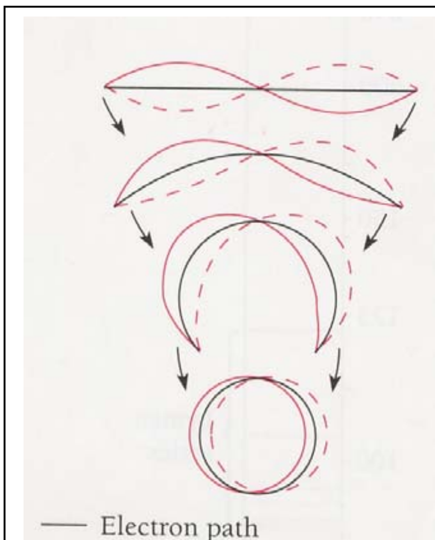
http://www-gap.dcs.st-and.ac.uk/~history/Mathematicians/Bohr_Niels.html

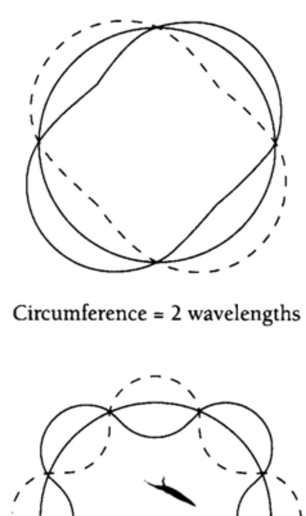
To resolve the infrared catastrophe, Bohr proposed his famous model (in 1913), which is a hybrid of the classical theory of atom (Rutherford model) and the wave nature of particle (de Broglie's matter wave). We call his theory the "old quantum theory". Bohr won the Nobel prize in 1923 for his Bohr model, in which he postulated that:

1) Mechanical stability: an electron in an atom moves in a circular orbit about the nucleus under Coulomb attraction obeying the law of classical mechanics

2) Condition for orbit stability: Instead of the infinite orbit which could be possible in classical mechanics (c.f the orbits of satellites), it is only possible for an electron to move in an orbit that contains an integral number of de Broglie wavelengths,

$$n\lambda = 2\pi r_n, \quad n = 1,2,3...$$





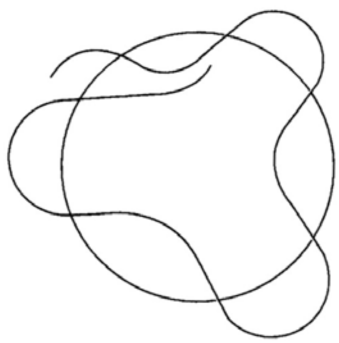


Figure 4.14 A fractional number of wavelengths cannot persist because destructive interference will occur.

As a result of the orbit quantisation, the of angular momentum (≡linear momentum × perpendicular radius to the centre of motion, $L = p \times r$) of the orbiting electron is also quantised,

$$L = n\hbar$$

3) Despite the fact that it is constantly accelerating, an electron moving in such an allowed orbit does not radiate EM energy (hence total energy remains constant). as far as the stability of atoms is concerned, classical physics is invalid here.

4) EM radiation is emitted if an electron initially moving in an orbit of total energy E_i, discontinuously changes it motion so that it moves in an orbit of total energy E_f. The frequency of the emitted radiation,

$$\nu = (E_i - E_i)/h$$

(Equivalent of Einstein's postulate of energy of a photon)

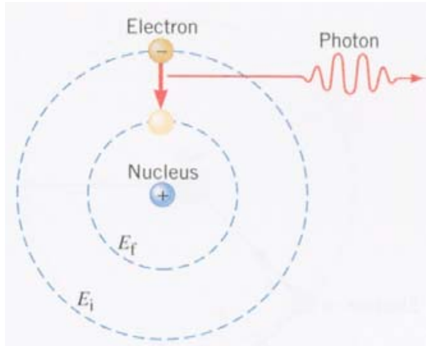


Figure 30.5 In the Bohr model, a photon is emitted when the electron drops from a larger, higher-energy orbit (energy = E_i) to a smaller, lower-energy orbit (energy = E_f).

Bohr's model of hydrogen

Consider a nucleus with charge $+Ze$ and mass $M >> m_e$. With this assumption the centre of the circular motion of the electron coincides with the centre of the nucleus. This picture is only approximate, and the result of the following calculation will be modified if this assumption is relaxed and the mass M is not taken to be infinite compared to m.

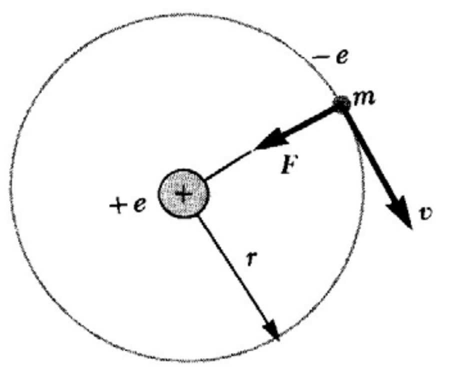


Figure 3.20 Diagram representing Bohr's model of the hydrogen atom.

Mechanical stability of the atom requires that

$$\frac{1}{4\pi\varepsilon_0}\frac{(Ze)e}{r^2} = \frac{m_e v^2}{r}$$

(MS)

Coulomb's attraction = centripetal force

The quantised angular momentum,

$$L = m_e v r = n\hbar$$

(QL)

Combining Eqs.(MS) and (QL), the allowed radius and velocity at a given orbit is also quantised:

$$r_n = 4\pi\varepsilon_0 \frac{n^2\hbar^2}{m_e Z e^2},$$

$$v_n = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{n\hbar}$$

(QR)

Comments:

(i) For smallest orbit of Hydrogen, $Z = 1$, $n=1$

$$r_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} = 0.5\,\overset{0}{A}$$ (the Bohr's radius)

= the typical size of an atom.

In general, the radius of the orbit n is expressed in terms of the Bohr's radius $r_n = n^2 \frac{r_0}{Z}$.

(ii) $v_0 = 2.2\times 10^6$ m/s << c, non-reletivistic

Energy of Bohr's atom:

Potential energy of the electron at a distance r from the nucleus is (you have learnt this from standard EM theory)

$$V = -\int_r^\infty \frac{Ze^2}{4\pi\varepsilon_0 r^2} dr = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

(-ve meaning that the EM force is attractive)

Kinetic energy:

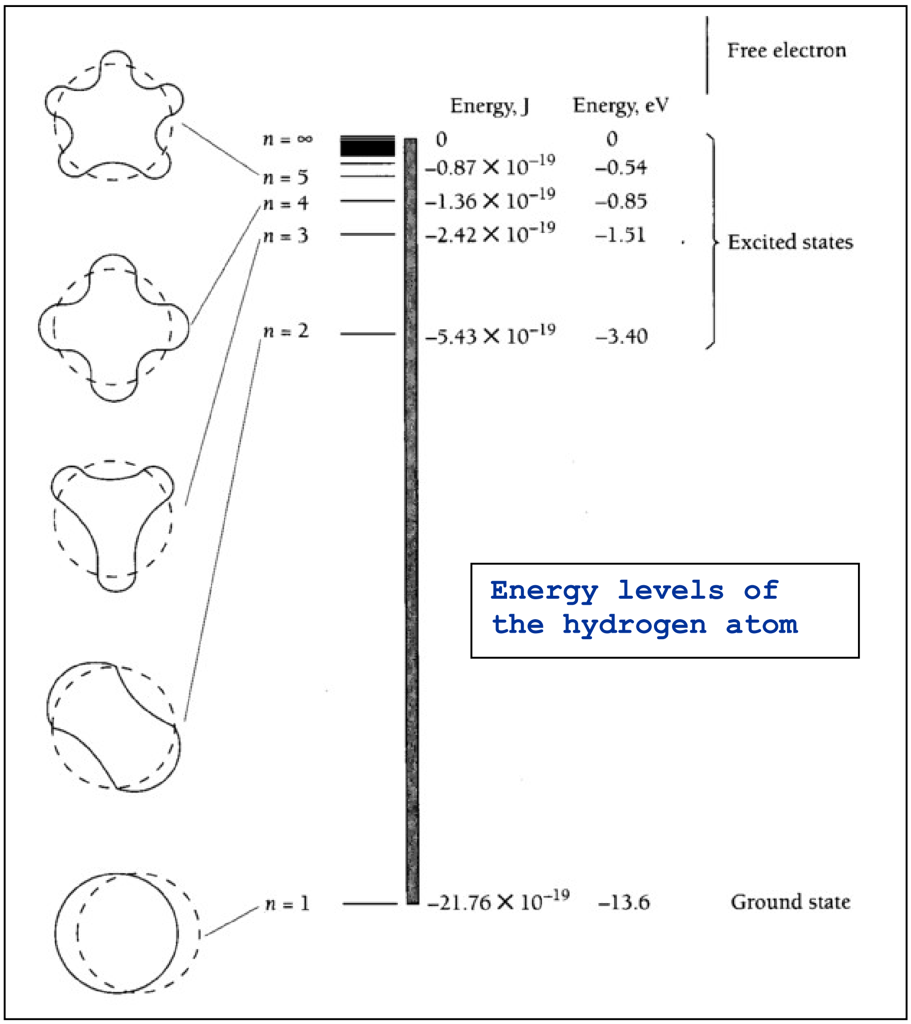
$$K = \frac{m_e v^2}{2} = \frac{Ze^2}{8\pi\varepsilon_0 r^2}$$

Total mechanical energy,

$$E = K + V = -\frac{Ze^2}{4\pi\varepsilon_0 r^2} = -\frac{m_e Z^2 e^4}{(4\pi\varepsilon_0)^2 2\hbar^2}\frac{1}{n^2} \equiv E_n$$

The last step followed after inserting r_n from Eq.(QR)
(-ve total energy means that the electron-nucleus is a bounded system)

The energy level of the electrons in the atomic orbit is quantised. The quantum number, n, that characterises the electronic states is called principle quantum number



For the hydrogen atom (Z = 1)

The ground state energy is given by

$$E_0 \equiv E_n(n=1) = -\frac{m_e e^4}{(4\pi\varepsilon_0)^2 2\hbar^2} = -13.6 \text{ eV}$$

Hence, the energy level can be expressed in terms of

$$E_n = \frac{E_0}{n^2} = -\frac{13.6}{n^2}\text{eV}$$

An electron occupying an orbit with very large n is almost free because its energy $E_n(n \to \infty) = 0$ eV. Electron at high n is not tightly bounded to the nucleus by the EM force. Energy levels at high n approaches to that of a continuum, as the energy gap between adjacent energy levels become infinitesimal in the large n limit.

The energy input required to remove the electron from its ground state to infinity (ie. to totally remove the electron from the bound of the nucleus) is simply $E_\infty - E_0 = 13.6$ eV - the ionisation energy of hydrogen

> As a practical rule, it is strongly advisable to remember the two very important values (i) the Bohr radius, r_0 = 0.53 $\overset{0}{A}$ and (ii) the ground state energy of the hydrogen atom, E_0 = -13.6 eV

When atoms are excited to an energy above its ground state, they shall radiate out energy (in forms of photon) within at the time scale of ~10^{-8} s. Atoms can be excited via (i) collisions with another particle (e.g. in neon lamp) (ii) absorption of radiation with wavelength that matches the allowed energy gaps of the atom. The absorbed radiation excite the electron to higher energy level, and then re-radiate out in all direction as it de-excites to lower energy level. This happens in absorption line spectrum.

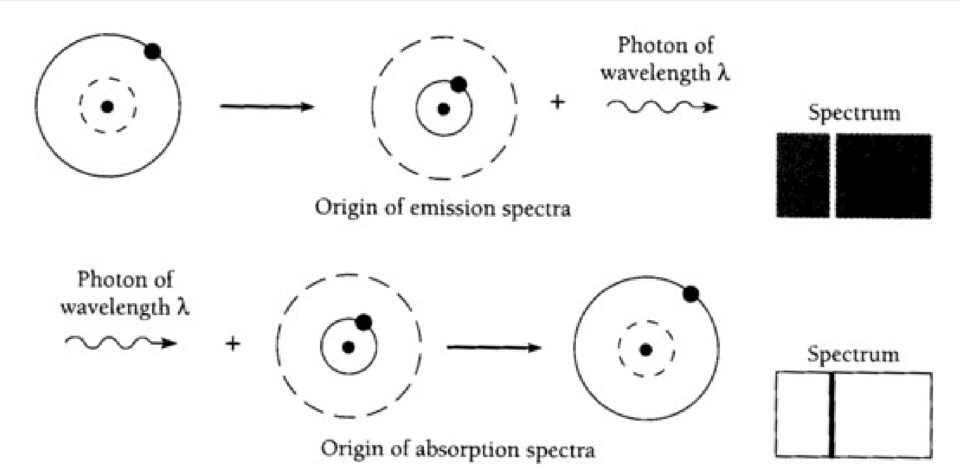


Figure 4.19 How emission and absorption spectral lines originate.

AURORA are caused by streams of fast photons and electrons from the sun that excite atoms in the upper atmosphere. The green hues of an auroral display come from oxygen.

When an electron makes a transition from a higher energy state, n_i to a lower state energy n_f, EM radiation is emitted is association with this transition. The energy of the photon radiated is simple the difference between the two energy states:

$$\frac{1}{\lambda} = \frac{\nu}{c} = \frac{E_i - E_f}{ch} = -\frac{E_0}{ch}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \equiv Z^2 R_\infty \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

(BSL)

where $R_\infty \equiv \frac{m_e e^4}{4c\pi\hbar^3(4\pi\varepsilon_0)^2} = 109{,}737\text{cm}^{-1}$ is the Rydberg constant with infinitely heavy nucleus (this is our assumption in the beginning, still remember?).

Question: What would happen if this assumption is lifted and a finite mass of the nuclear is taken into account?

Balmer series correspond to the set of spectral emitted when higher electron at n_i makes transition to the lower state at n_f = 2. The wavelength of this series fall in the visible

Lyman series correspond to the set of spectral emitted when higher electron at n_i makes transition to the lower state at n_f = 1. The wavelength of this series fall in the ultraviolet

Question: Brackett and Pfund series (correspond to n_f = 4,5). What is the range of the wavelengths of these series? (IR? Visible? Or ultraviolet?)

The spectral series of Hydrogen as seen in spectroscopy experiments

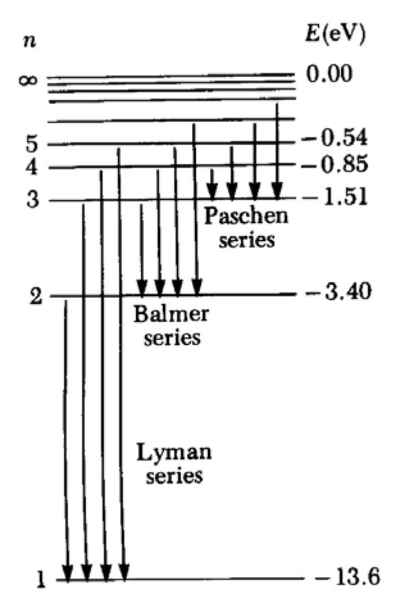
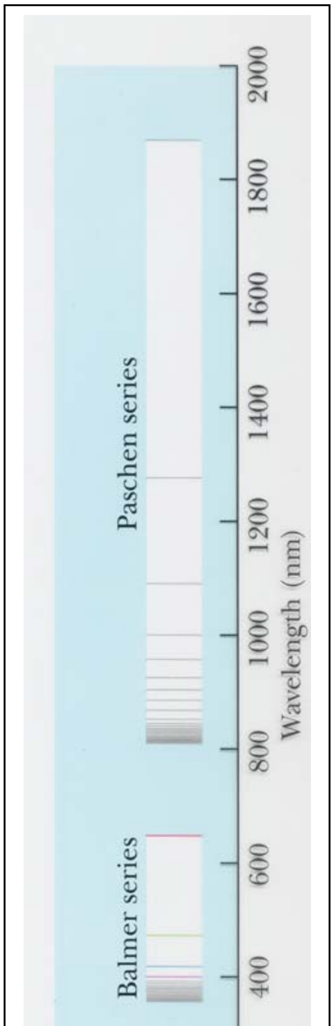


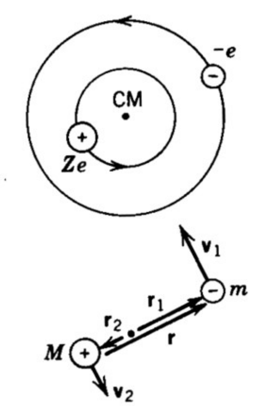
Figure 3.22 An energy level diagram for hydrogen. In such diagrams the discrete allowed energies are plotted on the vertical axis. Nothing is plotted on the horizontal axis, but the horizontal extent of the diagram is made large enough to show allowed transitions. Note that the quantum numbers are given on the left.



Relaxing the infinitely heavy mass of the nucleus

In the more general case where the nucleus mass is not infinitely heavy, we can no more picture the atom as a single electron circulating the centre of the nucleus while the nucleus is at rest. In the general picture, *both* the electron and nucleus are circulating around their common centre of mass.

Figure 3-14
Circular motion of two charged particles with center of mass at rest.



If the effect of finiteness of the nucleus mass is taken into appropriate account, all the results as discussed above remain the same except with the replacement of the electron mass m_e with the reduced mass $\mu = \frac{m_e M}{m_e + M}$. Note that in the limit $M \to \infty$, $\mu \to m_e$.

The Rydberg constant will then have to be corrected to

$$R_\infty \to R \equiv \frac{\mu e^4}{4c\pi\hbar^3(4\pi\varepsilon_0)^2} = 109{,}678\,\mathrm{cm}^{-1},$$

which is a more accurate theoretical value when compared to experimental data.

The theoretical value of Rydberg's constant R is almost perfectly matched with the observed spectral series of hydrogen with Eq. (BSL) etc. This serves as an excellent justification to the approximate correctness of Bohr's model to describe simple atomic system (with a single electron).

Example

Suppose that, as a result of a collision, the electron in a hydrogen atom is raised to the second excited state (n = 3). What is the energy and wavelength of the photon emitted if the electron makes a direct transition to the ground state? What are the energies and the wavelengths of the two photons emitted if, instead, the electron makes a transition to the first excited state (n=2) and from there a subsequent transition to the ground state?

ANS

The energy of the proton emitted in the transition from the n = 3 to the n = 1 state is

$\Delta E = E_3 - E_1 = 13.6\left(\frac{1}{1^2} - \frac{1}{3^2}\right)$ eV = 12.1 eV, and the wavelength of this photon is $\lambda = \frac{c}{\nu} = \frac{ch}{\Delta E} = \frac{1242 eV \cdot nm}{12.1 eV} = 102$ nm.

Likewise the energies of the two photons emitted in the transitions from n = 3 → n = 2 and n = 2 → n = 1 are, respectively,

$\Delta E = E_3 - E_2 = 13.6\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = 1.89$ eV, with wavelength

$$\lambda = \frac{ch}{\Delta E} = \frac{1242 eV \cdot nm}{1.89 eV} = 657 \text{ nm}$$

$\Delta E = E_2 - E_1 = 13.6\left(\frac{1}{1^2} - \frac{1}{2^2}\right) = 10.2$ eV, with wavelength

$$\lambda = \frac{ch}{\Delta E} = \frac{1242 eV \cdot nm}{10.2 eV} = 121 \text{ nm}$$

Example

The series limit of the Paschen (n_0 = 3) is 820.1 nm. (The series limit of a spectral series is the wavelength corresponds to $n \to \infty$). What are two longest wavelengths of the Paschen series?

ANS

By referring to the definition of the series limit, $\frac{1}{\lambda_\infty} = \frac{R_\infty}{n_f^2}$.

Hence, $\frac{1}{\lambda} = Z^2 R_\infty \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$ can be written in terms of the series limit as

$$\frac{1}{\lambda} = \frac{1}{\lambda_\infty} \left(1 - \frac{n_f^2}{n_i^2} \right).$$

For Paschen series, $\frac{1}{\lambda} = \frac{1}{820.1\,\text{nm}} \left(1 - \frac{3^2}{n_i^2} \right)$, n = 4,5,6…

The three longest wavelengths are:

n = 4, $\lambda = 820.1\,\text{nm} \left(\frac{n_i^2}{n_i^2 - 9} \right) = 820.1\,\text{nm} \left(\frac{4^2}{4^2 - 9} \right) = 1875\,\text{nm}$;

n = 5, $\lambda = 820.1\,\text{nm} \left(\frac{n_i^2}{n_i^2 - 9} \right) = 820.1\,\text{nm} \left(\frac{5^2}{5^2 - 9} \right) = 1281\,\text{nm}$

Frank-Hertz experiment

Experiment that show the excitation of atoms to discrete energy levels and is consistent with the results suggested by line spectra

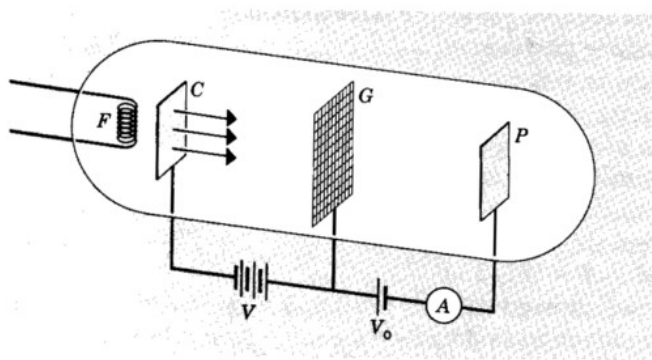


FIGURE 6.24 Franck-Hertz apparatus. Electrons leave the cathode *C*, are accelerated by the voltage *V* toward the grid *G*, and reach the plate *P* where they are recorded on the ammeter *A*.

Mercury vapour is bombarded with electron accelerated under the potential *V* (between the grid and the filament). A small potential V_0 between the grid and collecting plate prevents electrons having energies less than a certain minimum from contributing to the current measured by ammeter. As *V* increases, the current measured also increases.

After a first critical potential is reached (4.9 V in the case for mercury vapour), the current dropped abruptly.

Explanation: A electron having K.E. of 4.9 eV collides in an inelastic manner with an atom, as a result the atom get excited to an energy level above its ground state. At this critical point, the energy of the accelerating electron equals to that of the energy gap between the ground state and the excited state. This is an example of a `resonance' phenomena, in which the frequency of the external field that interacts with the system matches with that of the internal frequency of the system (in this case, the energy gap which takes only quantised values). After inelastically excite the atom, the original (the bombarding) electron move off with too little energy to overcome the small retarding potential and reach the plate. As the accelerating potential is raised further, the plate current again increases, since the electrons now have enough energy to reach the plate. Eventually another sharp drop (at 9.8 V) in the current occurs because, again, the electron has collected just the same energy to excite the same energy level in the other atoms. The higher critical potentials result from two or more inelastic collisions and are multiple of the lowest (4.9 V). The excited mercury atom will then de-excite by radiating out a photon of exactly the energy (4.9 eV).

Frank and Hertz have checked that during the electron bombardment, the mercury gas does give off a spectral line with 253.6 nm in wavelength - a photon has an energy of just 4.9 eV.

The critical potential verifies the existence of atomic levels.

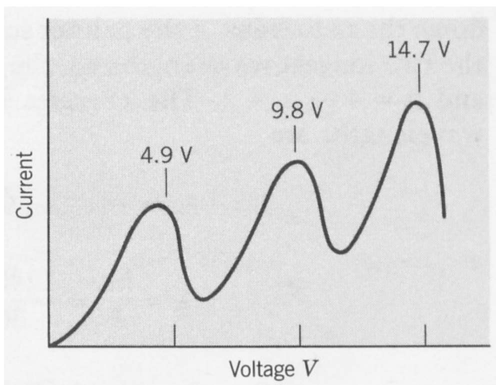


FIGURE 6.25 Result of Franck-Hertz experiment using mercury vapor. The current drops at $V = 4.9$ V, $V = 9.8$ V ($= 2 \times 4.9$ volts), $V = 14.7$ V ($= 3 \times 4.9$ V).

Bohr's correspondence principle

The predictions of the quantum theory for the behaviour of any physical system must correspond to the prediction of classical physics in the limit in which the quantum number specifying the state of the system becomes very large:

$$\lim_{n \to \infty} \text{quantum theory} = \text{classical theory}$$

Or, in other words, the laws of quantum physics are valid in the atomic domain; while the laws of classical physics is valid in the classical domain; where the two domains overlaps, both sets of laws must give the same result.

Example of the correspondence in Bohr's atom:

Classical EM prediction: an electron in a circular motion will radiate EM wave at the same frequency

Bohr's model: In the limit, $n = 10^3 - 10^4$, the Bohr's atom would has a size of 10^{-3} m, which is in classical domain. The prediction for the photon emitted during transition around the $n = 10^3 - 10^4$ states should equals to that predicted by classical EM theory. **(Question: How do you determine the size of the Bohr's radius for a hydrogen atom excited to the state of $n = 10^3 - 10^4$)**

Classical mechanics and EM:

The period of a circulating electron is

$$T = 2\pi r/(2K/m)^{1/2} = \pi r(2m)^{1/2}(8\pi\varepsilon_0 r)^{1/2}/e$$

Substitute the quantised atomic radius $r_n = n^2 r_0$ into T, we obtain the frequency as per

$$\nu_n = 1/T = me^4/32\pi^3\varepsilon_0^2\hbar^3 n^3$$

Now, for an electron in the Bohr atom at energy level $n = 10^3 - 10^4$, the frequency of an radiated photon when electron make a transition from the n state to $n-1$ state is given by

$$\nu_n = (me^4/64\pi^3\varepsilon_0^2\hbar^3)[(n-1)^{-2} - n^{-2}]$$

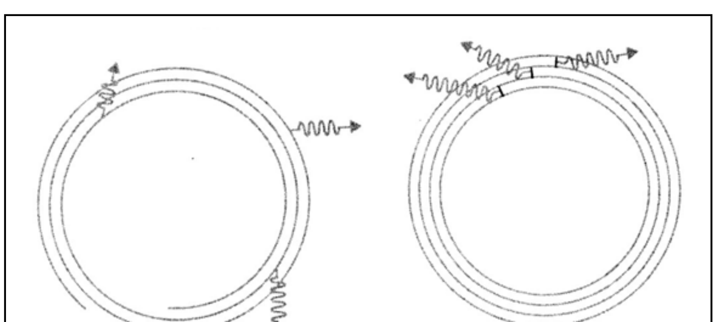
$$= (me^4/64\pi^3\varepsilon_0^2\hbar^3)[(2n-1)/n^2(n-1)^2]$$

In the limit of large n,

$$\nu \approx (me^4/64\pi^3\varepsilon_0^2\hbar^3)[2n/n^4]$$

$$= (me^4/32\pi^3\varepsilon_0^2\hbar^3)[1/n^3]$$

Hence, in the region of large n, where classical and quantum physics overlap, the classical prediction and that of the quantum one is identical.



The deficiency of the Bohr's model

- Not trivial to generalise the model to multielectron atoms (because Bohr's does not take into account of the interactions among the electrons themselves)
- Cannot explain the doublet of spectral lines (splitting of a spectral line into two very close ones) seen in spectroscopy (which is due to magnetic effects of the nucleus)
- Cannot predict the relative and absolute intensities of the spectral lines (because the *transition probability* among states is not given in the Bohr's model)
- It violates the uncertainty principle (in the radial components of r and p_r). For a given fixed energy state n, the radius of the orbit is a sharp circle with a know r_n, hence $\Delta r = 0$. So is p_r exact 0 (true for a uniform circular motion) $\Rightarrow \Delta p_r = 0$.

Need a full wave mechanical treatment of the atomic model to solve all this.

A Party of Famous Physicists

One day, all of the world's famous physicists decided to get together for a tea luncheon. Fortunately, the doorman was a grad student, and able to observe some of the guests...

- Everyone gravitated toward Newton, but he just kept moving around at a constant velocity and showed no reaction.
- Einstein thought it was a relatively good time.
- Thompson enjoyed the plum pudding
- Wien radiated a colourful personality.
- Millikan dropped his Italian oil dressing.
- de Broglie mostly just stood in the corner and waved
- Stefan and Boltzman got into some hot debates
- Compton was a little scatter-brained at times.
- Bohr ate too much and got atomic ache

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