

(c) Bohr Model of Hydrogen Atom

Bohr's determine the atomic energy states by considering an atom consisting of nucleus $+Ze$ and mass M , and single electron of charge $-e$ and mass m . The condition of stable electronic orbital is

Coulomb force = Centripetal force

$$\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2} = \frac{mv^2}{r},$$

where v is the electron speed and r is the orbital radius.

The orbital angular momentum of electron, $L = mvr$, must be a constant, because the force acting on the electron is entirely in the radial direction. Applying the quantization condition $L = n\hbar$, (where $n = 1, 2, 3, 4, 5, \dots$).

$$mvr_n = n\hbar \Rightarrow v = \frac{n\hbar}{mr_n} \Rightarrow \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_n^2} = \frac{mn^2\hbar^2}{m^2r_n^3}$$

we get the expression of velocity and radius.

Radius:

$$r_n = 4\pi\epsilon_0 \frac{n^2\hbar^2}{mZe^2} = a_0 \frac{n^2}{Z}$$

where, $a_0 = \text{Bohr radius} = 0.52\text{\AA}$

Velocity:

$$v_n = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{n\hbar} = \alpha c$$

where, α is the fine structure constant defined as

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137}$$

The total energy of the atom, which contain both kinetic energy and potential energy term is,

$$E = K + V = \frac{1}{2} \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_n} - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_n} = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_n}$$

$$E = -\frac{mZ^2e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2} = -\frac{me^4 Z^2}{8\epsilon_0^2 \hbar^2 n^2} = E_1 \frac{Z^2}{n^2}$$

This shows that, quantization of the orbital angular momentum of the electron leads to a quantization of its total energy.

(i) Energy levels for Hydrogen atom ($Z = 1$)

$$E_n = -\frac{me^4}{8\epsilon_0^2 h^2} \frac{1}{n^2} = \frac{E_1}{n^2}, \quad n = 1, 2, 3, \dots$$

where $E_1 = -\frac{me^4}{8\epsilon_0^2 h^2} = -13.6 \text{ eV}$

Thus, the energy of the hydrogen atom is

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

The total energy of the electron is negative. The lowest energy level E_1 is called the **ground state** of the atom, and the higher levels E_2, E_3, E_4, \dots are called **excited states**. As the quantum number n increases, the corresponding energy E_n approaches closer to 0. In the limit of $n = \infty$, $E_n = 0$ and the electron is no longer bound to the nucleus to form an atom.

(ii) Origin of line spectrum

Line spectrum arises when electron jump from one level to another level, with a difference in energy between the levels appears as a single photon.

Initial energy – Final energy = Photon energy

$$E_i - E_f = h\nu$$

Substituting the E_i and E_f , we have

$$E_i - E_f = E_1 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = -E_1 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

The frequency of the emitted photon ν is

$$\nu = \frac{E_i - E_f}{h} = -\frac{E_1}{h} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

Because the quantity actually measured is wavelength, it is convenient to convert frequency to wavelength using $c = \nu\lambda$ to get

$$\frac{1}{\lambda} = -\frac{E_1}{ch} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

where R is the Rydberg constant

$$R = -\frac{E_1}{ch} = 1.097 \times 10^7 \text{ m}^{-1}$$

Above equation states that the radiation emitted by excited hydrogen atoms should contain certain wavelengths only.

(iii) Effect of nuclear mass:

In the Bohr theory, we have assumed that the nucleus of the hydrogen atom is so heavy that it remains fixed at the centre of the circular orbit, while the electron revolves round it. But this will be true only when the mass of the nucleus is infinitely large as compared with the case of the electron. In fact the nucleus has finite mass. Therefore, the nucleus and the electron revolve round a common centre of mass with same angular velocity the nucleus in an orbit of smaller radius as compared to electron orbit.

Let us consider that the electron (m) and nucleus (M) revolve around their common center of mass O which remains fixed in space. By taking nuclear motion into account, the energy of the electron in the n^{th} orbit of a one electron atom is

$$E'_n = -\frac{2\pi^2 \mu Z^2 e^4}{(4\pi\epsilon_0)^2 n^2 h^2}$$

$$E'_n = E_n \frac{\mu}{m} = -\frac{13.6 \mu}{n^2 m} \text{ (eV)}$$

where $\mu = \frac{mM}{m+M}$ is called the reduced mass of the electron. Since, μ is slightly less

than m , the electron energies are slightly less negative than if the nucleus were at rest (i.e. infinitely heavy). The wavelengths of spectral line computed on the basis of the above energy equation are slightly larger than those corresponding to an infinitely heavy nucleus and agree more closely with the experimental values.

Orbital radius becomes

$$r_n = 4\pi \epsilon_0 \frac{n^2 \hbar^2}{\mu Z e^2} = a_0 \frac{m}{\mu}$$

Variation of the Rydberg constant

The finite nuclear mass causes a slight variation in the Rydberg constant from atom to atom. The Rydberg constant for an infinitely heavy mass is

$$R_{\infty} = \frac{2\pi^2 m e^4}{(4\pi \epsilon_0)^2 c h^3}$$

and that for a nucleus of mass M is

$$R_M = \frac{2\pi^2 \mu e^4}{(4\pi \epsilon_0)^2 c h^3} = \frac{2\pi^2 m e^4}{(4\pi \epsilon_0)^2 c h^3} \frac{\mu}{m} = R_{\infty} \frac{\mu}{m}$$

$$R_M = \frac{R_{\infty}}{1 + \frac{m}{M}}$$

