Atomic Structure and Atomic Models (3):

The Hydrogen Spectrum:

The light which is discontinuous in frequency distribution forms a discrete set of light images that are termed as spectral lines. One can analyze these lines by the distribution of their frequency or color. The wavelengths of the lines of a spectrum fall into definite sets which are called series. An element may display several series. Each series can be represented by an empirical formula which has a similarity for all the series of a given element. Balmer in 1885 discovered the “Blamer series of hydrogen atom” as shown in Fig.1.

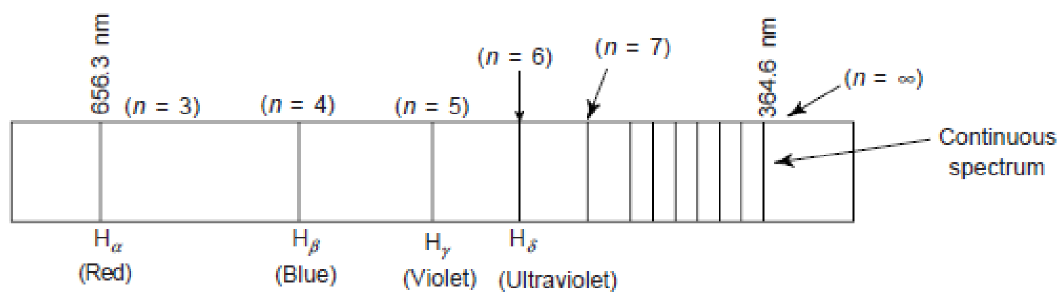

Figure 1

Starting from the line of longest wavelength 656.3 nm the various lines in this series are designated as H_β, H_γ, etc. The lines get closer together until we reach what is known as the series limit at 364.6 nm. Beyond this series limit there are no discrete lines but only a continuous spectrum. Balmer enunciated an empirical relation to represent the wavelength of this series as:

$$\bar{v} = \frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{n^2}\right]$$

Where (n=3,4,5, ….) and R= 1.0937 x 10^7 m^{-1} is the Rydberg constant.

An examination of the ultraviolet and infrared regions revealed the existence of other series in hydrogen spectrum. These other series are:

Lyman Series: $\bar{\nu} = \frac{1}{\lambda} = R\left[\frac{1}{1^2} - \frac{1}{n^2}\right]$ $(n = 2, 3, 4)$

Paschen Series: $\bar{\nu} = \frac{1}{\lambda} = R\left[\frac{1}{3^2} - \frac{1}{n^2}\right]$ $(n = 4, 5, 6)$

Brackett Series: $\bar{\nu} = \frac{1}{\lambda} = R\left[\frac{1}{4^2} - \frac{1}{n^2}\right]$ $(n = 5, 6, 7)$

Pfund Series: $\bar{\nu} = \frac{1}{\lambda} = R\left[\frac{1}{5^2} - \frac{1}{n^2}\right]$ $(n = 6, 7, 8)$

The value of R is the same for all the series. The origin of different spectral series of hydrogen due to transitions between the different orbits is shown in Fig. 2. The transitions are indicated by drawing arrows from the initial to the final orbits.

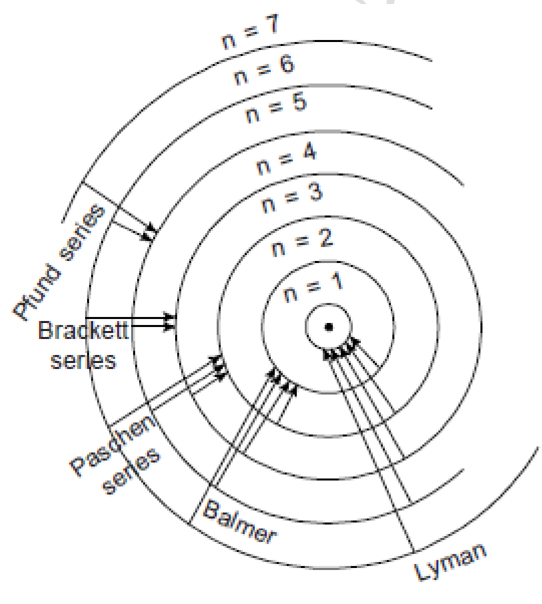

Figure 2

Normal and excited states of Atoms:

When the electron is completely removed from the atom, i.e. n = 1, the atom is said to the ionized. The corresponding potential (Vi) is known as the ionization potential. Ionization energy or ionization potential is expressed in units of electron volt (eV : 1 eV = 1.6 x 10^{-19} J). The inert or nobel gases have the highest ionization energy as these elements have stable electronic configuration. The electrons fill completely a shell or sub-shell. Alkali atoms, e.g. Lithium and Sodium have low ionization potential as they have one electron in outermost & sub-shell, beyond the stable configuration and hence can easily be removed out of the atom. The another term associated with ionization energy is electron affinity. This is the amount of energy released, when a neutral atom adds an electron. The energy required to transfer an electron from atom 1 to atom 2 is the difference between the ionization energy I_1 and the electronic affinity E_{12} of the respective atoms, i.e., $I_1 - E_{12}$. We see that Halogen atoms have the highest electron affinity. However, when the electron is forced into an outer orbit (say n = 2, 3, 4, 5, . . .) the atom is said to be excited. In the unexcited normal state, i.e. ground state, with n = 1, the electron is in its lowest energy state at the bottom. The electron moves in this orbit continuously without emitting or absorbing energy and is said to be in stable state. When electron is excited (say n = 2, 3, 4, 5 . . . orbits), it absorbs energy. When electron returns from the excited state to any of the lower states, it emits energy.

Energy Levels:

According to Bohr's theory of hydrogen atom, there are only certain discrete energy levels in the hydrogen atom. When an electron makes a spontaneous jump from an outer orbit to an inner orbit, energy is radiated which is equal to the difference in energy between the orbits or levels. According to theory, the electron has definite energy in a stationary orbit, given by:

$$E_n = -\frac{chRZ^2}{n^2}$$

For hydrogen Z = 1, so that:

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

We can represent the energies of the electron in the different orbits of hydrogen (or other hydrogen like atoms) given by drawing a set of horizontal lines for different values of n. This has been done for hydrogen in Fig. 3. These are known as the energy levels of hydrogen. Electron energy levels are most conveniently expressed in electrons volts (eV).

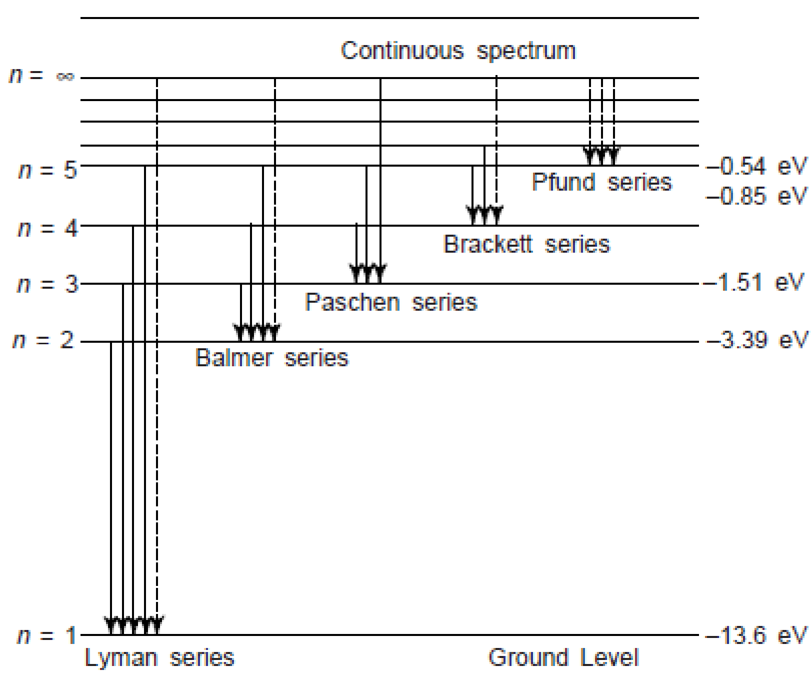

Figure 3

We can see that the minimum energy required to set free an electron originally bound in the lowest energy (n = 1) of the hydrogen atom is 13.6 eV, which is ionization energy for hydrogen. In the commonly known notations, an electron in a n = 1 is said to be in the K-shell. Correspondingly, if n = 2, n = 3 or n = 4, the electron is said to be in the L, M or N shells respectively. Obviously, K, L, M, N, O, P, and Q – shells correspond to quantum numbers n = 1, 2, 3, 4, 5, 6, and 7.

$$n = 1 \text{ (K-shell)} : E_1 = -13.6 \text{ eV}$$

$$n = 2 \text{ (L-shell)} : E_2 = -\frac{E_1}{2^2} = -3.4 \text{ eV}$$

$$n = 3 \text{ (M-shell)} : E_3 = -\frac{E_1}{3^2} = -1.51 \text{ eV}$$

$$n = 4 \text{ (N-shell)} : E_4 = -\frac{E_1}{4^2} = -0.86 \text{ eV}$$

$$n = 5 \text{ (O-shell)} : E_5 = \frac{E_1}{5^2} = -0.54 \text{ eV}$$

$$\cdots$$

$$\cdots$$

$$n = \infty \qquad E_\infty = 0 \text{ eV}.$$

Energy Levels Diagram of Multielectron Atoms:

An atom containing more than one electron is called a multielectron atom and a standard energy level diagram for such types of atoms is shown in Fig. 4. Now, we examine the sequence of filling up the electrons in various orbitals in the different energy levels of multielectron atoms:

(i) First Principal Energy Level (n = 1): This has only one orbital i.e., 1 s-orbital and accommodate only two electrons.

(ii) Second Principal Energy Level (n = 2): This has two orbitals 2s and 2p. 2s-orbtial has only one subsub-shell and can accommodate only two electrons. 2p orbital has three sub-sub-shells and can accommodate at the most 6 electrons and each sub-sub-shell cannot accommodate more than two electrons. The maximum number of electrons that can be accommodated in n = 2 energy level is 8 and the total number of maximum electrons that can be accommodated upto the second principal energy level is 10 (2 in n = 1 level and 8 in n = 2 level). However, the second principal energy level (n = 2) will only start accommodating electrons only after the first principal energy (n = 1) is completely filled up.

(iii) Third Principal Energy Level (n = 3): This has three orbitals: 3s, 3p and 3d orbitals. From Fig. 2.11(a), we note that the 3d-orbital does not fall within the range of n = 3 principal energy level, as the energy of the 3d-orbital is greater that of 4s orbital in the fourth principal energy level. This is why the 3d-orbital is filled only after filling up of 4s-orbital of the 4th principal energy level. The sequence of filling up 3s and 3p orbitals is as follows:

3s orbital has only one sub-sub-shell and can accommodate only two electrons.

3p-orbital has three sub-sub-shells and can accommodate at the most 6 electrons.

Thus the maximum number of electrons filled up in the n = 3 level is 8 and the total number of electrons which can be accommodated up to n = 3 level is 18. We must remember that n = 3 level will start accommodating the electrons only after the second principal energy level is completely filled up.

(iv) Fourth Principal Energy level (n = 4): This has four orbitals: 4s, 4p, 4d and 4f. The energy of 4d and 4f orbitals are greater than 5s and 6s orbitals respectively and they do not fall within the range of fourth principal energy level. Obviously, n = 4 energy level contains only 4s, 3d and 4p orbitals as shown. The sequence of filling these orbitals is as below:

4s-orbital: It has only one sub-shell and can accommodate only 2 electrons.

3d-orbtial: It has 5 sub-shells and can accommodate at the most 10 electrons but each sub-sub-shell of this orbital cannot accommodate more than 2 electrons.

4p-orbital: This has three sub-sub-shells and can accommodate at the most 6 electrons.

Thus n = 4 has the maximum capacity of 18 electrons and the total number of electrons which can be accommodated up to fourth principal energy level is 36. We must remember that n = 4 level will start accommodating the electrons only after the n = 3 level is completely filled up.

Similarly, 5th, 6th and 7th principal energy levels are filled with electrons. The maximum capacity of 5th, 6th and 7th levels are 18, 32 and 32 respectively. The sequence of filling up of the orbitals of n = 5 level is 5s, 4d and 5p; the sequence of filling up of the orbitals of n = 6 level is 6s, 4f, 5d and 6p and similarly that of n = 7 level is 7s, 5f, 6d and 7p. We must remember that each f-orbital has 7 sub-shells and each sub-shell cannot accommodate more than 2 electrons.