Fundamentals of Atomic Theory

Blackbody Radiation:

All substances at finite temperatures radiate electromagnetic waves. Isolated atoms (in a gas) emit discrete frequencies, molecules emit bands of frequencies, and solids radiate a continuous spectrum of frequencies.

The details of the spectrum emitted by a solid depend on its temperature and to some extent on its composition. At room temperature the spectrum is centered around the infrared; that is, most of the radiation emitted lies in the infrared part of the electromagnetic spectrum. As the temperature of the solid increases, more and more of the emitted radiation is in the visible part of the spectrum; we see it first glow red and then approach white as the temperature is increased.

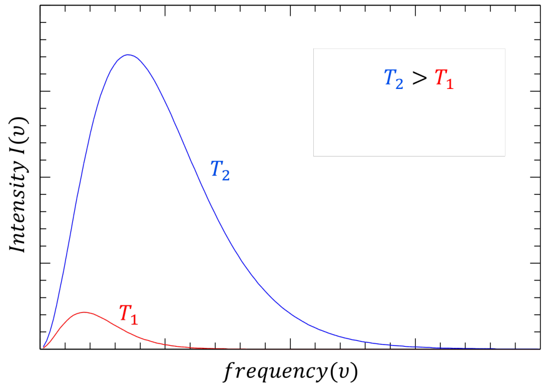

Figure 1: Intensity *vs* frequency in a blackbody radiation

Objects that emit a spectrum of *universal* character, one that does not depend on the composition of the object, are called blackbodies. The reason for the name is that these objects absorb all the radiation incident on them. They do not reflect light, and hence they appear black.

Character of the Spectrum of a Blackbody:

The main features of the spectrum emitted by a blackbody are:

1. The spectrum is continuous with a broad maximum. This fact is shown in figure, which is a plot of $I(\nu)$, the spectral radiancy at each frequency, versus the frequency of the radiation(ν). The spectral radiancy is the energy per frequency emitted per unit time per unit area of the blackbody. The two curves correspond to two different temperatures of the object.
2. The energy emitted per unit time per unit area is found to increase with the fourth power of the temperature, i.e.

   $$power\ per\ unit\ area = \sigma T^4 \quad \text{(Stefan-Boltzmann law)}$$

   where the constant $\sigma = 5.67 \times 10^{-8} W/m^2K^4$.
3. Figure also shows that the spectrum shifts toward higher frequencies as the temperature increases. In fact, one finds experimentally that the frequency ν_{max}, at which $I(\nu)$ is a maximum, increases linearly with the temperature of the blackbody, that is,

   $$\nu_{max} \propto T$$

Planck's Theory

Attempts by physicists to explain the blackbody spectrum using the laws of classical electromagnetism and thermodynamics proved unsuccessful.

Planck's approach to the problem was to find an empirical mathematical expression for $I(\nu)$ that would fit the experimental data. He then observed that he could derive the expression by making a revolutionary physical hypothesis.

According to Planck's hypothesis, *a system undergoing simple harmonic motion with frequency ν can only emit energies given by $E = nh\nu$, where $n = 1, 2, 3, \ldots$ and h is a constant now known as Planck's constant. The value of h is 6.63×10^{-34} Joule second (Js).* This phenomenon is called *quantization of energy*.

Planck derived an expression for $I(\nu)$ that matched the experimental data:

$$I(\nu) = \frac{2\pi h\nu^3}{c^2}\frac{1}{\exp(h\nu/k_BT) - 1}$$

where c is the velocity of light, k_B is the Boltzmann constant, ν is the frequency of the electromagnetic wave, and T is the absolute temperature of the blackbody.

Bohr Atom

Bohr's Postulates

Postulate 1 An electron cannot revolve round the nucleus in all possible orbits as suggested by classical theory. The electron can revolve round the nucleus only in those allowed or permissible orbits for which the angular momentum of the electrons is an integral multiple of $\frac{h}{2\pi}$, where h is Planck's constant.

If m is the mass of electron and v is velocity of the electron in an orbit of radius r, then,

$$Angular\ momentum(L) = mvr = n\frac{h}{2\pi} = n\hbar$$

$$\boxed{L = n\hbar}$$

where n is an integer and can take values $n = 1, 2, 3, 4, ...$ It is called principal quantum number. This equation is called Bohr's quantization condition.

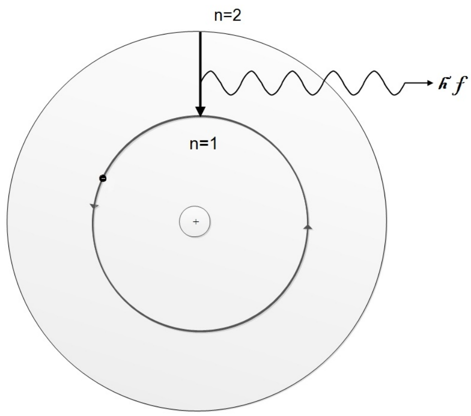

Figure 2: Bohr's atom

Postulate 2 When electron revolves in permitted orbits they do not radiate energy. An atom radiates energy only when an electron jumps from a higher energy state to the lower energy state and the energy is absorbed, when it jumps from lower to higher energy orbit.

If E_{n_1} and E_{n_2} are energies associated with first and second orbits respectively, then the frequency ν of the radiation emitted is given by

$$\nu = \frac{E_{n_2} - E_{n_1}}{h}$$

This is called Bohr's frequency condition.

Bohr's Theory of Hydrogen Atom

Bohr assumed that a hydrogen atom consists of a nucleus with one unit positive charge $+e$ (i.e. a proton)and a single electron of charge $-e$, revolving around it in a circular orbit of radius r. The electrostatic force of attraction between the proton and the electron is given by

$$F = \frac{1}{4\pi\epsilon_0}\frac{e^2}{r^2} \tag{1}$$

If m and v are mass and velocity of the electron in the orbit, then the centripetal force required by the electron to move in circular orbit of radius r is given by

$$F = \frac{mv^2}{r} \tag{2}$$

The electrostatic force of attraction between the electron and the nucleus provides the necessary centripetal force. Therefore,

$$\frac{mv^2}{r} = \frac{1}{4\pi\epsilon_0}\frac{e^2}{r^2} \tag{3}$$

According to Bohr's first postulate,

$$mvr = n\frac{h}{2\pi}$$

$$\boxed{v = \frac{nh}{2\pi rm}} \tag{4}$$

$$v^2 = \frac{n^2h^2}{4\pi^2r^2m^2}$$

substituting this value ofv^2 in equation (3), we get

$$\frac{m}{r}\left(\frac{n^2h^2}{4\pi^2r^2m^2}\right) = \frac{1}{4\pi\epsilon_0}\frac{e^2}{r^2}$$

$$r = \frac{\epsilon_0 n^2h^2}{\pi me^2} \tag{5}$$

Radius of the n^{th} permissible orbit for hydrogen is given by

$$\boxed{r_n = \frac{\epsilon_0 n^2h^2}{\pi me^2}} \tag{6}$$

As $n = 1, 2, 3, ...$ it follows from equation (6) that the radii of the stationary orbits are proportional to n^2.

Bohr Radius

The radius of the innermost orbit in hydrogen atom is called Bohr's radius and is denoted by a_00.
For $n = 1$,

$$r = a_0 = \frac{\epsilon_0 h^2}{\pi me^2}$$

Substituting the known values of ϵ_0, h, m, and e, we get,

$$a_0 = 0.529\text{Å}$$

$$r_n = 0.529 \times n^2 \text{ Å} \tag{7}$$

$1\text{Å} = 10^{-10}m$

Velocity of the Electron

The velocity of the electron in the n^{th} orbit, v_n is given by

$$v_n = \frac{nh}{2\pi r_n m}$$

Substituting the value of r_n from equation (6) we get,

$$v_n = \frac{nh}{2\pi m}\left(\frac{\pi me^2}{\epsilon_0 n^2h^2}\right)$$

$$\boxed{v_n = \frac{e^2}{2\epsilon_0 nh}} \tag{8}$$

Therefore $v_n \propto \frac{1}{n}$, the electrons closer to the nucleus move with higher velocity than lying farther.

Energy of the Electron in n^{th} orbit
As electron is revolving round the nucleus, it has kinetic energy.

$$K.E. = \frac{1}{2}mv_n^2$$

And,

$$P.E. = -\frac{1}{4\pi\epsilon_0}\frac{e.e}{r_n^2}$$

Therefore, total energy of the electron in the n^{th} orbit is

$$E_n = K.E. + P.E.$$

$$E_n = \frac{1}{2}mv_n^2 - \frac{1}{4\pi\epsilon_0}\frac{e.e}{r_n^2}$$

Substituting values of r_n and v_n from (6) and (8), we get,

$$\boxed{E_n = -\frac{me^4}{8\epsilon_0^2 n^2 h^2}} \tag{9}$$

Bohrs Interpretation of the Hydrogen Spectrum
If an electron jumps from an outer orbit n_2 of higher energy level to an inner orbit n_1 of lower energy level, the energy of photon of the radiation emitted is given by,

$$h\nu = E_{n_2} - E_{n_1}$$

where E_{n_2} and E_{n_1} are energies of the electron in the stationary orbits then

$$E_{n_1} = -\frac{me^4}{8\epsilon_0^2 n_1^2 h^2} \quad \text{and} \quad E_{n_2} = -\frac{me^4}{8\epsilon_0^2 n_2^2 h^2}$$

therefore, the energy of photon emitted is given by

$$h\nu = \left(-\frac{me^4}{8\epsilon_0^2 n_2^2 h^2}\right) - \left(-\frac{me^4}{8\epsilon_0^2 n_1^2 h^2}\right) \quad \Rightarrow \quad h\nu = \frac{me^4}{8\epsilon_0^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Therefore,

$$\boxed{\nu = \frac{me^4}{8\epsilon_0^2 h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)} \tag{10}$$

Wavenumber($\overline{\nu}$): Reciprocal of wavelength of radiation is called wavenumber. i.e. $\overline{\nu} = \frac{1}{\lambda}$

$$\overline{\nu} = \frac{1}{\lambda} = \frac{f}{c}$$

Therefore,

$$\overline{\nu} = \frac{\nu}{c} = \frac{me^4}{8\epsilon_0^2 ch^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\boxed{\overline{\nu} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)} \tag{11}$$

where $R = \frac{me^4}{8\epsilon_0^2 ch^3}$ known as Rydberg's constant. The value of Rydberg's constant is $1.097 \times 10^7 m^{-1}$

Spectral Series of Hydrogen Atom

When an electron jumps from the higher energy state to the lower energy state, the difference of energies of two states is emitted as a radiation of definite frequency. It is called *spectral line*. The spectral lines are divided into a number of series.

1. Lyman Series The spectral lines of this series correspond to the transition of an electron from some higher energy state to the innermost orbit ($n = 1$). Therefore, for Lyman series $n_1 = 1$ and $n_2 = 2, 3, 4, 5, ...$

2. Balmer Series The spectral lines of this series correspond to the transition of an electron from some higher energy state to the orbit having $n = 2$. Therefore, for Balmer series $n_1 = 2$ and $n_2 = 3, 4, 5, 6....$

3. Paschen Series The spectral lines of this series correspond to the transition of an electron from some higher energy state to the orbit having $n = 3$. Therefore, for Paschen series $n_1 = 3$ and $n_2 = 4, 5, 6, 7....$

4. Brackett Series The spectral lines of this series correspond to the transition of an electron from some higher energy state to the orbit having $n = 4$. Therefore, for Brackett series $n_1 = 4$ and $n_2 = 5, 6, 7, 8....$

5. P-fund Series The spectral lines of this series correspond to the transition of an electron from some higher energy state to the orbit having $n = 5$. Therefore, for P-fund series $n_1 = 5$ and $n_2 = 6, 7, 8, ...$

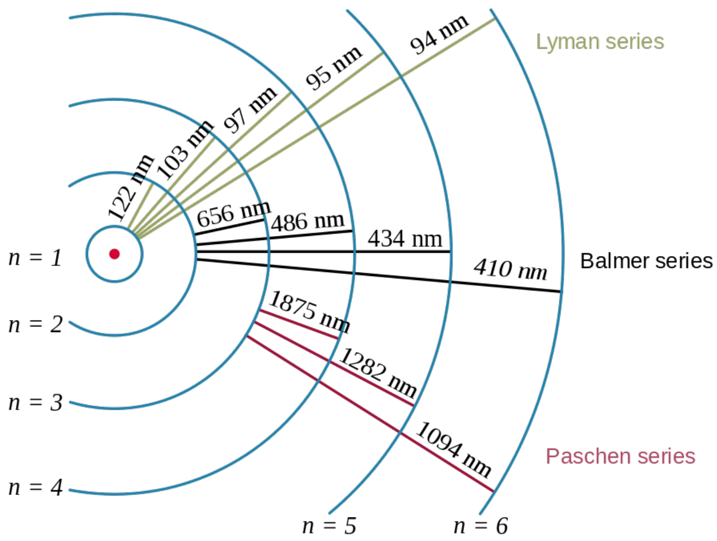

Figure 3: Spectral series of Hydrogen atom

Limitations of Bohrs Theory of Hydrogen Atom

1. Elliptical orbits are possible for the electron orbits, but Bohrs theory does not tell us why only elliptical orbits are possible.
2. Bohrs theory does explain the spectra of only simple atoms like hydrogen but fails to explain the spectra of multi-electron atoms.
3. The fine structure of certain spectral lines of hydrogen could not be explained by Bohrs theory.
4. It does not explain the relative intensities of spectral lines.
5. This theory does not account for the wave nature of electrons.