2.4 DUAL NATURE OF RADIATION

In order to explain several phenomena like *interference, diffraction* and *polarization*, it is necessary to assume that electromagnetic *radiation has wave nature*.

To explain the observed results connected with the interaction of radiation with matter, such as the *blackbody radiation*, the *photoelectric effect* and the *Compton effect*, it becomes necessary to assume that *radiation has particle nature*—it is emitted or absorbed in the form of discrete quanta called photons. Thus, we have to accept the paradoxical situation that ***radiation has dual nature.***

1.4 ATOMIC SPECTRA

- All elements in atomic state emit line spectra.
- A line spectrum consists of narrow bright lines separated by dark intervals.
- It is characteristic of the atoms of the element which emits it.
- This makes spectroscopy a very important tool of chemical analysis because measurement of the wavelengths emitted by a material allows us to identify the elements present in it, even in very small amounts.
- It was found that the wavelengths present in the atomic spectrum of an element fall into sets which exhibit some definite pattern. Such a set is called a *spectral series*.
- In 1885, Johann Balmer showed that the wavelengths of all the spectral lines of the hydrogen atom known till then could be expressed by the formula

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad n = 3,\ 4,\ 5,\ \ldots$$

The constant R is known as the Rydberg constant. Its value is $1.097 \times 10^7 m^{-1}$. This set of lines lies in the visible part of the electromagnetic spectrum and is called the ***Balmer series.***

Other series of lines were discovered for the hydrogen atom in different regions of the electromagnetic spectrum.

Lyman Series: Ultraviolet Region

$$\frac{1}{\lambda} = R\left(\frac{1}{1^2} - \frac{1}{n^2}\right) \quad n = 2, 3, 4, \ldots$$

Paschen Series: Infrared Region

$$\frac{1}{\lambda} = R\left(\frac{1}{3^2} - \frac{1}{n^2}\right) \quad n = 4, 5, 6, \ldots$$

Brackett Series : Infrared Region

$$\frac{1}{\lambda} = R\left(\frac{1}{4^2} - \frac{1}{n^2}\right) \quad n = 5, 6, 7, \ldots$$

Pfund Series : Infrared Region

$$\frac{1}{\lambda} = R\left(\frac{1}{5^2} - \frac{1}{n^2}\right) \quad n = 6, 7, 8, \ldots$$

All the above formulae are special cases of the general formula

$$\boxed{\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)} \quad \ldots(1.19)$$

where n_1 and n_2 are positive integers with $n_1 < n_2$ and $n_2 = n_1 + 1, n_1 + 2, \ldots$. This is known as the **Rydberg-Ritz formula**.

It may be noted that the above formula expresses the wave number $(1/\lambda)$ of any line as the difference of two terms of the type

$$T_n = \frac{R}{n^2} \quad n = 1, 2, \ldots$$

1.5 BOHR MODEL OF HYDROGENIC ATOMS

In 1913, a major step forward was taken by Niels Bohr. He suggested that the classical electromagnetic theory is not applicable to the processes at the atomic scale. He then combined Rutherford's nuclear model with the quantum idea of Planck and Einstein to develop a theory of hydrogenic atoms. These are also called hydrogen-like atoms. The theory was remarkably successful in explaining the observed spectrum of hydrogen.

Though Bohr's theory is incorrect and has now been replaced by the quantum mechanical treatment, it still remains an important milestone in the development of atomic physics and it is essential for the student to understand it before proceeding to the more correct theories.

The Bohr model is based on the following **postulates**:

1. The electron can revolve around the nucleus only in certain allowed circular orbits of definite energy and in these orbits it does not radiated. These orbits are called **stationary orbits**.
2. The angular momentum of the electron in a stationary orbit is an integral multiple of $\hbar(= h/2\pi)$, h being Planck's constant:

$$l = mvr = n\hbar$$

where m is the mass of the electron, v is its speed, r is the radius of the orbit and n is a positive integer.

3. The electron can make a transition from one orbit to another. The emission of radiation takes place as a single photon when an electron "jumps" from a higher orbit to a lower orbit. The frequency of the photon is

$$\nu = \frac{E_2 - E_1}{h}$$

where E_2 and E_1 are the energies of the electron in the higher and lower orbits, respectively. Conversely, an electron in the lower orbit can jump to the higher orbit by absorbing a photon of this frequency.

Let Z be the atomic number of the nucleus. If e is the electronic charge, then the charge of the nucleus is Ze. The centripetal acceleration for circular motion is provided by the Coulomb attraction between the electron and the nucleus. Therefore,

$$\frac{mv^2}{r} = \frac{k(Ze)e}{r^2} \qquad \ldots(1.20)$$

$$\frac{mv^2}{r} = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r^2} \qquad \ldots(1.21)$$

The expressions for the radius of the nth Bohr orbit and the speed of the electron in this orbit, respectively, as

$$\boxed{r_n = \frac{(4\pi\varepsilon_0)\hbar^2 n^2}{Ze^2 m}} \qquad \ldots(1.22)$$

and

$$\boxed{v_n = \frac{Ze^2}{(4\pi\varepsilon_0)\hbar n}} \qquad \ldots(1.23)$$

The integer n is called the *quantum number*. Substituting the values of ε_0, $\hbar$, e, and m,

For the first Bohr orbit, also called the *ground state*, of hydrogen, $Z = 1$, $n = 1$. Therefore, the radius and the speed are 0.53 Å and 2.18×10^6 m/s, respectively. The first Bohr radius of hydrogen is generally denoted by the symbol a_0:

Energy of the Electron in the *n*th Bohr Orbit

The total energy E_n of the electron is the sum of the kinetic and potential energies:

$$E_n = \frac{1}{2} m v_n^2 - \frac{Ze^2}{(4\pi\varepsilon_0) r_n}$$

$$= \frac{m}{2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{n^2} - \frac{m}{\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{n^2}$$

or

$$\boxed{E_n = -\frac{m}{2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{n^2}}$$

Sometimes it is convenient to express the energy in terms of the *Bohr radius*

$$\boxed{E_n = -\frac{\hbar^2}{2ma_0^2}\frac{Z^2}{n^2}} \qquad \ldots(1.25)$$

Substituting the values of the constants,

$$\boxed{E_n = -2.2 \times 10^{-18}\frac{Z^2}{n^2}\ \text{J} = -13.6\frac{Z^2}{n^2}\ \text{eV}}$$

This shows that the energy of the ground state of hydrogen is (–13.6 eV).

The negative sign indicates that the electron is bound.

The minimum energy required to movere the electron from the ground state of hydrogen atom is 13.6 eV. This energy is, therefore, called the ionization energy of the hydrogen atom.

Frequency and Wavelength of the Radiation in the Transition $n_1 \rightarrow n_2$

From Bohr theory; $\nu = \dfrac{E_2 - E_1}{h}$

This equation gives the frequency of the radiation emitted when the electron makes a transition from an orbit of higher energy with quantum number n_2 to one of lower energy with quantum number n_1:

$$\nu = \frac{E_{n_2} - E_{n_1}}{h} = \frac{E_{n_2} - E_{n_1}}{2\pi\hbar} \qquad \ldots(1.26)$$

And by using;

$$E_n = -\frac{m}{2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{n^2} \qquad \ldots(1.27)$$

Then the frequency of the radiation emitted is,

$$\nu = \frac{m}{4\pi\hbar^3}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \ldots(1.28)$$

The inverse of the corresponding wavelength (λ), also called **wave number** ($\bar{\nu}$), is given by

$$\bar{\nu} = \frac{1}{\lambda} = \frac{m}{4\pi c\hbar^3}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \ldots(1.29)$$

This can be written as

$$\boxed{\bar{\nu} = \frac{1}{\lambda} = R_\infty Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)} \qquad \ldots(1.30)$$

where

$$\boxed{R_\infty = \frac{m}{4\pi c\hbar^3}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2}$$

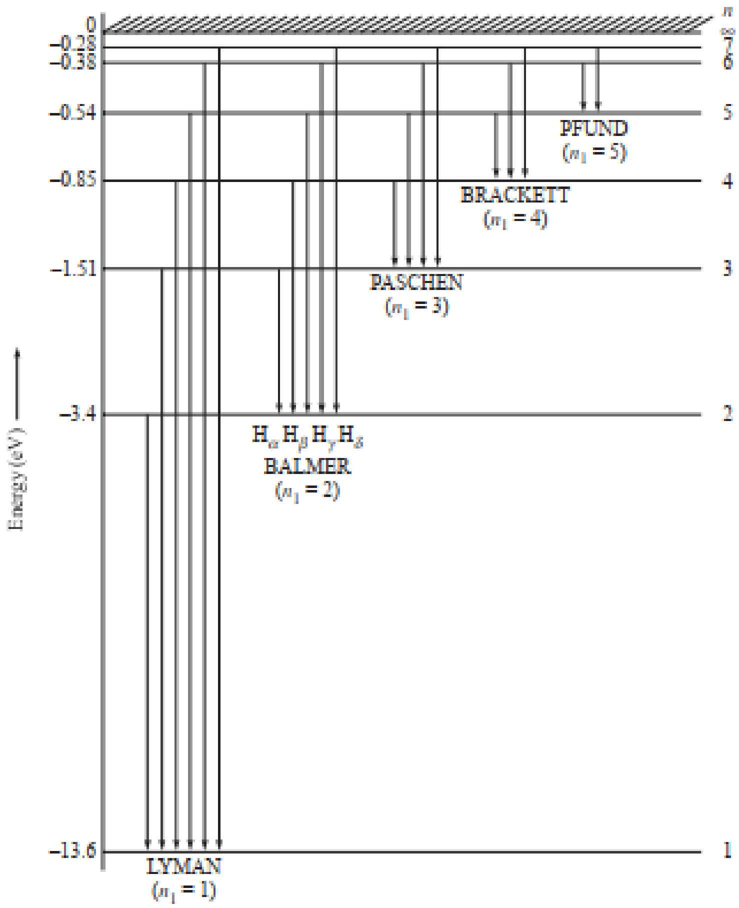
The constant R_∞ is obviously the Rydberg constant. (R_∞ empirical value $1.09737 \times 10^7 m^{-1}$)

1.6 EXPLANATION OF THE HYDROGEN SPECTRUM

If we put $z = 1, n_1 = 1$ and $n_2 = 2, 3, 4, \ldots$ in formula of wave number

$$\boxed{\bar{\nu} = \frac{1}{\lambda} = R_\infty Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)}$$

We find that the values of λ so obtained agree with the experimentally observed wavelengths.



Energy level diagram for hydrogen atome

PROBLEM: The energy of an excited hydrogen atom is –3.4 eV.Calculate the angular momentum of the electron according to Bohr theory.

Solution: The energy of the electron in the nth orbit is

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

Therefore,

$$n^2 = \frac{-13.6}{E_n} = \frac{-13.6}{-3.4} = 4$$

or $$n = 2$$

$$\text{Angular momentum} = \frac{nh}{2\pi}$$

$$= \frac{2 \times 6.63 \times 10^{-34}}{2 \times 3.14}$$

$$= \boxed{2.11 \times 10^{-34}\ \text{Js}}$$

H.W.

1. The energy of the ground state of hydrogen atom is –13.6 eV. Find the energy of the photon emitted in the transition from n = 4 to n = 2.

2. The H line of Balmer series is obtained from the transition n = 3 (energy = – 1.5 eV) to n = 2 (energy = – 3.4 eV). Calculate the wavelength for this line.