Quadrant II – Transcript and Related Materials

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Module No: 4

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Notes

Line Spectra

Consider a discharge tube containing hydrogen gas at low pressure (refer figure 1). When a high-voltage electrical discharge is passed through this sample, the resulting H atoms obtained due to dissociation emit light. When the emitted light is passed through a prism, the prism disperses the light into its constituent light. When this light is allowed to strike a photographic plate a line spectrum is obtained, i.e. a spectrum of narrow lines corresponding to certain wavelengths rather than continuous range of wavelengths. Hydrogen atom has four characteristic lines in its spectrum out of which the most intense line is in the red portion of the visible spectrum, at 656 nm.

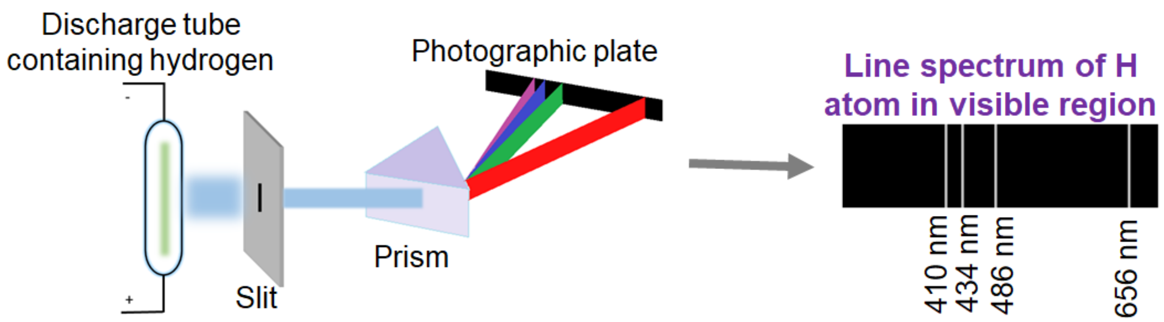

Figure 1: Discharge tube experiment with hydrogen gas giving line spectrum of hydrogen atom in visible region

In 1885, Johann Balmer showed that the frequencies of the lines observed in the visible region of the spectrum of hydrogen can be expressed as follows:

$$\gamma = \text{constant}\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

where n = 3, 4, 5, 6.

These lines are known as the Balmer series.

Johannes Rydberg later restated and expanded Balmer's result in the Rydberg equation:

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

where n_1 and n_2 are positive integers, $n_2 > n_1$, and R is the Rydberg constant (1.09737×10^7 m^{-1}).

Balmer's equation described the wavelengths of only the visible lines in the emission spectrum of hydrogen (with $n_1 = 2$, $n_2 = 3, 4, 5,…$). However, Rydberg's equation described the wavelengths of other series of lines also that would be observed in the emission spectrum of hydrogen: one in the ultraviolet ($n_1 = 1$, $n_2 = 2, 3, 4,…$) and one in the infrared ($n_1 = 3$, $n_2 = 4, 5, 6$). The theoretical justification for equation of these form was provided by Bohr's Model of hydrogen atom.

Bohr's Model

The emission spectrum of hydrogen atom could be explained by a theoretical model for the hydrogen atom which was proposed by Niels Bohr in 1913. According to this model the electron moves around the nucleus in circular orbits that can have only certain allowed radii (refer figure 2). It was shown that the energy of an electron in a particular orbit can be given as:

$$E_n = -\frac{Rhc}{n^2} \quad \text{---------------- eqn.1}$$

Where R is the Rydberg constant, h is Planck's constant, c is the speed of light, and n is a positive integer which can take values from 1 to ∞. This n corresponding to the number assigned to the orbit, i.e. n = 1 for the orbit closest to the nucleus and n = ∞ corresponds to the level where the energy holding the electron and the nucleus together is zero.

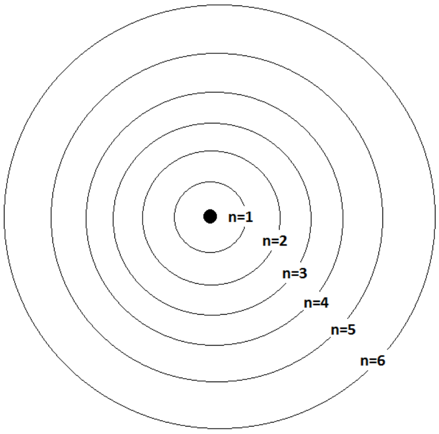

Figure 2: Bohr's model of hydrogen atom

As n decreases, the radius of the orbit shrinks and the electron is held more tightly by the nucleus. The orbit with n = 1 is the lowest lying and most tightly bound. Hydrogen atom has only one electron, and in the ground state this electron is present in the orbit with n=1. A hydrogen atom with an electron in an orbit with n > 1 is therefore in an excited state. Atom in excited state is highly unstable as a result it immediately wants to return back to ground state. The excited atom does so by undergoing a transition to the ground state in a process called decay (refer figure 3). During decay the excited atom loses energy by emitting a photon whose energy corresponds to the difference in energy between the two states.

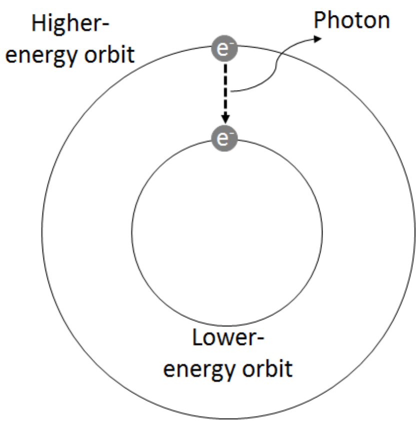

Figure 3: The emission of photon by a hydrogen atom in an excited state.

The difference in energy (ΔE) between any two orbits or energy levels is given as:

$$\Delta E = n_f - n_i$$

where n_f is the final orbit and n_i the initial orbit. Substituting from Bohr's equation for energy (eqn.1) we get:

$$\triangle E = E_{n_f} - E_{n_i} = -\frac{Rhc}{n_f^2} - \left(-\frac{Rhc}{n_i^2}\right) = -Rhc\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \quad \text{--------- eqn.2}$$

We know that $\Delta E = hc/\lambda$ and hence by substituting in eqn.2 we get:

$$\frac{hc}{\lambda} = -Rhc\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

Cancelling hc on both sides gives:

$$\frac{1}{\lambda} = -R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

If we ignore the negative sign, this is the same equation that Rydberg obtained experimentally. The negative sign in above equation indicates that energy is released as the electron moves from higher-energy orbit to lower-energy orbit.

The value of R (1.09737×10^7 m^{-1}) calculated by Bohr from fundamental constants is the same number Rydberg had obtained by analysing the emission spectra.

The origin of Balmer series of lines in the emission spectrum of hydrogen can now be understood (refer figure 4). The lines in this series correspond to transitions from higher-energy orbits ($n > 2$) to the second orbit ($n = 2$). Thus, the hydrogen atoms undergo excitation by absorbing energy from electrical discharge and decays from a higher-energy excited state ($n > 2$) to a lower-energy state ($n = 2$) by emitting a photon of electromagnetic radiation whose energy equals the difference in energy between the two states. The line at 656 nm (red) is due to transition from $n = 3$ to $n = 2$, the line at 486 nm (green) is due to $n = 4$ to $n = 2$ transition, the line at 434 nm (blue) is due to $n = 5$ to $n = 2$ transition, and the line at 410 nm (violet) is due to $n = 6$ to $n = 2$ transition.

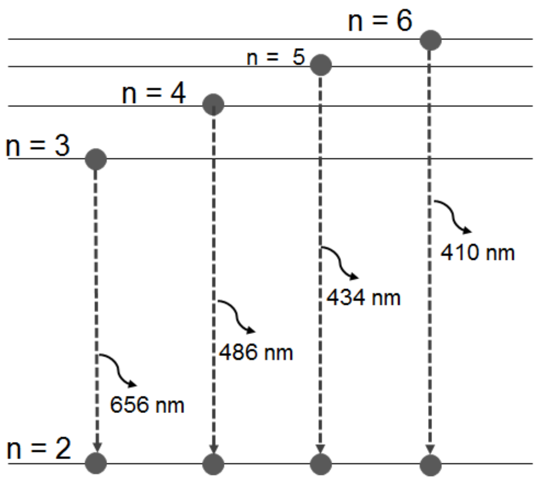

Figure 4: Balmer series transitions

The intensity of the various lines in a line spectrum depends on the number of atoms in each excited state. The line at 656 nm (red) is most intense because at the temperature in the gas discharge tube, more atoms are in the n = 3 than the n ≥ 4 levels. Similarly, the origin of other series can be explained (refer figure 5).

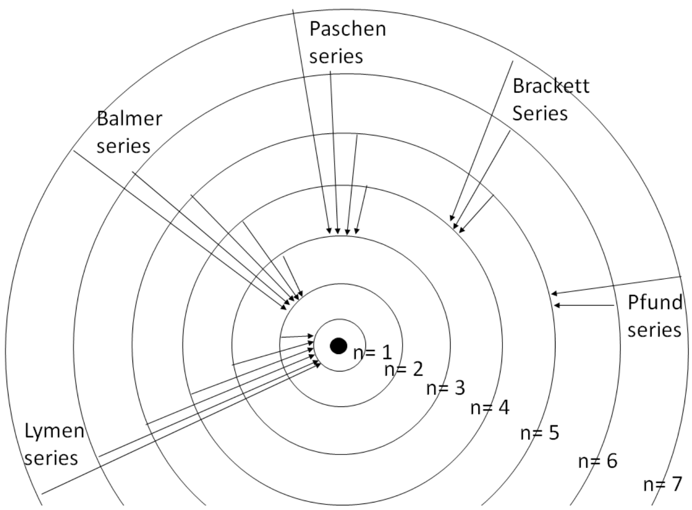

Figure 5: Electronic transitions responsible for the various series of lines observed in the hydrogen atom spectrum. The lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release energy corresponding to ultraviolet radiation. The paschen, brackett, and pfund series of lines are due to transitions from higher-energy orbits to orbits with n = 3, 4, and 5, respectively; these transitions release energy corresponding to infrared radiation.