Question 24. The first four spectral in the Lyman series of a H-atom are λ = 1218 Å, 1028 Å, 974.3 Å and 951.4 Å. If instead of Hydrogen, we consider deuterium, calculate the shift in the wavelength of these lines.

Solution: Let μ_H and μ_D are the reduced masses of electron for hydrogen and deuterium respectively.

We know that
$$\frac{1}{\lambda} = R \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right]$$

As n_i and n_f are fixed for by mass series for hydrogen and deuterium.

$$\lambda \propto \frac{1}{R} \text{ or } \frac{\lambda_D}{\lambda_H} = \frac{R_H}{R_D} \qquad ...(i)$$

$$R_R = \frac{m_e e^4}{8 \varepsilon_0 c h^3} = \frac{\mu_H e^4}{8 \varepsilon_0 c h^3}$$

$$R_D = \frac{m_e e}{8 \, \varepsilon_0 \, ch^3} = \frac{\mu_D e^4}{8 \, \varepsilon_0 ch^3}$$

$$\frac{R_H}{R_D} = \frac{\mu_H}{R_D} \qquad \dots (ii)$$

 $R_D = \mu_D$ From equation (i) and (ii)

$$\frac{\lambda_D}{\lambda_H} = \frac{\mu_H}{\mu_D} \qquad ...(iii)$$

Reduced mass for hydrogen,

$$\mu_H = \frac{m_e}{1 + m_e/M} \simeq m_e \left(1 - \frac{m_e}{M} \right)$$

Reduced mass for deuterium,

$$\mu_D = \frac{2M \cdot m_e}{2M\left(1 + \frac{m_e}{2M}\right)} \simeq m_e \left(1 - \frac{m_e}{2M}\right)$$

where M is mass of proton

$$\begin{split} \frac{\mu_{H}}{\mu_{D}} &= \frac{m_{e} \left(1 - \frac{m_{e}}{2M}\right)}{m_{e} \left(1 - \frac{m_{e}}{2M}\right)} = \left(1 - \frac{m_{e}}{M}\right) \left(1 - \frac{m_{e}}{2M}\right)^{-1} \\ &= \left(1 - \frac{m_{e}}{M}\right) \left(1 + \frac{m_{e}}{2M}\right) \\ &\Rightarrow \quad \frac{\mu_{H}}{\mu_{D}} = \left(1 - \frac{m_{e}}{2M}\right) \\ \text{or} \quad \frac{\mu_{H}}{\mu_{D}} &= \left(1 - \frac{1}{2 \times 1840}\right) = 0.99973 \\ &\quad (\because \quad M = 1840 \ m_{e}) \end{split}$$
From (iii) and (iv)

$$\frac{\lambda_D}{\lambda_H} = 0.99973, \quad \lambda_D = 0.99973 \,\lambda_H.$$

Using $\lambda_H = 1218 \text{ Å}, 1028 \text{ Å}, 974.3 \text{ Å} and 951.4 \text{ Å}, we get$

$$\lambda_D = 1217.7 \text{ Å}, 1027.7 \text{ Å}, 974.04 \text{ Å}, 951.1 \text{ Å}$$

Shift in wavelength $(\lambda_H - \lambda_D) \approx 0.3 \text{ Å}$.