## 1. Details of Module and its structure

| Module Detail | |
|---|---|
| Subject Name | Chemistry |
| Course Name | Chemistry 01 (Class XI, Semester 01) |
| Module Name/Title | Structure of Atom: Part 3 |
| Module Id | kech_10203 |
| Pre-requisites | Knowledge of Electron, proton, Rutherford's model, Hydrogen spectrum |
| Objectives | After going through this module you will be able to:<br>1. Describe Bohr's Model for Hydrogen atom<br>2. Explain the line spectrum of Hydrogen<br>3. Understand the dual behaviour of matter and Heisenberg<br>4. Uncertainty Principle<br>5. Understand the reason for the failure of Bohr's model of atom |
| Keywords | Orbit, Spectral lines, Angular momentum, Quantum Number, Rydberg constant, Bohr radius, Dual behaviour, Uncertainty Principle |

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## 4. SUMMARY

## 1. INTRODUCTION

In the previous module you have learnt about the dual character of electromagnetic radiations, photoelectric effect and the line spectrum of hydrogen atom. On the basis of these observations, Bohr proposed a model for the structure of atom which could explain the line spectrum of hydrogen like species which you will study in this module.

## 2. BOHR'S MODEL FOR HYDROGEN ATOM

Neils Bohr (1913) was the first to explain quantitatively the general features of hydrogen atom structure and its spectrum. Though the theory is not the modern quantum mechanics, it can still be used to rationalize many points in the atomic structure and spectra. Bohr's model for hydrogen atom is based on the following postulates:

**i)** The electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called **orbits**, stationary states or allowed energy states. These orbits are arranged concentrically around the nucleus.

**ii)** The energy of an electron in the orbit does not change with time. However, the electron will move from a lower stationary state to a higher stationary state when required amount of energy is absorbed by the electron or energy is emitted when electron moves from higher stationary state to lower stationary state. The energy change does not take place in a continuous manner.

**Angular Momentum**

Just as linear momentum is the product of mass (m) and linear velocity (v), angular momentum is the product of moment of inertia (I) and angular velocity (ω). For an electron of mass $m_e$, moving in a circular path of radius r around the nucleus,

angular momentum = $I \times \omega$

Since $I = m_e r^2$ , and $\omega = v/r$ where $v$ is the linear velocity,

angular momentum = $m_e r^2 \times v/r = m_e vr$

**iii)** The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by $\Delta E$, is given by :

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h} \qquad (1)$$

Where $E_1$ and $E_2$ are the energies of the lower and higher allowed energy states respectively. This expression is commonly known as Bohr's frequency rule.

**iv)** The angular momentum of an electron in a given stationary state can be expressed as in equation (2)

$$m_e vr = n\frac{h}{2\pi} \qquad (2)$$

n = 1, 2, 3.....

Thus an electron can move only in those orbits for which its angular momentum is integral multiple of $h/2\pi$ that is why only certain fixed orbits are allowed.

The details regarding the derivation of energies of the stationary states used by Bohr, are quite complicated and will be discussed in higher classes. However, according to Bohr's theory for hydrogen atom:

a) The stationary states for electron are numbered n = 1,2,3.......... These integral numbers are known as **Principal quantum numbers**.

b) The radii of the stationary states are expressed as :

$$r_n = n^2 a_0 \qquad (3)$$

where $a_0$ = 52.9 pm. Thus the radius of the first stationary state (n =1), called the **Bohr orbit**, is 52.9 pm. Normally the electron in the hydrogen atom is found in this orbit. As n increases the value of r will increase. In other words, as n increases, the electron will be present away from the nucleus.

c) The most important property associated with the electron, is the energy of its stationary state. It is given by the expression.

$$E_n = -R_H\left(\frac{1}{n^2}\right) \qquad (4)$$

n = 1,2,3....

where $R_H$ is called **Rydberg constant** and its value is $2.18\times10^{-18}$ J. The lowest state ( n =1) is called as the ground state. Its energy is equal to

$$E_1 = -2.18\times10^{-18}\left(\frac{1}{1^2}\right) = -2.18\times10^{-18}\text{J}.$$

The energy of the stationary state for n = 2, will be

$$E_2 = -2.18\times10^{-18}\text{J}\left(\frac{1}{2^2}\right) = -0.545\times10^{-18}\text{ J}.$$

Fig. 1 depicts the energies of different stationary states or energy levels of hydrogen atom. This representation is called an energy level diagram.

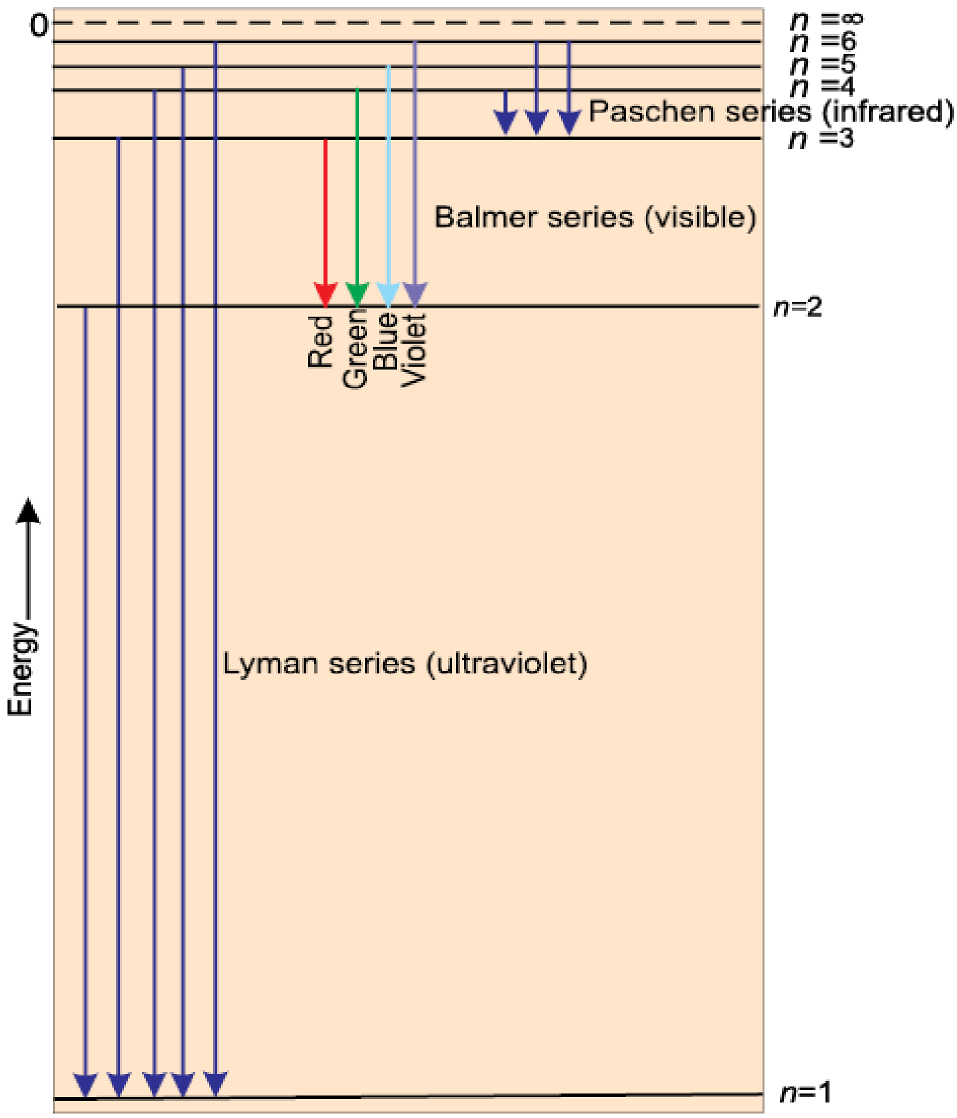


***Fig. 1*** *Transitions of the electron in the hydrogen atom*
*(The diagram shows the Lyman, Balmer and Paschen series of transitions)*

**What does the negative electronic energy ($E_n$) for hydrogen atom mean?**
The energy of the electron in a hydrogen atom has a negative sign for all possible orbits. What does this negative sign convey? This negative sign means that the energy of the electron in the atom is lower than the energy of a free electron at rest. A free electron at rest is an electron that is infinitely far away from the nucleus and is assigned the energy value of zero. Mathematically, this corresponds to setting n equal to infinity in the equation (4) so that $E_\infty=0$. As the electron gets closer to the nucleus (as n decreases), $E_n$ becomes larger in absolute value and more and more negative. The most negative energy value is given by n=1 which corresponds to the most stable orbit. We call this the ground state.

When the electron is free from the influence of nucleus, the energy is taken as zero. The electron in this situation is associated with the stationary state of Principal Quantum number, $n = \infty$ and the hydrogen atom is called as ionized hydrogen atom. When the electron, in $n = \infty$, is attracted by the nucleus and goes in orbit n, the energy is emitted and therefore, the

energy of electron is lowered. This is the reason for the presence of negative sign in equation (4) . It depicts the stability of electron relative to the reference state of zero energy and n = ∞.
d) Bohr's theory can also be applied to the ions containing only one electron, similar to that present in hydrogen atom, for example, $He^{+}$, $Li^{2+}$, $Be^{3+}$. The energies of the stationary states associated with these kinds of ions (also known as hydrogen like species) are given by the expression.

$$E_n = -2.18 \times 10^{-18} \left(\frac{Z^2}{n^2}\right) \quad (5)$$

and radii by the expression

$$r_n = \frac{52.9(n^2)}{Z} \text{pm} \quad (6)$$

where Z is the atomic number and has values 2 and 3 for the helium and lithium atoms respectively. From the above equations, it is evident that the value of energy becomes more negative and that of radius becomes smaller with increase of Z. This means that electron will be tightly bound to the nucleus.
e) It is also possible to calculate the velocities of electrons moving in these orbits. Although the precise equation is not given here, qualitatively the magnitude of velocity of electron increases with increase of positive charge on the nucleus and decreases with increase of principal quantum number.

## 2.1. Explanation of Line Spectrum of Hydrogen

Line spectrum observed in case of hydrogen atom can be explained quantitatively using Bohr's model. According to assumption 2, radiation (energy) is absorbed if the electron moves from the orbit of smaller Principal quantum number to the orbit of higher Principal quantum number, whereas the radiation (energy) is emitted if the electron moves from higher orbit to lower orbit. The energy gap between the two orbits is given by equation (7)

$$\Delta E = E_f - E_i \quad (7)$$

Combining equations (4) and (7)

$$\Delta E = \left(\frac{-R_H}{n_f^2}\right) - \left(\frac{-R_H}{n_i^2}\right)$$ (where $n_i$ and $n_f$ stand for initial orbit and final orbits)

$$\Delta E = R_H \left(\frac{1}{n_i^2}\right) - \left(\frac{1}{n_f^2}\right) = 2.18 \times 10^{-18}\text{J} \left(\frac{1}{n_i^2}\right) - \left(\frac{1}{n_f^2}\right) \quad (8)$$

The frequency (ν) associated with the absorption and emission of the photon can be evaluated by using equation (9)

$$\nu = \frac{\Delta E}{h} = \frac{R_H}{h}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \quad (9)$$

$$= \frac{2.18 \times 10^{-18}\text{J}}{6.626 \times 10^{-34}\text{J s}}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$= 3.29 \times 10^{15}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)\text{Hz} \quad (10)$$

and in terms of wavenumbers ($\bar{\nu}$)

$$\bar{\nu} = \frac{\nu}{c} = \frac{R_H}{hc}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \quad (11)$$

$$= \frac{3.29 \times 10^{15}\,\text{s}^{-1}}{3 \times 10^{8}\text{ms}^{-1}}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$=1.09677 \times 10^{7}\left(\frac{1}{n_i^2}-\frac{1}{n_f^2}\right) \qquad (12)$$

In case of absorption spectrum, $n_f > n_i$ and the term in the parenthesis is positive and energy is absorbed. On the other hand in case of emission spectrum $n_i > n_f$ , $\Delta E$ is negative and energy is released.

The expression (8) is similar to that used by Rydberg which was derived empirically using the experimental data available at that time. Further, each spectral line, whether in absorption or emission spectrum, can be associated to the particular transition in hydrogen atom. In case of a large number of hydrogen atoms, different possible transitions can be observed and thus leading to large number of spectral lines. The brightness or intensity of spectral lines depends upon the number of photons of same wavelength or frequency absorbed or emitted.

**Problem 1**

What are the frequency and wavelength of a photon emitted during a transition from n = 5 state to the n = 2 state in the hydrogen atom?

**Solution**

Since $n_i = 5$ and $n_f = 2$, this transition gives rise to a spectral line in the visible region of the Balmer series. From equation (8)

$$\Delta E = 2.18 \times 10^{-18}\mathrm{J}\left(\frac{1}{5^2}-\frac{1}{2^2}\right)$$

$$=-4.58 \times 10^{-19}\mathrm{J}$$

The negative sign indicates that the energy is released during the transition.

The frequency of the photon (taking energy in terms of magnitude) is given by

$$\nu = \frac{\Delta E}{h}$$

$$=\frac{4.58 \times 10^{-19}\mathrm{J}}{6.626 \times 10^{-34}\mathrm{J\,s}}$$

$$= 6.91\times10^{14}\ \mathrm{Hz}$$

$$\lambda = \frac{c}{\nu} = \frac{3.0 \times 10^{8}\mathrm{m\,s^{-1}}}{6.91 \times 10^{14}\mathrm{Hz}} = 434\mathrm{nm}$$

**Problem 2**

Calculate the energy associated with the first orbit of $He^+$ . What is the radius of this orbit?

**Solution**

$$E_n = \frac{-(2.18 \times 10^{-18}\mathrm{J})Z^2}{n^2}\mathrm{atom^{-1}}$$

For $He^+$, n = 1, Z = 2

$$E_n = \frac{-(2.18 \times 10^{-18}\mathrm{J})2^2}{1^2} = -8.72 \times 10^{-18}\mathrm{J}$$

The radius of the orbit is given by equation (6)

$$r_n = \frac{(0.0529\ \mathrm{nm})n^2}{Z}$$

Since n = 1, and Z = 2

$$r_n = \frac{(0.0529\ \mathrm{nm})1^2}{2} = 0.02645\ \mathrm{nm}$$

## 2.2 Limitations of Bohr's Model

Bohr's model of the hydrogen atom was no doubt an improvement over Rutherford's nuclear model, as it could account for the stability and line spectra of hydrogen atom and hydrogen like ions (for example, $He^{+}$, $Li^{2+}$, $Be^{3+}$). However, Bohr's model was too simple to account for the following points.

i. It fails to account for the finer details (doublet, that is two closely spaced lines) of the hydrogen atom spectrum which are observed by using sophisticated spectroscopic techniques.
ii. This model is also unable to explain the spectrum of atoms other than hydrogen, for example, helium atom which possesses only two electrons.
iii. Bohr's theory was also unable to explain the splitting of spectral lines in the presence of magnetic field (Zeeman effect) or an electric field (Stark effect).
iv. It could not explain the ability of atoms to form molecules by chemical bonds.

In other words, taking into account the points mentioned above, one needs a better theory which can explain the salient features of the structure of complex atoms.

## 3. TOWARDS QUANTUM MECHANICAL MODEL OF THE ATOM

In view of the shortcoming of the Bohr's model, attempts were made to develop a more suitable and general model for atoms. Two important developments which contributed significantly in the formulation of such a model were:

1. Dual behaviour of matter,
2. Heisenberg uncertainty principle.

### 3.1 Dual Behaviour of Matter

The French physicist, de Broglie in 1924 proposed that matter, like radiation, should also exhibit dual behaviour i.e., both particle and wavelike properties. This means that just as the photon has momentum as well as wavelength, electrons should also have momentum as well as wavelength. de Broglie, from this analogy, gave the following relation between wavelength ($\lambda$) and momentum ($p$) of a material particle.

$$\lambda = \frac{h}{mv} = \frac{h}{p} \qquad (13)$$

where $m$ is the mass of the particle, $v$ its velocity and $p$ its momentum. de Broglie's prediction was confirmed experimentally when it was found that an electron beam undergoes diffraction, which is a characteristic phenomenon of waves. This fact has been put to use in making of an electron microscope, which is based on the wavelike behaviour of electrons just as an ordinary microscope utilises the wave nature of light. An electron microscope is a powerful tool in modern scientific research because it achieves a magnification of about 15 million times.

It needs to be noted that according to de Broglie, every object in motion has a wave character. The wavelengths associated with ordinary objects are so short (because of their large masses) that their wave properties cannot be detected. The wavelengths associated with electrons and other subatomic particles (with very small mass) can however be detected experimentally. Results obtained from the following problems prove these points qualitatively.

**Problem 3**

What will be the wavelength of a ball of mass 0.1 kg moving with a velocity of 10 m $s^{-1}$ ?

**Solution**

According to de Brogile equation (13)

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{J s}}{(0.1 \text{ kg})(10\text{ms}^{-1})}$$

$= 6.626 \times 10^{-34}$ m ( 1J = 1 kg $m^2$ $s^{-2}$)

**Problem 4**

The mass of an electron is $9.1 \times 10^{-31}$ kg. If its K.E. is $3.0 \times 10^{-25}$ J, calculate its wavelength.

**Solution**

Since K. E. = ½ $mv^2$

$$\bar{v} = \left(\frac{2\text{K.E.}}{m}\right)^{(1/2)} = \left(\frac{2 \times 3.0 \times 10^{-25} \text{kg m}^2\text{s}^{-2}}{9.1 \times 10^{-31} \text{kg}}\right)$$

$= 812$ m $s^{-1}$

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{J s}}{(9.1 \times 10^{-31} \text{kg})(812 \text{m s}^{-1})}$$

$= 8967 \times 10^{-10}$ m = 896.7 nm

**Problem 5**

Calculate the mass of a photon with wavelength 3.6 Å.

**Solution**

$\lambda$ = 3.6Å = $3.6 \times 10^{-10}$ m

Velocity of photon = velocity of light

$$m = \frac{h}{\lambda v} = \frac{6.626 \times 10^{-34} \text{J s}}{(3.6 \times 10^{-10} \text{m})(3 \times 10^{8} \text{ ms}^{-1})}$$

$= 6.135 \times 10^{-29}$ kg

## 3.2 Heisenberg's Uncertainty Principle

Werner Heisenberg a German physicist in 1927, gave uncertainty principle which is the consequence of dual behaviour of matter and radiation. According to Heisenberg's Uncertainty principle, **it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron.**

Mathematically, it can be given as in equation (14).

$$\Delta x \times \Delta p_x \geq \frac{h}{4\pi} \qquad (14)$$

or $\Delta x \times \Delta m v_x \geq \frac{h}{4\pi}$

or $\Delta x \times \Delta v_x \geq \frac{h}{4\pi m}$

where Δx is the uncertainty in position and $\Delta p_x$ (or $\Delta v_x$) is the uncertainty in momentum (or velocity) of the particle. If the position of the electron is known with high degree of accuracy (Δx is small), then the velocity of the electron will be uncertain ($\Delta v_x$ is large). On the other hand, if the velocity of the electron is known precisely ($\Delta v_x$ is small), then the position of the electron will be uncertain (Δx will be large). Thus, if we carry out some physical measurements on the electron's position or velocity, the outcome will always depict a fuzzy or blur picture.

The uncertainty principle can be best understood with the help of an example. Suppose you are asked to measure the thickness of a sheet of paper with an unmarked metre stick.

Obviously, the results obtained would be extremely inaccurate and meaningless. In order to obtain any accuracy, you should use an instrument graduated in units smaller than the thickness of a sheet of the paper. Similarly, in order to determine the position of an electron, we must use a meter stick calibrated in units of smaller than the dimensions of electron (keep in mind that an electron is considered as a point charge and is therefore, dimensionless). To observe an electron, we can illuminate it with "light" or electromagnetic radiation. The "light" used must have a wavelength smaller than the dimensions of an electron. The high momentum photons of such light $\left(p = \frac{h}{\lambda}\right)$would change the energy of electrons on collision. In this process we, no doubt, would be able to calculate the position of the electron, but we would know very little about the velocity of the electron after the collision.

**3.3 Significance of Uncertainty Principle**

One of the important implications of the Heisenberg Uncertainty Principle is that **it rules out existence of definite paths or trajectories of electrons and other similar particles.** If the position of a body is known at a particular instant and if its velocity and the forces acting on it at that instant are also known, then the position of the body can be determined at a different instant. Therefore, it can be concluded that the position of an object and its velocity fixes its trajectory. Since for a sub-atomic object such as an electron, it is not possible to determine the position and velocity simultaneously at any given instant to an arbitrary degree of precision, it is not possible to talk of the trajectory of an electron.

**The effect of Heisenberg Uncertainty Principle is significant only for motion of microscopic objects and is negligible for that of macroscopic objects.** This can be seen from the following examples.

If uncertainty principle is applied to an object of mass, say about a milligram ($10^{-6}$ kg), then

$$\Delta x \times \Delta v_x = \frac{h}{4\pi m}$$

$$= \frac{6.626 \times 10^{-34}\,\mathrm{J\,s}}{4 \times 3.1416 \times 10^{-6}\,\mathrm{kg}} \approx 10^{-28}\,\mathrm{m^2 s^{-1}}$$

The value of $\Delta v \Delta x$ obtained is extremely small and is insignificant. Therefore, one may say that **in dealing with milligram-sized or heavier objects, the associated uncertainties are hardly of any real consequence.**

In the case of a microscopic object like an electron on the other hand, $\Delta v \Delta x$ obtained is much larger and such uncertainties are of real consequence. For example, for an electron having mass of $9.11\times10^{-31}$ kg., according to Heisenberg uncertainty principle,

$$\Delta x \times \Delta v_x = \frac{h}{4\pi m}$$

$$= \frac{6.626\times10^{-34}\,\mathrm{J\,s}}{4\times3.1416\times9.1\times10^{-31}\,\mathrm{kg}} = 10^{-4}\,\mathrm{m^2 s^{-1}}$$

It, therefore, means that if one tries to find the exact location of the electron, with an uncertainty of only $10^{-8}$ m, then the uncertainty $\Delta v$ in velocity would be

$$\frac{10^{-4}\mathrm{m}^2\mathrm{s}^{-1}}{10^{-8}\mathrm{m}} \approx 10^4 \mathrm{ms}^{-1}$$

This is so large that the classical picture of electrons moving in Bohr's orbits (fixed) cannot hold good. **It, therefore, means that the precise statements of the position and momentum of electrons have to be replaced by the statements of probability, that the electron has at a given position and momentum. This is what happens in the quantum mechanical model of atom.**

**Problem 6**

A microscope using suitable photons is employed to locate an electron in an atom within a distance of 0.1 Å. What is the uncertainty involved in the measurement of its velocity?

**Solution**

$$\Delta x \times \Delta v_x = \frac{h}{4\pi m} \text{ or } \Delta v = \frac{h}{4\pi\, \Delta x m}$$

$$\Delta v = \frac{6.626 \times 10^{-34}\mathrm{J\,s}}{4 \times 3.14 \times 0.1 \times 10^{-10}\mathrm{m} \times 9.11 \times 10^{-31}\mathrm{kg}}$$

$= 0.579\times10^{7}$ m $s^{-1}$ (1J = 1 kg $m^2$ $s^{-2}$)

$= 5.79\times10^{6}$ m $s^{-1}$

**Problem 7**

A golf ball has a mass of 40g, and a speed of 45 m/s. If the speed can be measured within accuracy of 2%, calculate the uncertainty in the position.

**Solution**

The uncertainty in the speed is 2%, i.e.,

$$\frac{45 \times 2}{100} = 0.9 \mathrm{~m~s}^{-1}$$

Using the equation

$$\Delta x = \frac{h}{4\pi m \Delta v}$$

$$= \frac{6.626\times10^{-34}\mathrm{J\,s}}{4\times3.14\times40\mathrm{g}\times10^{-3}\mathrm{~kg~g}^{-1}(0.9\mathrm{m~s}^{-1})}$$

$= 1.46\times10^{-33}$ m

This is nearly ~ $10^{18}$ times smaller than the diameter of a typical atomic nucleus. As mentioned earlier for large particles, the uncertainty principle sets no meaningful limit to the precision of measurements.

**3.4 Reasons for the Failure of the Bohr Model**

One can now understand the reasons for the failure of the Bohr model. In Bohr model, an electron is regarded as a charged particle moving in well defined circular orbits about the nucleus.

The wave character of the electron is not considered in Bohr model. Further, an orbit is a clearly defined path and this path can completely be defined only if both the position and the velocity of the electron are known exactly at the same time. This is not possible according to the Heisenberg uncertainty principle. Bohr model of the hydrogen atom, therefore, not only ignores dual behaviour of matter but also contradicts Heisenberg uncertainty principle. In view of these inherent weaknesses in the Bohr model, there was no point in extending Bohr model to other atoms. In fact an insight into the structure of the atom was needed which could account for wave-particle duality of matter and be consistent with Heisenberg uncertainty principle. This came with the advent of quantum mechanics.

## 4. SUMMARY

- Bohr postulated that electron moves around the nucleus in circular orbits in an atom.
- For an atom, only certain orbits can exist and each orbit corresponds to a specific energy.
- Bohr could explain the line spectrum of hydrogen atom or hydrogen like species but could not explain the spectra of multi-electron atoms.
- Each spectral line in the spectrum can e associated to the transition of electron from one orbit to another.
- de Broglie suggested that matter exhibits both particle and wave like properties and also gave an expression for the calculation of wavelength, called de Broglie wave equation.
- Heisenberg's uncertainty principle states that it is impossible to determine simultaneously, the exact position and exact velocity of an electron.