AIM OF COURSE:

The overall aim of this course is to show that the bulk properties of matter depend on structure at the atomic, molecular, microscopic, macroscopic levels. Armed with such knowledge, the student should be able to choose and use various materials judiciously.
LECTURE 1: THE ATOM AND MOLECULE (MODELS)

Objectives:
At the end of the lecture you should be able to:
1: Describe the Thomson’s atomic model and explain its limitations
2: Describe the Rutherford’s model of an atom, and identify its inadequacies
3: Explain Bohr’s model of an atom, and be able to calculate the energy change when an atom makes a transition from one orbit to another
4: Point out the limitations of the Bohr’s model.

1.1 Introduction

Solids, liquids and gases are made of atoms; the diameter of whose is about $10^{-10}$m. In recent years direct visual evidence of atoms have been obtained by scientists using powerful microscopes (e.g. atomic force microscope). For details of the internal structure of atoms these microscopes are not yet sufficiently powerful. In this context, an atom is the smallest indivisible component of a chemical element. It is important to note that an atom has its constituents, the electrons, protons, and neutrons; hence an atom is not the fundamental component of matter.

Atoms are made up of positive and negative electric charges, and the attraction and repulsion of these charges are the basis of all the chemical and physical phenomena observed in solids, liquids, and gases. The arrangement of electric charges in the atoms remained a mystery until the discovery of the nucleus by Rutherford, while Niels Bohr explained the factors determining the characteristic colours of light emitted by atoms.

1.2 J.J. Thomson’s Model (Plum-pudding Model)

The features of this model are:
- All the atoms contain electrons, which are negatively charged.
- Atoms are electrically neutral entities; every atom thus contains enough positively charged matter to balance the negative charges of the electrons.
- Electrons are several times much lighter than the whole atom, implying that the positively charged constituent provides nearly all the entire mass of the atoms.
- Thomson proposed that atoms are uniform spheres of positively charged matter in which electrons are embedded.

I am sure most of you are aware of the ‘guava fruit’. The seeds of the guava fruit can be taken to represent the electrons, whereas the flesh of the fruit represents the positively charged matter. This picture of the atom is shown in Fig. 1.1.
It is important to point out that the Thomson’s model of an atom is not in accord with experiment, and with time, had to be discarded.

1.3: Rutherford’s Model

The model explains the experimental results of Geiger and Marsden (1913) wherein some of the alpha (α) particles directed at the atoms (tiny metallic (gold) foil) were scattered through large angles. The Rutherford’s scattering experiment shown in Fig. 2, as conducted by Geiger and Marsden, disapproved the Thomson’s model of an atom.
The key features of the Rutherford’s model are:

- In this model an atom comprises a tiny nucleus, in which its positive charge and nearly all of its mass are concentrated, with the electrons some distance away, as shown in Fig. 3.

![Figure 3. The Rutherford’s model of an atom.](image)

- The large scattering of the alpha (\(\alpha\)) particle (~7000 times more massive than an electron) is due to intense electric field (and hence force) it encounters at the nucleus.
- The atomic electrons, because of their very small mass do not affect the motion of the incident alpha (\(\alpha\)) particles.
- The deflection an alpha (\(\alpha\)) particle experiences when it nears the nucleus depends on the magnitude of the nuclear charge. From this fact, the nuclear charges of various atoms can be estimated by comparing the relative scattering angles, showing that:

  1. All the atoms of a given element have the same nuclear charge.
  2. The nuclear charge increased regularly from element to element in the Periodic Table.
  3. The nuclear charge = \(+eZ\). (\(e\) is the electronic charge and has a magnitude of 1.6x10\(^{-19}\) Coulombs, \(Z\) is the atomic number of the element and is equivalent to the number of the protons in the nuclei of the atoms).

- From the Rutherford’s nuclear model, the scattering (deflection) angle (\(\theta\)) of the alpha (\(\alpha\)) particles can be calculated. Shown in Fig. 4 is the trajectory of the scattered alpha particles. The trajectories are hyperbolas.
The perpendicular distance between the nucleus and the original (undeflected) line of motion is called the **impact parameter** \((b)\).

![Diagram showing the impact parameter (b) and the angle of deflection (θ) between the nucleus and the undeflected line of motion.](image)

**Figure 4. The trajectories of scattered alpha particle**

According to classical mechanics, the angle of deflection \((θ)\) can be expressed in terms of the impact parameter \((b)\), the energy \((E)\) of the \(α\)-particle, and the charge of the nucleus \((Ze)\) as

\[
θ = 2 \cot^{-1} \left( \frac{2 \pi \varepsilon_o E b}{Z e^2} \right). \tag{1.1}
\]

\(\varepsilon_o\) is the dielectric constant of free space and has a value of \(8.85 \times 10^{-12} \text{ C}^2\text{m}^{-2}\text{N}^{-1}\)

In order to undergo sufficiently large deflection, the \(α\)-particle must strike an atom within the impact parameter, \(10^{-13}\text{m}\) or less.

**Example 1:**
What impact parameter will give a deflection of \(1°\) for an \(α\)-particle of 7.7 MeV incident on a gold nucleus? What parameter will give a deflection of \(30°\)?

**Solution:**

With \(E = 7.7\text{MeV} = 7.7 \times 10^6 \times 1.6 \times 10^{-19} = 1.2 \times 10^{-12} \text{J}\) and \(Z_{\text{gold}} = 79\), Eqn. (i) yields

\[
b = \frac{Z e^2}{4 \pi \varepsilon_o E} \cot \left( \frac{θ}{2} \right) = \frac{79 \times (1.6 \times 10^{-19} C)^2}{4 \pi \times 8.85 \times 10^{-12} F / m \times 1.2 \times 10^{-12} J} \cot \left( \frac{θ}{2} \right).
\]
\[ b = \left(1.48 \times 10^{-14} \, m\right) \cot\left(\frac{\theta}{2}\right) \]

For \( \theta = 1^\circ \), and \( \theta = 30^\circ \), we obtain
\[ b = 1.7 \times 10^{-12} \, m, \quad \text{and} \quad b = 5.5 \times 10^{-14} \, m \]
respectively.

**Example 2.**

Compare the probabilities for deflection by angles in excess of 1° with the probabilities of deflection by angles in excess of 30° for an \( \alpha \)-particle of 7.7 Mev on a gold atom.

**Solution:**

From example 1,
\[ b_1 = 1.7 \times 10^{-12} \, m \]
implies that its line of motion must strike within a circular area of \( \pi \left(1.7 \times 10^{-12} \, m\right)^2 \) centred on the nucleus, while \( b_{30} = 5.5 \times 10^{-14} \, m \), means that the original line of motion must strike within an area of \( \pi \left(5.5 \times 10^{-14} \, m\right)^2 \) centred on the nucleus. The probabilities \( P_1 \) and \( P_{30} \) are proportional to the target areas. Thus
\[
\frac{P_1}{P_{30}} = \frac{\pi \left(1.7 \times 10^{-12} \, m\right)^2}{\pi \left(5.5 \times 10^{-14} \, m\right)^2} = 940.
\]

Thus, whenever 940 incident particles are deflected by more than 1° only one of these will be deflected by an angle larger than 30° (on the average). This shows that very large deflections are rare.

The number \( (N) \) of particles scattered at different angles was calculated by Rutherford and he found out that the number of particles scattered at an angle \( (\theta) \) is given by the relation

\[ N \propto \frac{1}{\sin^4\left(\frac{\theta}{2}\right)} \quad (1.2) \]
The target area that corresponds to a given deflection is called the **cross section** \((\sigma)\) for the deflection. The deflection of the particles of a beam by impact on a target is called **scattering**.

### 1.3.1 Limitations of Rutherford’s Model:

The two limitations of the model are:

(i) It could not account for the stability of the atom.

(ii) It predicts that electrons (due to ever changing radii of circular orbits) will radiate electromagnetic (em) waves of all frequencies, that is, a continuous spectrum of these waves will result. Experimental evidence, on the contrary show that atomic spectra are not continuous but discrete, i.e., are single spectral lines corresponding to specific frequencies.

#### Reading exercises:

1) Describe an experiment which confirms the view that an atom contains a small central nucleus.

2) Why was gold used in the \(\alpha\)-scattering experiment? What would happen if different thin foils of metals such as platinum, or silver were used? What conclusion can you draw from such observations? (Hint: Think of the atomic masses)

3) The Rutherford’s \(\alpha\)-experiments shows that most of the \(\alpha\)-particles exit the thin metallic foil almost undeflected while some are deflected through large angles. What information about the atomic structure can you gather from this observation?
1.4 The Bohr’s model of an atom

We have noted that Rutherford proposed an atom comprising a central positively charged nucleus surrounded by negative charges, identified as electrons. The nucleus must exert an attraction on the electrons, so it is necessary to postulate that they would circulate in orbits in a way that the centrifugal force balances the electrostatic attraction. From the classical theory of electromagnetism, when an electron (or a charge) moves in an orbit, it emits electromagnetic (em) waves. Thus from classical theory we expect electrons circulating around the nucleus to emit em radiations of the same frequency as the orbital frequency. This would involve loss of energy and an approach of the electron nearer the nucleus. A consequence is a continual change of frequency and also a final collapse of the electron into the nucleus—neither of which is observed to happen. Atoms, when they do, emit radiations of fixed frequency. This prediction of Rutherford’s model is not in accord with experiment.

Bohr (1915) proposed a model of the atoms as follows:

(i) The electrons exist only in stable circular orbits of fixed energy, the angular momentum of an electron in an orbit being an integral multiple of \( h/2\pi \), where \( h \) is Planck’s constant.

(ii) An electron will emit or absorb energy only when making a transition (change) from one orbit to another possible orbit.

![Bohr’s model of an atom](image-url)

Figure 5. Bohr’s model of an atom showing electrons in stable orbits and an electron making a transition from one orbit to the other resulting in radiation of energy
Bohr's hypothesis was an attempt to explain the possible electron orbits, the energy differences between which would account for the observed spectral lines.

Let us now consider a single-electron atom. If \( m \) is the mass of the electron moving with a velocity \( \mathbf{v} \) in the circular orbit or radius \( r \) around a fixed nucleus of charge \( +Ze \), then from Coulomb's law we obtain the attractive force \( F_c \) between the electron and the nucleus as

\[
F_c = \frac{Ze^2}{4\pi\varepsilon_0 r^2}
\]  

(1.3)

where \( \varepsilon_0 \) is the permittivity of free space.

(Recall Coulomb's law, as you learnt in electrostatics, is the law that gives the force between charged particles).

Assuming Newton's law of motion (i.e., force is the product of mass and acceleration) applies then the centrifugal force \( F_{cf} \) on the electron is \( m\mathbf{v}^2/r \). If the electron remains in its orbit, these forces (electrostatic and centrifugal) must be then equal or balance out, i.e.,

**NB: Planck's idea:** Light and all other forms of electromagnetic radiation possess energy, the smallest unit of which is a quantum or photon, has energy \( h\nu \), where \( \nu \) is the frequency of radiation \( \nu = \frac{c}{\lambda} \) and \( h = 6.62 \times 10^{-34} \) Js, \( c = 3.0 \times 10^8 \) ms\(^{-1} \) is the velocity of light, and \( \lambda \) is the wavelength.
\[ m\nu^2/r = \frac{Ze^2}{4\pi\varepsilon_o r^2} \]

so that

\[ \nu^2 = \frac{Ze^2}{4\pi\varepsilon_o mr} \]  \hspace{1cm} (1.4)

Equation (1.4) shows that for any particular value of \( r \) there is a particular value of \( \nu \).

The energy of the electron consists of the potential energy (P.E) and kinetic energy (K.E) components.

\[ K.E = \frac{1}{2} m\nu^2 \quad \text{and} \quad P.E = -\frac{Ze^2}{4\pi\varepsilon_o r} = -m\nu^2 \]

(Note: Reference for P.E. point is at taken as the zero position).

The total energy (T) is the sum of P.E and K.E, thus

\[ T = K.E + P.E = \frac{1}{2} m\nu^2 - m\nu^2 = -\frac{1}{2} m\nu^2. \]

If we now introduce Bohr’s condition that the angular momentum \( m\nu r \) of an electron can have only certain value which is an integral multiple of \( \hbar/2\pi \), then

\[ m\nu r = \frac{nh}{2\pi} \]

where \( n = 1,2,3,4, \ldots \) is an integer. Combining equations (1.4) and (1.5) we obtain

\[ \nu = \frac{Ze^2}{2nh\varepsilon_o} \]

(1.6)

and the total energy is

\[ T = -\frac{1}{2} m\nu^2 = -\frac{Z^2 me^4}{8\hbar^2 \varepsilon_o^2} \left( \frac{1}{n^2} \right) \]

(1.7).

Inserting the appropriate numerical values of the constants, the total energy becomes
\[ T = -2.18 \frac{Z^2}{n^2} \times 10^{-18} \, J. \]

\( n \) is called the principal quantum number.

As an electron jumps from an outer orbit (say \( n_2 \)) to an inner orbit (say, \( n_1 \)) nearer the nucleus, there will be a decrease in its total energy equal to the difference in its energies in the two orbits. This change in energy (\( \Delta E = E_{2} - E_{1} \)) is expressed as

\[ \Delta E = 2.18 \times 10^{-18} Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) J. \]  \( \text{(1.8)} \)

This energy is released as a quantum of e.m. radiation (photon) of frequency \( \nu = \frac{\Delta E}{h} \) or wavelength \( \lambda = \frac{c}{\nu} = \frac{c h}{\Delta E} \).

When we combine equations (1.5) and (1.6) we can obtain the expression for \( r \), i.e.,

\[ r = n^2 \frac{\hbar^2 c}{mZ e^2} \]  \( \text{(1.9)} \)

Equation (1.9) shows that \( r \propto n^2 \). For hydrogen atom (\( Z=1 \)), the radius of the first orbit (\( n=1 \)) we get

\[ r = \frac{\hbar^2 c}{m e^2}. \]

This is called Bohr’s radius and its numerical value is \( 0.53 \times 10^{-10} \text{m} \) (or \( 0.53 \text{Å} \)).

Exercise: Calculate the velocity of electron in the 1st orbit (\( n=1 \)) of hydrogen atom (\( Z=1 \))
SUMMARY

1: The atom is electrically is neutral, i.e., the number of electrons in the atom is such that their negative charge is equal to the positive charge of the atom.

2: The entire positive charge of the atom is concentrated in quite a small volume of the atom.

3: The angular momentum of the electron in an orbit is quantised, i.e., takes only specific values that are integral multiple of the Planck’s constant. Thus electrons can only be in discrete orbits, known as stable (stationary) orbits.

4: The electrons only radiate energy when they make transitions from one orbit to the other. The transition could be as a result of the electron receiving energy from an external source. An electron that has received energy from an external source is said to be ‘excited’.

5: The total energy of an electron in an orbit is

\[ E = -\frac{Z^2 m e^4}{8 h^2 n^2} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \]

6: The change in energy during a transition of an electron from one state to the other is

\[ \Delta E = 2.18 \times 10^{-18} Z^2 \frac{1}{n_1^2} \frac{1}{n_2^2} \]

EXERCISES

1. Calculate the distance of closest approach for an \( \alpha \)-particle with a kinetic energy of 10\(^7\) eV approaching a stationary nucleus of atomic number 50. (Answer: 1.44x10\(^{-14}\)m).

2. The number of particles scattered at 60\(^\circ\) is 100 per minute in an alpha-particle scattering experiment, using gold foil. Determine the number of particles per minute scattered at 90\(^\circ\) angle. (Answer: 25/minute).

3. Show, using the Bohr’s model, that the radius of the 3rd orbit of a hydrogen atom is 4.77\(\AA\).

4. What is the angular momentum of an electron in hydrogen atom, if the energy of the electron in an excited state is –3.4eV? (Answer: 2.108x10\(^{-34}\) J-s).

5. The radius of the first electron-orbit in hydrogen atom is \( r_o \). What is the radius of the second orbit? What of the second orbit of singly-ionised helium atom? (Answer: 4 \( r_o \), 2 \( r_o \)).

6. An electron moves about a proton in a circular orbit of radius 5x10\(^{-11}\) m. Express the total energy in electron-volts (eV). (Answer: -14.4 eV)
FURTHER READINGS