UNIT 1 OLD QUANTUM THEORY

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1.1 INTRODUCTION

The ideas of classical mechanics developed by Galileo, Kepler and Newton, when applied to atomic and molecular systems were found to be inadequate. Need was felt for a theory to describe, correlate and predict the behaviour of the sub-atomic particles. The quantum theory, proposed by Max Planck and applied by Einstein and Bohr to explain different aspects of behaviour of matter, is an important milestone in the formulation of the modern concept of atom.

In this unit, we will study how black body radiation, heat capacity variation, photoelectric effect and atomic spectra of hydrogen can be explained on the basis of theories proposed by Max Planck, Einstein and Bohr. They based their theories on the postulate that all interactions between matter and radiation occur in terms of definite packets of energy, known as quanta. Their ideas, when extended further, led to the evolution of wave mechanics, which shows the dual nature of matter and energy.

Objectives
After studying this unit, you should be able to:
• describe the discovery of electron, proton and neutron,
• explain the atom models of Thomson and Rutherford,
• list the wave parameters of light,
• describe the shortcomings of classical physics,
• state Planck’s theory and explain its application to black body radiation and heat capacity variation,
• define photoelectric effect and explain it in the light of Einstein’s theory,
• list Bohr’s postulates and derive an expression useful in calculating the radius of the hydrogen atom,
• explain the atomic spectra of hydrogen in the light of Bohr’s theory,
• analyse critically the advantages and limitations of Bohr’s theory, and
• state the refinements in the atomic spectra theory.

1.2 DISCOVERY OF SUB-ATOMIC PARTICLES

The atomic theory of the Greek philosophers, Leucippus and Democretus (400 B.C.) held that continued subdivision of matter would ultimately yield atoms which would
Structure of Matter

Cathode rays are a stream of negatively charged particles, known as electrons.
Mass of the electron
\[ = 9.109 \times 10^{-31} \text{ kg} \]
Charge of the electron
\[ = -1.602 \times 10^{-19} \text{ C} \]
The unit for charge of the electron is coulomb, C.

not be further divided. The word ‘atom’ is derived from the Greek word, atomos, which means “uncut” or indivisible. Dalton (1808) based his atomic theory on the ideas of Democretus and was able to explain the laws of chemical combination. Toward the end of nineteenth century, it began to appear that the atom itself might be composed of even smaller particles. This discovery was brought about by experiments with electricity.

Attempts to pass a high voltage electric current through gases under reduced pressure led to Julius Plucker’s discovery (1859) of cathode rays, Fig. 1.1. The cathode rays stream from the negative electrode, which is called the cathode. These rays consist of negatively charged particles which travel in straight lines. The cathode rays give off flashes of light, when they strike a screen coated with substances like zinc sulphide. The picture tubes in television sets and computer monitors, function on this principle.

The particles in cathode rays were later called electrons, as suggested by Stoney. The determination of charge to mass ratio of electrons by Thomson (1897) confirmed the fact that the electrons, which originate from the metal of which the cathode is constituted, are the same no matter what metal is employed as the cathode. In other words, electrons are fundamental particles of all types of matter.

If one or more electrons are removed from a neutral atom or molecule, the residual entity is positively charged. During the formation of cathode rays in an electric discharge tube, one or more electrons are removed from each of the atoms, and the positive particles so produced, move toward the negative electrode. If this electrode has holes in it, the positive ions pass through them, as shown in Fig. 1.2.

These streams of positive ions, called positive rays, were first observed by Goldstein (1886). The charge to mass ratios of positive ions depend on the nature of gases taken in the discharge tube. For example, charge to mass ratios for the positive rays obtained from hydrogen and neon are not the same. You can compare this fact with the earlier statement that the charge to mass ratio value of electrons is the same irrespective of the nature of gases kept in the discharge tube.

The positive particles produced, when hydrogen is taken in the discharge tube, are called protons in accordance with the suggestion of Rutherford (1920). In Greek ‘protes’ means first. The protons, like electrons are assumed to be constituents of all atoms. The proton has positive charge, although equal in magnitude to that of the electron.
In the same year, Rutherford suggested that there might exist particles which he called neutrons, having a mass equivalent to a proton but without charge. Chadwick (1932) discovered neutrons during his experiments on the bombardment of beryllium by α-particles. The properties of electron, proton and neutron are summarised in Table 1.1. Although other sub-atomic particles have also been identified, atomic structure is adequately explained on the basis of the number of electrons, protons and neutrons in an atom.

### Table 1.1: Sub-atomic Particles

<table>
<thead>
<tr>
<th>Particle</th>
<th>Mass/kg</th>
<th>Charge/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron</td>
<td>$9.109 \times 10^{-31}$</td>
<td>$-1.602 \times 10^{-19}$</td>
</tr>
<tr>
<td>Proton</td>
<td>$1.673 \times 10^{-27}$</td>
<td>$+1.602 \times 10^{-19}$</td>
</tr>
<tr>
<td>Neutron</td>
<td>$1.675 \times 10^{-27}$</td>
<td></td>
</tr>
</tbody>
</table>

Along with discoveries of sub-atomic particles, various theories were put forward to explain the structure of the atom.

### 1.3 EARLIER ATOM MODELS

As mentioned in the last section, Dalton proposed a theory that atom is indivisible. But the discovery of sub-atomic particles like electron, led to a revision of this theory. Thomson (1904) proposed a model for the atomic structure, known as "plum pudding" model, which is pictorially described in Fig. 1.3. He considered an atom to be a uniform sphere of positive electricity of about $10^{-8}$ cm radius, with the electrons embedded in such a way as to give the most stable electrostatic arrangement.

This model was not able to explain the observation of Geiger and Marsden (1909) regarding the scattering of the α-particles directed towards thin gold foil. Some were deflected from their straight-line path and a few recoiled back toward their source (Fig. 1.4). A uniform sphere of positive charge, would mean only a gradual deflection of the α-particle, but not scattering as it progressed through the foil.

Rutherford (1911), on the basis of the α-ray scattering experiment, suggested that positive charge and mass of the atom are concentrated in a space which is very much smaller than that occupied by the atom as a whole. He suggested an atomic model, known as nuclear model which consisted of a nucleus at the centre and negative particles surrounding it. The nucleus accounted for mass and positive charge. To support the fact that the electrons did not fall into a nucleus as a result of electrostatic attraction, Rutherford found it necessary to postulate rapid rotation of the electrons about the nucleus just as planets go round the sun. This analogy is misleading since according to classical electromagnetic theory, an electron in orbit is subject to continual acceleration towards the centre and the accelerated electric charge must emit radiation. The consequent loss of energy, should bring the electron down in a spiral path to the nucleus — that is the collapse of the atom.
A wave is a travelling disturbance that transports energy. Electromagnetic theory of light depicts propagation of light through space, as oscillating electric and magnetic fields; these fields are mutually perpendicular and also perpendicular to the direction of propagation of light. Further, the energy of a wave depends on the square of its amplitude.

Within two years, Niels Bohr suggested a better theory of the atom. Before studying Bohr's theory, let us analyse the wave properties of light and the reason for the failure of classical physics in describing the properties of sub-atomic particles like electrons.

**SAQ 1**
What is the essential difference between the atomic models proposed by Thomson and Rutherford?

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**1.4 LIGHT AS ELECTROMAGNETIC WAVE**

A beam of light has oscillating electric and magnetic fields associated with it. It is characterised by the properties such as frequency, wavelength and wave number. We can understand all these properties by considering, in general, a wave propagating in one dimension only (Fig. 1.5) along ABCDEFGHI.....

Electromagnetic theory of light depicts propagation of light through space, as oscillating electric and magnetic fields; these fields are mutually perpendicular and also perpendicular to the direction of propagation of light. Further, the energy of a wave depends on the square of its amplitude.

**Wavelength** $\lambda$ (Greek: *lambda*) is the distance between two successive crests or troughs. The length BF or DH in Fig 1.5 is equal to the wavelength and it is expressed in the unit, metre (m). The **frequency** is the number of waves per second. It is represented by the Greek letter $\nu$ (nu). Its unit is hertz (Hz). In fact, one hertz is equal to second$^{-1}$ ($s^{-1}$). Wavelength and frequency are related by the expression (1.1) where $c$ is the velocity of the light wave in the medium.

$$\lambda = \frac{c}{\nu} \quad \ldots \ldots (1.1)$$

In vacuum, $c = 2.998 \times 10^8 \text{ m s}^{-1}$, and we use this value for $c$ in our calculations. From the above expression, we understand that wavelength is inversely proportional to frequency.

The reciprocal of frequency is the period of oscillation, $T = \frac{1}{\nu}$. It indicates the time for one oscillation. Similarly the reciprocal of wavelength is the **wave number** ($\tilde{\nu}$: nu tilde). Wave number is related to frequency and wavelength as per Eq. 1.2.

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{c}{\nu} \quad \ldots \ldots (1.2)$$

The SI unit of $\tilde{\nu}$ is $\text{m}^{-1}$ although most of the literature values are in $\text{cm}^{-1}$. The peak height (KB or MF) or trough depth (LD or NH) is called the **amplitude** of the wave.

In section 1.6, we shall see how energy of a light wave is related to its frequency and wavelength. The electromagnetic spectrum describes the range of values of frequency and wavelength in the electromagnetic radiation. The characteristics of electromagnetic spectrum are given in Table 1.2.
Old Quantum Theory

Table 1.2: Characteristics of Electromagnetic Spectrum

<table>
<thead>
<tr>
<th>Description</th>
<th>Wavelength Range cm⁻¹</th>
<th>Wave Number cm⁻¹</th>
<th>Frequency Hz</th>
<th>Energy kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radio waves</td>
<td>3 x 10⁶ m</td>
<td>3.33 x 10⁶</td>
<td>10⁵</td>
<td>3.98 x 10⁻⁸</td>
</tr>
<tr>
<td>Microwave</td>
<td>0.30 m (600 μm)</td>
<td>0.0333</td>
<td>10⁹</td>
<td>3.98 x 10⁻⁸</td>
</tr>
<tr>
<td>Far infrared</td>
<td>0.8 μm (800 nm)</td>
<td>1.25 x 10⁴</td>
<td>3.75 x 10¹⁴</td>
<td>149.8</td>
</tr>
<tr>
<td>Near infrared</td>
<td>30 μm</td>
<td>333</td>
<td>10¹³</td>
<td>3.98</td>
</tr>
<tr>
<td>Visible</td>
<td>0.0006 m (600 μm)</td>
<td>16.6</td>
<td>4.98 x 10¹¹</td>
<td>0.191</td>
</tr>
<tr>
<td>Ultraviolet</td>
<td>0.8 μm (800 nm)</td>
<td>1.25 x 10⁴</td>
<td>3.75 x 10¹⁴</td>
<td>149.8</td>
</tr>
<tr>
<td>Vacuum ultraviolet</td>
<td>400 nm</td>
<td>2.5 x 10⁴</td>
<td>7.5 x 10¹⁴</td>
<td>299.2</td>
</tr>
<tr>
<td>X-rays and gamma-rays</td>
<td>5 nm</td>
<td>2 x 10⁹</td>
<td>6 x 10¹⁵</td>
<td>2.39 x 10⁴</td>
</tr>
</tbody>
</table>

At one end of the spectrum, there are X-rays and gamma-rays with low wavelength and high frequency; at the other end, we find radio waves and microwaves with high wavelength and low frequency. In Table 1.3 you can find the wavelength values of ultraviolet and visible light of different colours.

Table 1.3: Expanded Ultraviolet—Visible Region

<table>
<thead>
<tr>
<th>Colour</th>
<th>Wavelength/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultraviolet</td>
<td>200</td>
</tr>
<tr>
<td>Violet</td>
<td>410</td>
</tr>
<tr>
<td>Indigo</td>
<td>430</td>
</tr>
<tr>
<td>Blue</td>
<td>470</td>
</tr>
<tr>
<td>Green</td>
<td>520</td>
</tr>
<tr>
<td>Yellow</td>
<td>570</td>
</tr>
<tr>
<td>Orange</td>
<td>620</td>
</tr>
<tr>
<td>Red</td>
<td>710</td>
</tr>
</tbody>
</table>

It is seen that violet light has lower wavelength than the light of the red colour.

Let us calculate λ and ν values for a light having ν, 10¹⁵ Hz. According to the Eq. 1.1, \( \lambda = \frac{c}{\nu} \).

\[
= \frac{2.998 \times 10^8}{10^{15}} = 2.998 \times 10^{-7} \text{ m}
\]

= 299.8 nm.

using Eq. 1.2, \( \nu = \frac{c}{\lambda} \).

\[
= \frac{10^{15}}{2.998 \times 10^8} = 3.336 \times 10^6 \text{ m}^{-1} = 3.336 \times 10^4 \text{ cm}^{-1}.
\]

You can verify Eqs. 1.1 and 1.2 by substituting λ, ν and ν values for various regions, given in Table 1.2.

Using the above ideas, attempt the following SAQ.

SAQ 2
a) Calculate the frequency of yellow light, \( \lambda = 560 \) nm.

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1 millimetre = 1 mm = 10³ m
1 micrometre = 1 μm = 10⁻⁶ m
1 nanometre = 1 nm = 10⁻⁹ m
1 picometre = 1 pm = 10⁻¹² m
1 Ångstrom unit = 1 Å = 10⁻¹⁰ m

Calculation of energy in Table 1.2 is done using Eq. 1.6 given in sec. 1.6, where \( n \) is equal to Avogadro number \( (6.022 \times 10^{23}) \)
b) In VIBGYOR, relate the frequencies of different colours

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### 1.5 FAILURES OF CLASSICAL PHYSICS

The laws of motion put forward by Newton are the pillars of classical mechanics. Till 1900, it was thought that these classical concepts and laws hold good both for celestial bodies like planets and sub-atomic entities like electrons. Is this assumption quite acceptable? Is it advisable to use a lorry weigh-bridge to find the weight of a safety pin? Before trying to see whether classical mechanics is applicable to sub-atomic system, we have to be familiar with important assumptions of classical mechanics, viz.,

i) No restriction on the value that a dynamic variable (e.g. energy, momentum etc.) can have.

ii) No limit to the accuracy with which one or more of the dynamic variables of a system can be measured except the limit imposed by the precision of the measuring instruments.

iii) No restriction on the number of dynamic variables that can be accurately measured at the same time.

Added to classical mechanics, other tools in the bag of classical physics were thermodynamics, optics and electromagnetic theory. A number of experiments done in the latter half of nineteenth century and the first two decades of the present century gave results totally at variance with the predictions of classical physics. Let us now consider four specific cases given below, which indicated the inadequacy of classical physics:

i) black body radiation

ii) heat capacity variation

iii) photoelectric effect

iv) atomic spectra

As a first case, we shall take up black body radiation.

#### 1.5.1 Black Body Radiation

Black body radiation is the radiation emitted by a non-reflecting solid body. A **perfect black body is one which absorbs all the radiation falling on it.** Experimentally, a hollow body, blackened on the inside and with a small opening, is considered a typical black body. Any radiation that enters through the small opening is reflected repeatedly from the walls until all of the energy eventually becomes absorbed (Fig. 1.6a). A black body is both a good absorber and radiator of energy. Of the various types of bodies heated to particular temperature, only black body, radiates the maximum amount of energy. It radiates the same amount of energy as it absorbs.

![Fig. 1.6: (a) Black body radiation. The walls reflect and absorb light, entering the cavity; (b) Distribution of energy in black body radiation.](image)
The main aspects of black body radiation which emerge from experimental observations, are:

i) At shorter wavelength region, that is at higher frequency region, intensity of radiation is low.

ii) At every temperature, there is a wavelength at which energy radiated is maximum. This wavelength is called $\lambda_{\text{max}}$ value of that temperature.

iii) At higher temperatures, there is increased intensity of radiation in the shorter wavelength region.

These facts are pictorially represented in Fig. 1.6 (b).

A piece of iron, say at 375 K, is hot for the hand to touch but no visible radiation, i.e., shorter wavelength radiation, is emitted by the metal. However, with increase of temperature, it becomes progressively dull red, bright red, orange, yellow and white hot. In general, as temperature is increased, the radiation emitted, contains more of shorter wavelength region, whether it is from black body or an iron piece.

In contrast to the above experimental fact, the classical theory predicts that the black body ought to radiate over the whole wavelength region including visible region even at room temperature. As temperature is increased, the radiation emitted should get uniformly more intense. In other words, an iron piece even at room temperature, should radiate a little in the visible range.

When the evidence of eyes and fingers does not fit the predictions of the classical theory, it is time for this theory to be modified. In section 1.6, we shall see how quantum theory successfully explains the experimental facts regarding black body radiation.

1.5.2 Heat Capacity Variation

The second drawback of classical physics is its inadequacy in explaining heat capacity variation with temperature. Dulong and Petit, based on experimental evidence then available, proposed that the molar heat capacity at constant volume for metals must be equal to 24.93 J mol$^{-1}$ K$^{-1}$ irrespective of temperature. Molar heat capacity is the quantity of heat required to raise the temperature of one mole of a substance through one degree kelvin. Anyhow, the experiments performed at low temperatures reveal significant deviation from Dulong and Petit law. All metals are found to have molar heat capacities lower than 24.93 J mol$^{-1}$ K$^{-1}$ at low temperatures and the values appear to approach zero as temperature chosen is near absolute zero. In Section 1.6, we shall see how quantum theory explains heat capacity variation with temperature.

1.5.3 Photoelectric Effect

Let us now take up the third major setback to classical theory. The emission of electrons when metals are irradiated with ultraviolet light is known as photoelectric effect. This was observed by Hertz in 1887. The electrons, so emitted, are known as photoelectrons, to differentiate them from the electrons remaining inside the metal atoms. The main feature of this phenomenon is that a minimum frequency of light, known as threshold frequency ($\nu_0$), is required to emit photoelectrons. If the frequency of the incident light is less than this value, then photoelectrons are not emitted. The value of $\nu_0$ is a characteristic of the metallic surface used. Increasing the frequency of the light beyond threshold frequency value, only increases the velocity of the photoelectrons. These observations could not be explained by the nineteenth century view of light as wave phenomenon. In section 1.7, we shall see how Einstein's theory explains the experimental facts concerning photoelectric effect.

1.5.4 Atomic Spectra

The fourth front, where again classical theory failed, is the atomic spectra. Let us first understand what atomic spectrum is. When gases or vapours of a chemical substance are heated in an electric arc or bunsen flame, light is emitted. If a ray of this light is passed through a prism, a line spectrum is produced (Fig. 1.7).

This spectrum consists of a limited number of coloured lines, each of which corresponds to different wavelength of light. The line spectrum of each element is...
In the case of atoms, only electric transitions are possible and therefore, the spectrum is very simple consisting of electronic spectral lines. In the case of molecules, on the other hand, besides electronic transitions, transitions between rotational and vibrational energy levels are also possible and therefore molecular spectrum is relatively complex and has a large number of closely spaced lines and looks like a band (called band spectra).

On careful examination, it was found that in the atomic spectra of elements, spectral lines occur discretely at lower frequencies followed by a continuous spectrum at very high frequencies. An examination of a part of the spectrum of hydrogen as in Fig. 1.8a, indicates the presence of three groups of lines. One of them is in the visible region, and it was discovered by Balmer in 1885 (Fig. 1.8b). This series, known as Balmer series, has a mathematical relationship as shown by Eq. 1.3.

![Diagram of atomic spectra](image)

**Fig. 1.7: Apparatus for atomic spectra.**

**Fig. 1.8: (a) Atomic spectra of hydrogen. Only a few discrete lines followed by a continuum in the three series shown. Note the spacing \( \Delta V \) decreases as frequency increases in each series; that is, in each series, \( \Delta V_2 > \Delta V_3 > \Delta V_4 \).**

**Fig. 1.8: (b) Discrete lines followed by a continuum in Balmer series. Reproduced from the actual spectrum.**
In this equation, \( R \) is a constant, now known as Rydberg constant, having a value of \( 1.097 \times 10^7 \text{ m}^{-1} \) and \( n \) is a whole number having values 3, 4 etc.

You can see in Fig. 1.8b that the Balmer series consists of a series of spectral lines in which the distance of separation or spacing between the lines decreases, as the frequency increases. At very high frequencies, the spectral lines, converge to give a continuous spectrum or continuum. The other two series known as Lyman and Paschen series, with a similar pattern, occur in the far ultraviolet and infrared regions, respectively.

Further work by Rydberg showed that the lines in the atomic spectra of the alkali metals could be classified into a number of spectral series, each of which could be described by a relationship of the following type:

\[
\hat{\nu} = \frac{1}{\lambda} = R \left( \frac{1}{2^2} - \frac{1}{n^2} \right)
\]

In this relation, \( n \) is an integer and \( d \) is a constant. The Rydberg constant, \( R \), was shown to have the same value as mentioned above for all the elements and for the first time indicated a common link between the spectra of different elements.

Ritz (1908) showed experimentally that in any spectrum, it was possible to set up charts of quantities called terms, having dimensions of \( \text{cm}^{-1} \), such that the wave numbers of the observed spectral lines could be written as the difference of two terms. This is known as Ritz combination principle and in case of hydrogen, new spectral series were predicted for which the frequencies were given by:

\[
\hat{\nu} = R \left( \frac{1}{m^2} - \frac{1}{n^2} \right)
\]

Here \( m \) and \( n \) are integers and \( m \) is constant for a given series. This principle applies to two other series as well, namely, Lyman series and Paschen series.

Classical physics failed in its attempts to account for the appearance of various spectral series, each of which has discrete spectral lines at lower frequencies and a continuous spectra at higher frequencies. On the basis of classical physics, the atomic spectra was assumed to be consisting of a continuous band throughout. We shall see in section 1.11 as to how Bohr was partly successful in explaining the above observations.

### 1.6 PLANCK'S QUANTUM THEORY, BLACK BODY RADIATION AND HEAT CAPACITY VARIATION

The Quantum Theory, proposed by Max Planck in 1900, is the result of the realisation that the failure of classical physics is due to the wrong assumption that the energy of the system may take any arbitrary value. He suggested a detailed model for the processes taking place at the cavity walls. He considered the black body to consist of oscillators of molecular dimensions, each with a fundamental vibration frequency \( \nu \), and that each oscillator could emit energy only by a specified amount, known as quanta, but not continuously. His assumptions are given below:

i) An oscillator cannot have any energy, but only energies given by Eq. 1.6.

\[
E = n \hbar \nu = nE
\]

In this expression, \( \nu \) is the frequency of emitted radiation, while \( \hbar \) is a constant and \( n \) is an integer. Presently \( \hbar \) is called Planck's constant and \( n \) is known as quantum number. One quantum of energy, \( \epsilon \), is equal to the product \( \hbar \nu \). Planck evaluated the value of the constant \( \hbar \) as \( 6.626 \times 10^{-34} \text{ J s} \). So Eq. 1.6 asserts that the oscillator energy is quantised. It is interesting to know that \( \hbar \) is related to angular momentum, which is equal to linear momentum (mass \( \times \) velocity) multiplied by length.

ii) The oscillators do not radiate energy continuously but only in quanta. These quanta of energy are emitted when an oscillator changes from one quantised energy state to another. Thus, if the oscillator goes from the level \( n+1 \) to \( n \), we get from Eq. 1.6, the amount of energy radiated as,

\[
\Delta E = E_2 - E_1 = (n+1)\hbar \nu - n\hbar \nu = \hbar \nu
\]

\( \epsilon, \epsilon \), epsilon, stands for one quantum of energy, \( \hbar \nu \).

Unit of \( \hbar = J \text{ s} \)

\( = \text{kg m}^2 \text{ s}^{-2} \cdot \text{s} = \text{kg m}^2 \text{ s}^{-1} = (\text{kg m s}^{-1}) \text{ m} = (\text{Unit of mass \times unit of velocity}) \times \text{unit of length} = (\text{Unit of linear momentum}) \times \text{unit of length} = \text{Unit of angular momentum} \)

\( h \) is also known as action constant; later in Unit 2, we shall see how \( h \) relates wave and particle aspects of sub-atomic particles.
Also an oscillator neither absorbs nor emits energy as long as it remains in the same quantised state.

Let us now see in a qualitative way how Planck's theory is useful in explaining black body radiation. The number of oscillators possessing sufficient energy \( e \), otherwise known as oscillator population at that energy level, is proportional to the exponential term, \( e^{-\frac{E}{kT}} \), known as Boltzmann factor. Here \( T \) is the temperature and \( k \), the Boltzmann constant. The intensity of radiation is proportional to the oscillator population at a particular energy level. Hence the intensity of radiation is proportional to \( e^{-\frac{E}{kT}} \). Using Eq. 1.6, we can say that the intensity of radiation is proportional to the quantity, \( e^{-\frac{E}{kT}} \). The term \( e^{-\frac{E}{kT}} \) is in fact equal to \( e^{\frac{h\nu}{kT}} \) and hence is a fraction. As \( \nu \) increases, the value of the fraction \( e^{-\frac{E}{kT}} \) and also the population of the oscillators decrease. It is something like decreasing the percentage of successful students at an examination by increasing the minimum pass marks! This means, the intensity of radiation of higher frequency region or shorter wavelength region is low (Fig. 1.6b).

The intensity of radiation is increased, once the temperature is increased. Since \( T \) is in the denominator of the exponential term, when \( T \) increases, \( e^{\frac{h\nu}{kT}} \) decreases. Hence, increase of temperature increases the value of \( 1/e^{\frac{h\nu}{kT}} \) and the intensity of radiation. That is, more radiation of even shorter wavelengths will be emitted at higher temperatures (Fig. 1.6b). Planck, using a mathematical approach, was able to explain the \( \lambda_{max} \) value at each temperature.

Apart from explaining the black body radiation, Planck's theory is useful in calculating the energy of oscillators from the frequency values. The values of energy are given in Table 1.2 in kJ mol\(^{-1}\) as per Eq. 1.6 for each constituent of electromagnetic radiation, assuming that \( n \) is numerically equal to Avogadro number.

A ray of light having frequency \( \nu \) can be considered as a stream of particles, each one having energy \( h\nu \). These particles are now known as photons. This means that if a ray carries an energy \( E \) into some region, then the number of photons \( n \), arriving is \( \frac{E}{h\nu} \).

Planck's theory was extended by Einstein to explain heat capacity variation with temperature. Energy was considered to be taken up by the vibrations of particles. Einstein assumed that each atom could vibrate about its equilibrium position with a single frequency \( \nu \). He derived an expression to calculate the heat capacity and used it successfully to explain the decrease of heat capacity at low temperatures. The physical reason for this success is that at low temperatures only a few oscillators possess enough energy to begin oscillating. At higher temperatures, energy is available for all the oscillators to become active and the heat capacity approaches its classical value as predicted by Dulong and Petit law. The essence of Einstein's theory of heat capacities is that quantisation must be introduced in order to explain thermal properties of matter.

Using the above ideas, try the following SAQ.

**SAQ 3**
A yellow bulb generates \( 2.80 \times 10^{20} \) photons with \( \lambda = 560 \) nm. Calculate the total energy generated.

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**1.7 EINSTEIN'S THEORY OF PHOTOELECTRIC EFFECT**

Applying the photon concept to the photoelectric effect, Einstein proposed that an electron at the surface of the metal gains an energy \( h\nu \) by the absorption of a photon from the electromagnetic radiation. If the frequency \( \nu \) of the photon is greater than the minimum value \( \nu_0 \), called threshold frequency which is characteristic of a particular metal, then the emission of photoelectron occurs. The difference, \( h\nu - \nu_0 \),
is transformed as the kinetic energy of the photoelectron which is equal to \( m^2/2 \). In conformity with the principle of conservation of energy, Einstein's theory can be stated as:

\[
\hbar \nu - \hbar \nu_0 = m^2/2
\]  

...(1.8)

In this expression, \( \nu \) and \( \nu_0 \) are the photon and threshold frequencies, respectively while \( m \) and \( v \) are the mass and velocity of the photoelectron. If \( \nu < \nu_0 \), then \( m^2/2 \) is negative which is meaningless. That is, **photoelectron emission does not take place when \( \nu \) is less than \( \nu_0 \).** Using Eq. 1.8, you try the following SAQ.

**SAQ 4**

Calculate the frequency of the radiation required to eject photoelectrons at a velocity of \( 9 \times 10^5 \) m s\(^{-1} \) from sodium metal surface, having a threshold frequency of \( 4.61 \times 10^{14} \) Hz (mass of the photoelectron = \( 9.109 \times 10^{-31} \) kg).

---

### 1.8 BOHR ATOM MODEL

The quantum theory was applied by the Danish physicist, Niels Bohr (1913) to explain the spectrum of hydrogen atom. He suggested an atom model which is an improvement over Rutherford model described in section 1.3.

Bohr based his theory on the following postulates:

i) An electron can exist only in orbits of definite angular momentum and energy. Each orbit is known as a **stationary state**.

ii) The electron does not radiate energy when it is in an allowed orbit.

iii) While in an orbit, the angular momentum of the electron, \( mvr \), is an integral multiple of \( \hbar/2\pi \) units.

\[
\frac{mvr}{2\pi} = \frac{\hbar n}{2\pi} 
\]  

...(1.9)

Where \( m \) and \( v \) stand for the mass and velocity of the electron, \( r \) is the orbit radius and \( n \) is an **integer called principal quantum number**. The orbits are called \( K, L, M, N, \ldots \) depending on the values of \( n \), viz., 1, 2, 3, 4, \ldots At the time this view was proposed, there was no reason for the quantisation of angular momentum. Anyhow, in section 1.6 you saw, how \( \hbar \) has the units of angular momentum.

iv) Each spectral line is produced by a single electron. When an electron jumps from one orbit to another, radiation of a definite frequency is emitted or absorbed giving rise to a definite spectral line. The frequency of the spectral line is related to the difference in energy, \( \Delta E \), between initial and final levels, as per the equation:

\[
\Delta E = h\nu = h\nu_0
\]  

...(1.10)

Using the above postulates, he was able to calculate the radius of different orbits in hydrogen atom, the energy of the electron in its orbits and the frequency of the spectral lines.

---

### 1.9 CALCULATION OF RADIUS OF ORBITS

Bohr atom model considers an electron of charge \( -e \) and mass \( m \) revolving round the nucleus of charge \( +Ze \) with velocity \( v \) in a stationary orbit of radius \( r \) (Fig. 1.9). The nuclear charge is taken as \( +Ze \) since the nucleus is assumed to contain \( Z \) protons and each proton has charge \( +e \).

For attaining mechanical stability, the electrostatic force of attraction, \( f_a \), between the electron and the nucleus must be equal to the centrifugal force, \( f_c \), which is operating in the opposite direction.

\[
i.e., \quad f_a = -f_c
\]  

...(1.11)
Note the negative sign in Eq. 1.11 which indicates that one type of force opposes the other. The electrical force of attraction, \( f_a \), is proportional directly to the product of charges, \( -e \) and \( Ze \), and inversely to the square of the distance of separation, \( r^2 \), between the nucleus and the electron.

\[
f_a \propto \frac{(-e)(+Ze)}{r^2}
\]

i.e. \( f_a = \frac{-Ze^2}{(4\pi\varepsilon_0)r^2} \) ....(1.12)

Here \( (4\pi\varepsilon_0)^{-1} \) is a proportionality constant in SI units. The term, \( \varepsilon_0 \), is the permittivity in vacuum, and it is equal to \( 8.854 \times 10^{-12} \text{C}^2\text{N}^{-1}\text{m}^{-2} \). The terms \( e \) and \( r \) have coulomb (C) and metre (m) units, respectively while \( Z \) is unitless.

The centrifugal force, \( f_c = \frac{mv^2}{r} \) ....(1.13)

Substituting Eq. 1.12 and Eq. 1.13 in Eq. 1.11,

\[
\frac{-Ze^2}{(4\pi\varepsilon_0)r^2} = \frac{-mv^2}{r}
\]

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

Rearranging Eq. 1.9, we can write, \( v = \frac{n\hbar}{2\pi mr} \)

Squaring both sides, \( v^2 = \frac{n^2\hbar^2}{4\pi^2m^2r^2} \)

Multiplying both sides by \( m \),

\[
m^2v^2 = \frac{n^2\hbar^2}{4\pi^2mr^2} \]

Substituting Eq. 1.14 in Eq. 1.15 we get,

\[
\frac{Ze^2}{4\pi\varepsilon_0 r} = \frac{n^2\hbar^2}{4\pi^2mr^2}
\]

\[
r = \frac{n^2\hbar^2}{\pi mZe^2} \]

Eq. 1.16 is useful in calculating the radius of the orbits with different \( n \) values. As an illustration, we calculate the radius of the first Bohr orbit \( (r_1) \) for hydrogen atom \( (n=1, Z=1) \).

\[
r_1 = \frac{1^2 \times 8.854 \times 10^{-12}}{3.142 \times 9.109 \times 10^{-31} \times 1 \times (1.602 \times 10^{-19})^2}
\]

\[
= 53 \times 10^{-12} \text{m} = 53 \text{ pm (rounded to whole number)}
\]

Using this value in Eq. 1.16, a general expression for the radius of the different orbits of hydrogen atom is given below:

\[
r = 53 n^2 \text{ pm} \] ....(1.17)

From Eq. 1.17, you can infer that radius of a particular orbit in hydrogen atom is proportional to the square of its principal quantum number value. This is illustrated in Fig. 1.10.

![Fig. 1.10: The radius of the orbits in hydrogen atom is proportional to \( n^2 \) values. First three orbits only shown; \( r_1 : r_2 : r_3 = 1:4:9 \).](image)
The unit, picometre (pm), is quite convenient in describing the radius of the orbits in atoms.

**SAQ 5**
Calculate the radius of the second orbit in hydrogen atom.

---

### 1.10 ENERGY OF AN ELECTRON IN AN ORBIT

The total energy, \( E_n \), of an electron in \( n \)th orbit, is given by the sum of its potential energy (P.E.) and kinetic energy (K.E.), i.e.,
\[
E_n = \text{P.E.} + \text{K.E.}
\]... (1.18)

The potential energy of the electron is defined as the work necessary to take the electron to infinity from its equilibrium distance \( r \), with respect to the nucleus. Since the coulombic force \( (f_a) \) between the electron and nucleus is \( -\frac{Ze^2}{4\pi\epsilon_0 r^2} \), as per Eq. 1.12, potential energy is calculated as follows:

\[
P.E. = \int_r^\infty f_a \cdot dr
= \int_r^\infty -\frac{Ze^2}{4\pi\epsilon_0 r^2} \cdot dr
= -\frac{Ze^2}{4\pi\epsilon_0} \left[ -\frac{1}{r} \right]^\infty_r
= -\frac{Ze^2}{4\pi\epsilon_0r}.
\]

P.E. = \( -\frac{Ze^2}{4\pi\epsilon_0r} \); also, K.E. = \( \frac{mv^2}{2} \)

The negative sign indicates that work must be done on the electron to remove it to infinity.

So substituting the values of P.E. and K.E. in Eq. 1.18, we get,
\[
E_n = \frac{mv^2}{2} - \frac{Ze^2}{4\pi\epsilon_0r} \quad \ldots(1.19)
\]

From Eq. 1.14, \( \frac{mv^2}{2} = \frac{Ze^2}{8\pi\epsilon_0r} \) \ldots(1.20)

Substituting Eq. 1.20 in Eq. 1.19,
\[
E_n = \frac{Ze^2}{8\pi\epsilon_0r} - \frac{Ze^2}{4\pi\epsilon_0r}
= \frac{-Ze^2}{8\pi\epsilon_0r} \quad \ldots(1.21)
\]

Substituting for \( r \) from Eq. 1.16,
\[
E_n = \frac{-Ze^2}{8\pi\epsilon_0} \cdot \frac{\pi m Ze^2}{n^2\epsilon_0 h^2}
= \frac{-Ze^4 m}{8\pi^2 \epsilon_0^2 h^2 n^2} \quad \ldots(1.22)
\]

The negative sign in this expression denotes the fact that there is attraction between the nucleus and the electron; so work must be done to move it to a distance greater than the equilibrium distance \( r \) from the nucleus.

Substituting the values of \( e, m, \epsilon_0 \) and \( h \) in Eq. 1.22, the energy of the electron in the \( n \)th orbit of hydrogen atom is obtained as,
You must remember that \( Z = 1 \) for hydrogen atom. In the first orbit, \( n = 1 \), the energy of the electron is equal to \(-2.178 \times 10^{-18} \text{ J}\). Since \( E_n \) is related to \( n^2 \) in Eq. 1.22, the increase in energy with the value of \( n \) is, as shown, in Table 1.4.

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \frac{E_n}{J} = \frac{-2.178 \times 10^{-18}}{n^2} )</th>
<th>( \frac{E_n - E_{n-1}}{J} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(-2.178 \times 10^{-18})</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>(-5.445 \times 10^{-19})</td>
<td>(1.634 \times 10^{-18})</td>
</tr>
<tr>
<td>3</td>
<td>(-2.42 \times 10^{-19})</td>
<td>(3.025 \times 10^{-19})</td>
</tr>
<tr>
<td>4</td>
<td>(-1.361 \times 10^{-19})</td>
<td>(1.059 \times 10^{-19})</td>
</tr>
<tr>
<td>5</td>
<td>(-8.712 \times 10^{-20})</td>
<td>(4.898 \times 10^{-20})</td>
</tr>
</tbody>
</table>

The successive differences in energy values in Table 1.4 are obtained to show how successive energy levels become closer. So energy levels are distinctly discrete at lower \( n \) values. As \( n \) becomes sufficiently large, the energy levels differ only slightly. This is called convergence of the energy levels. This principle will be helpful to you in understanding the atomic spectra of hydrogen described in the next section. But before proceeding to the next section, why don’t you try the following SAQ?

**SAQ 6**

What is the energy value of an electron if \( n = \infty \)?

---

**1.11 ATOMIC SPECTRA AND BOHR’S THEORY**

Bohr’s theory is useful in calculating the frequencies of spectral lines in the atomic spectra of hydrogen. Let us assume that \( E_1 \) and \( E_2 \) represent the energies at the inner and outer quantum number values \( n_1 \) and \( n_2 \), respectively. Using Eq. 1.22 we can write,

\[
E_1 = \frac{-Z^2 e^4 m}{8e_0^2 h^2} \cdot \frac{1}{n_1^2} \quad \ldots (1.24)
\]

\[
E_2 = \frac{-Z^2 e^4 m}{8e_0^2 h^2} \cdot \frac{1}{n_2^2} \quad \ldots (1.25)
\]

The amount of energy emitted when an electron jumps from an outer level \( n_2 \) to an inner level \( n_1 \) is given by,

\[
E_2 - E_1 = \frac{-Z^2 e^4 m}{8e_0^2 h^2} \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right)
\]

Representing this quantity as \( \Delta E \),

\[
\Delta E = \frac{Z^2 e^4 m}{8e_0^2 h^2} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \ldots (1.26)
\]

Substituting Eq. 1.10 in Eq. 1.26, it is possible to get the wave numbers of spectral lines as given by the expression,

\[
\tilde{\nu} = \frac{\Delta E}{\hbar c} = \frac{Z^2 e^4 m}{8e_0^2 h^3 c} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \ldots (1.27)
\]
The term \( \frac{Z^2 e^4 m}{8 \epsilon_0^2 \hbar^2 c} \) is called Rydberg constant for hydrogen atom. It is equal to

\[ 1.097 \times 10^7 \text{m}^{-1} \]

and is denoted by the symbol \( R_s \). Equation for hydrogen atom can be written as

\[ \tilde{\nu} = R_s \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \cdots(1.28) \]

You can see that Eq. 1.28 is similar in form to Eqs. 1.3, 1.4 or 1.5 given in Subsec 1.5.4. In the above derivation, it has been assumed that the nucleus is fixed at the centre of the orbits. In fact, nucleus and the electrons are both rotating about the common centre of mass. Anyhow, by using Eq. 1.28, we can calculate the frequencies of the spectral lines in Lyman, Balmer, Paschen, Brackett and Pfund series although at the time Bohr formulated his theory, only Balmer and Paschen series were known. For these five series in the atomic hydrogen spectra, the values of \( n_1 \) and \( n_2 \) are given in Table 1.5.

<table>
<thead>
<tr>
<th>Name of the series</th>
<th>( n_1 )</th>
<th>( n_2 )</th>
<th>Region</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lyman</td>
<td>1</td>
<td>2,3,4…</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>Balmer</td>
<td>2</td>
<td>3,4,5…</td>
<td>Visible</td>
</tr>
<tr>
<td>Paschen</td>
<td>3</td>
<td>4,5,6…</td>
<td>Infrared</td>
</tr>
<tr>
<td>Brackett</td>
<td>4</td>
<td>5,6,7…</td>
<td>Infrared</td>
</tr>
<tr>
<td>Pfund</td>
<td>5</td>
<td>6,7,8…</td>
<td>Infrared</td>
</tr>
</tbody>
</table>

A diagrammatic representation of spectral transitions among the different energy levels is given in Fig. 1.11.

![Spectral transitions among different energy levels. Note, for Balmer series, the corresponding spectral lines are shown.](image_url)
Note that the spacing between two successive levels becomes smaller, as \( n \) increases. We have mentioned about the converging nature of energy levels in section 1.10 also. Experimentally it has been found that within a particular series, for example, Lyman series, the lines in the spectrum of atomic hydrogen are discrete at lower frequencies and they converge as the frequency increases. Each successive line becomes closer to the previous one. This is quite evident from the spacings of the first four lines in Lyman series, as entered in the last column of Table 1.6.

### Table 1.6: Wave Number Values in Lyman Series

<table>
<thead>
<tr>
<th>Number of the spectral line ( n )</th>
<th>( n_1 )</th>
<th>( n_2 )</th>
<th>( \frac{\nu}{m^3} = 1.097 \times 10^7 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) )</th>
<th>Spacing ( \left( \nu_n - \nu_{n+1} \right)/m^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>2</td>
<td>8.228 \times 10^6</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>3</td>
<td>9.751 \times 10^6</td>
<td>1.523 \times 10^6</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>4</td>
<td>1.028 \times 10^7</td>
<td>5.29 \times 10^6</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>5</td>
<td>1.053 \times 10^7</td>
<td>2.5 \times 10^5</td>
</tr>
</tbody>
</table>

As Eq. 1.26 predicts, each series of lines converges towards a limit beyond which the spectrum is continuous. At this point, electron responsible for the spectral line has been excited into an orbit of such high energy \( (n_2 = \infty) \) that it has effectively escaped from the influence of the nucleus. In other words, the atom has lost its electron and formed a positive ion:

\[
\text{H}(g) \rightarrow \text{H}^+(g) + e^-
\]

The energy difference between the ground state of hydrogen atom, and the excited state that corresponds to convergence limit of the spectral lines, \( n_2 = \infty \), is called the ionisation energy of hydrogen atom. Note that ionisation energies refer to the removal of an electron in the gas phase. We will study more about ionisation energies in section 1.12 and in Unit 3.

Thus, Bohr's theory can explain the appearance of discrete spectral lines at lower frequencies and a continuous spectra at higher frequencies in the atomic spectra of hydrogen. In the light of what you have studied above, answer the following SAQ.

**SAQ 7**

What is the reason for the increase in the spectral frequency as \( n_2 \) increases?

Let us examine how the theoretical model of Bohr is able to explain some of the features given below:

- atomic spectra of hydrogen
- Rydberg constant value
- ionisation energy of hydrogen
- prediction of new elements

Bohr's theory is successful as an atom model to the extent that its findings are consistent with atomic spectra of hydrogen. The agreement between the theoretical and experimental values of spectral frequencies is a testimony to the validity of this theory. Again, the value of Rydberg constant, calculated according to Bohr's theory, is in agreement with the experimental value.

Ionisation energy of hydrogen atom is defined as the minimum energy necessary to remove the electron from \( n = 1 \) state to infinite distance \( (n_2 = \infty) \) leaving it without any kinetic energy and it can be calculated using Eq. 1.28 For hydrogen atom, the ionisation energy in the wave number unit,

\[
R_{1\infty} \left( \frac{1}{1^2} - \frac{1}{\infty^2} \right) = R_{1\infty} = 1.097 \times 10^7 \text{ m}^{-1}
\]
For the purposes of chemical calculation, ionisation energy of hydrogen may be defined as the energy required to remove one mole of electrons, i.e., 6.022 x 10^{23} electrons from one mole hydrogen atoms in the ground state. Hence, ionisation energy

\[
\begin{align*}
&= 6.022 \times 10^{23} \times 9.109 \times 10^{-31} \\
&= 6.022 \times 10^{-19} \times 9.109 \times 10^{-31} \\
&= 5.50 \times 10^{-19} \text{ J mol}^{-1} \\
&= 1.312 \times 10^3 \text{ J mol}^{-1} \\
&= 1312 \text{ kJ mol}^{-1}.
\end{align*}
\]

Thus Bohr's theory offers a method of calculating ionisation energy of hydrogen and this principle has been extended to other elements in calculating their ionisation energies.

From spectral studies, Bohr constructed a theoretical periodic chart which agreed with Mendeleev's chart. On the basis of atomic spectra, Bohr was able to predict that the element with \( Z = 72 \), has properties similar to titanium \( (Z = 22) \), and zirconium \( (Z = 40) \), and this element was later discovered and named hafnium.

**Limitations of Bohr's Theory**

According to Bohr's theory, angular momentum of the electron can never be zero. However, later on, wave mechanics (Unit 2) shows that in \( n = 1 \) state, electron has zero angular momentum.

The hyperfine structure in the atomic spectra of hydrogen is not well explained by Bohr's theory. Further this theory does not explain how molecules are formed from atoms. It does not recognise the wave properties of electrons. Just like electromagnetic radiation, the electron also has both particle and wave aspects. Using the crystal spacings in a nickel crystal as a diffraction grating, it is possible to obtain diffraction patterns that could be understood in terms of wave motion of the electron. But Bohr's theory has not provided any explanation for this phenomenon. According to Bohr's theory, electron moves in orbits known as stationary states. The path of this orbit (or its trajectory) can be known only if we know simultaneously both the position and the velocity of electron. It, therefore, assumes the accurate and simultaneous determination of both position and velocity of the electron. But this assumption is not in conformity with the wave nature of electron. In the next unit, we shall see, how theories were developed by Heisenberg and Schrödinger to explain the wave characteristics of electrons.

**1.13 REFINEMENTS IN THE ATOMIC SPECTRA THEORY**

Sommerfeld (1916) modified Bohr's theory and tried to interpret the fine structure in the atomic spectra of hydrogen as due to elliptical path of the electron. He introduced another quantum number, known as azimuthal quantum number, which was by later modifications represented as \( l \) and shown to have values \( 0,1,\ldots,(n-1) \) where \( n \) is the principal quantum number. Thus if \( n = 2 \), then \( l \) can have values \( 0 \) and \( 1 \).

The splitting of spectral lines when atoms are placed in a strong magnetic field, known as Zeeman effect, could also be partially explained by introducing magnetic quantum number \( m_l \) describing the allowed orientations of electron orbits in space. It was shown that for each value of \( l \), \( m_l \) can have \( 2l + 1 \) values namely from \(+l\) to \(-l\). Hence if \( l = 1 \), \( m_l \) can have three values, \(+1\), \(0\) and \(-1\). You will see in the next unit, an alternate way of arriving at the quantum numbers \( n \), \( l \) and \( m_l \).

**SAQ 8**

a) If \( n = 3 \), what are the possible values of \( l \)?
b) If \( l = 2 \), what are the values of \( m_l \)?

---

1.14 SUMMARY

In this unit, we have focused our attention on the developments leading to Bohr atom model. The instances and reasons for the failure of classical physics are given. Using quantum theory, Planck, Einstein and Bohr explained black body radiation, heat capacity variation, photoelectric effect and atomic spectra of hydrogen. But each of the above theories had limited success. No doubt these theories rejected the classical concept of the arbitrary energy values for an atomic system. But with regard to other major cracks in the classical theory, namely simultaneous and precise determination of position and momentum, no remedy has been suggested. This loophole was plugged by de Broglie, Heisenberg and Schrödinger and we shall study in the next unit about their concepts, collectively known as Wave Mechanics. Since wave mechanics is based on new quantum postulates, the theories proposed by Planck, Einstein and Bohr are collectively called Old Quantum Theory.

1.15 TERMINAL QUESTIONS

1) Explain the significance of \( \alpha \)-ray scattering experiment.

2) In what way is the analogy between an atom and solar system contradicting classical electromagnetic theory?

3) For a light of wavelength 300 nm, calculate frequency, wave number, energy per quantum and energy per mole.

4) Specify three major theoretical routes used for explaining atomic structure.

5) For the following statements, mark T for correct statements and F for false ones.
   a) The cathode rays carry positive charge.
   b) Neutrons were discovered when beryllium was bombarded by \( \alpha \)-particles.
   c) The frequency of X-rays is less than that of microwaves.
   d) The unit for wave number is \( \text{m}^{-1} \).
   e) The threshold frequency is the same for all the metals.

6) Explain the two main reasons for the failure of classical mechanics.

7) a) Explain the salient features of black body radiation.
   b) In what way, classical theory is inadequate in explaining black body radiation?

8) a) Define photoelectric effect.
   b) State the mathematical form of Einstein’s theory of photoelectric effect.

9) Calculate the wavelength of the light required to eject a photoelectron from caesium metal with a kinetic energy of \( 2.0 \times 10^{-19} \) J \( (\nu_0 \text{ for caesium is } 4.55 \times 10^{14} \text{ Hz}) \).

10) State Ritz combination principle.

11) What do you think is the most novel idea among Bohr’s postulates?

12) Derive an expression relating radius of the atom to the mass, charge and orbit number of the electron.

13) Calculate the radius of the third orbit in hydrogen atom using Bohr’s theory.

14) Derive an expression useful in calculating the energy of an electron in \( n \)th orbit of hydrogen atom.

15) What are the energy values of the electron in the third and fourth orbits of hydrogen atom?

16) a) From the expression, \( R_n = \frac{Z^2e^4m}{8\varepsilon_0^2\hbar^3c} \), find the value of \( R_4 \).
   
   b) What is the value of \( R_4 \) in \( \text{cm}^{-1} \)?
17) Calculate the wave numbers of the first two lines in Balmer series.

18) Explain the limitations of Bohr’s theory.

### 1.16 ANSWERS

**SAQs**

1) Thomson proposed that electrons are distributed within a sphere of positive electricity whereas Rutherford thought that the electrons move around a central positively charged nucleus.

2) a) \( \nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8}{560 \times 10^{-9}} \) Hz = \( 5.35 \times 10^{14} \) Hz.

   b) \( \nu_R < \nu_G < \nu_I < \nu_H < \nu_A < \nu_V \).

3) \( E = n h \nu = \frac{n h c}{\lambda} \)
   
   \[
   = \frac{2.80 \times 10^{20} \times 6.626 \times 10^{-34} \times 2.998 \times 10^8}{560 \times 10^{-9}} \quad J = 99.3 \text{ J}.
   \]

4) \( \nu = \frac{(h \nu_i + \frac{mv^2}{2})}{h} \)
   
   \[
   = \frac{(6.626 \times 10^{-34} \times 4.61 \times 10^{14} \times \frac{1}{2} \times 9.109 \times 10^{-31} \times (9 \times 10^8)^2)}{6.626 \times 10^{-34}} \text{ Hz}
   \]
   
   \[
   = 1.02 \times 10^{15} \text{ Hz}.
   \]

5) \( r_2 = 53 n^2 \text{ pm} = 53 \times 2^2 \text{ pm} = 212 \text{ pm} \).

6) \( E_{\infty} = 0 \).

7) The electron in an outer orbit has higher energy than while in an inner orbit, i.e., as \( n_2 \) increases, \( E_2 \) also increases. Since \( E_1 \) remains constant, the spectral frequency increases with increase of \( n_2 \).

8) a) \( l = 0, 1 \) and \( 2 \),

   b) \( m_l = +2, +1, 0, -1, -2 \).

**Terminal Questions**

1) This experiment was utilised by Rutherford to formulate nuclear atom model.

2) According to classical theory, an electron being a charged particle, as it moves, must gradually lose its energy and fall into the nucleus.

3) \( \nu = 9.993 \times 10^{14} \text{ Hz}; \quad \nu = 3.333 \times 10^8 \text{ m}^{-1}; \quad c = 6.621 \times 10^{-19} \text{ J}; \quad E = 398.8 \text{ kJ mol}^{-1} \).

4) Classical mechanics, old quantum theory and wave mechanics.

5) a) F  b) T  c) F  d) T  e) F.

6) i) Energy can have any arbitrary value,

   ii) Simultaneous fixation of position and momentum is possible.

7) a) i) At shorter wavelength region, intensity of radiation is low.

   ii) As temperature increases, the intensity of radiation in the shorter wavelength region also increases.

   b) Classical theory suggested that black body must radiate over the whole wavelength region.

8) a) Emission of photoelectrons when a metal is irradiated with ultraviolet light.

   b) \( h \nu - h \nu_o = \frac{mv^2}{2} \).

9) \[
\frac{hc}{\lambda} = h \nu_o + \frac{mv^2}{2}
\]
   
   \[
= \left[ (6.626 \times 10^{-34} \times 4.55 \times 10^{14} \right] + 2.0 \times 10^{-19} \right) J
\]

   \[
\lambda = 396.1 \text{ nm}.
\]

10) The wavelength of each spectral line could be written as difference between two terms.
11) Quantisation of angular momentum.

12) By balancing the force of attraction with centrifugal force, the equation can be derived. The final expression is,

\[ r = \frac{n^2 \epsilon_0 h^2}{\pi m Z e^2}. \]

13) \( r_3 = 9r_1 = 477 \text{ pm}. \)

14) Total energy of the electron is calculated by adding its kinetic energy and potential energy terms. The final expression is

\[ E_n = \frac{-Z^2 e^4 m}{8 \epsilon_0^2 n^2 h^2}. \]

15) \(-2.42 \times 10^{-19} \text{ J}; -1.361 \times 10^{-19} \text{ J}. \)

16) a) Substitution of the values of the various parameters gives:

\[ R_{14} = 1.091 \times 10^7 \text{ m}^{-1}, \]

b) \(1.097 \times 10^8 \text{ cm}^{-1}. \)

17) \(1.524 \times 10^6 \text{ m}^{-1}; 2.057 \times 10^6 \text{ m}^{-1}. \)

18) Bohr's theory cannot explain the hyperfine structure in the atomic spectra of hydrogen or the atomic spectra of multi-electron elements. It cannot explain the formation of molecules from atoms. It does not take into account the wave property of electron.