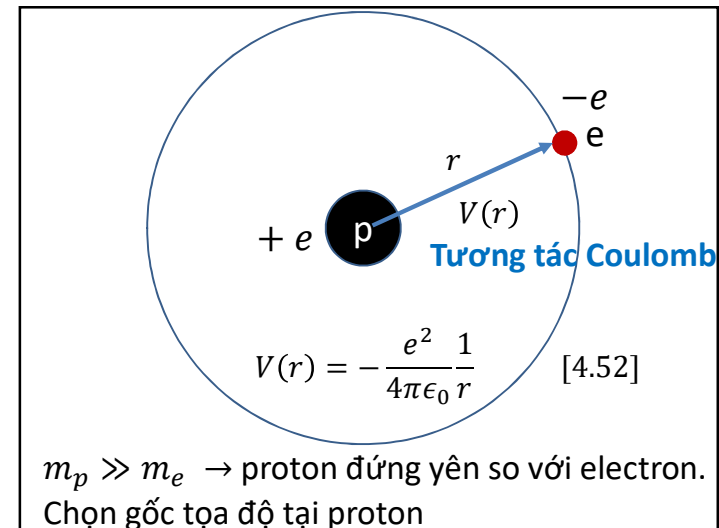


Nguyên tử hydro



Tọa độ cầu – Ph. trình bán kính

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[V(r) + \frac{\hbar^2 l(l+1)}{2m r^2} \right] u = Eu \quad [4.37]$$

V_{eff}

$$V_{eff}(r) = V(r) + \frac{\hbar^2 l(l+1)}{2m r^2} \quad [4.38]$$

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + V_{eff} u = Eu$$

PT cho nguyên tử hydro

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2 l(l+1)}{2m r^2} \right] u = Eu \quad [4.53]$$

Tìm $u(r)$ và năng lượng E

Xét trạng thái liên kết ($E < 0$)

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar} \quad [4.54]$$

$$\frac{1}{\kappa^2} \frac{d^2 u}{dr^2} = \left[1 - \frac{me^2}{2\pi\epsilon_0 \hbar^2 \kappa} \frac{1}{kr} + \frac{l(l+1)}{(kr)^2} \right] u$$

$$\rho \equiv \kappa r, \quad \text{và} \quad \rho_0 \equiv \frac{me^2}{2\pi\epsilon_0 \hbar^2 \kappa} \quad [4.55]$$

$$\frac{d^2 u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2} \right] u \quad [4.56]$$

Giải PT – xét tiệm cận

$$\frac{d^2 u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2} \right] u \quad [4.56]$$

$$\rho \rightarrow \infty \Rightarrow 1 \gg \frac{\rho_0}{\rho} \gg \frac{l(l+1)}{\rho^2} \Rightarrow \frac{d^2 u}{d\rho^2} = u$$

$$u(\rho) = Ae^{-\rho} + Be^{\rho} \quad [4.57]$$

$$\rho \rightarrow \infty \Rightarrow e^{\rho} \rightarrow \infty \Rightarrow B=0$$

$$u(\rho) \sim Ae^{-\rho} \quad [4.58]$$

Giải PT – xét tiệm cận

$$\frac{d^2 u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2} \right] u \quad [4.56]$$

$$\rho \rightarrow 0$$

$$\Rightarrow 1 \ll \frac{\rho_0}{\rho} \ll \frac{l(l+1)}{\rho^2} \Rightarrow \frac{d^2 u}{d\rho^2} = \frac{l(l+1)}{\rho^2} u$$

$$\Rightarrow u(\rho) = C\rho^{l+1} + D\rho^{-l}$$

$$\rho \rightarrow 0 \Rightarrow \rho^{-l} \rightarrow \infty \Rightarrow D=0$$

$$u(\rho) \sim C\rho^{l+1} \quad [4.59]$$

$$\begin{aligned} \rho \rightarrow \infty & \quad u(\rho) \sim Ae^{-\rho} \quad [4.58] \\ \rho \rightarrow 0 & \quad u(\rho) \sim C\rho^{l+1} \quad [4.59] \end{aligned} \Rightarrow u(\rho) = \rho^{l+1} e^{-\rho} v(\rho) \quad [4.60]$$

Cần tìm $v(\rho)$.

$$\frac{d^2 u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2} \right] u$$

$$\frac{du}{d\rho} = \rho^l e^{-\rho} \left[(l+1-\rho)v + \frac{\rho dv}{d\rho} \right]$$

$$\frac{d^2 u}{d\rho^2} = \rho^l e^{-\rho} \times \left\{ \left[-2l-2+\rho + \frac{l(l+1)}{\rho} \right] v + 2(l+1-\rho) \frac{dv}{d\rho} + \rho \frac{d^2 v}{d\rho^2} \right\}$$

$$\rho \frac{d^2 v}{d\rho^2} + 2(l+1-\rho) \frac{dv}{d\rho} + [\rho_0 - 2(l+1)]v = 0 \quad [4.61]$$

$$\rho \frac{d^2 v}{d\rho^2} + 2(l+1-\rho) \frac{dv}{d\rho} + [\rho_0 - 2(l+1)]v = 0 \quad [4.61]$$

Giải PTVP 4.61 bằng chuỗi lũy thừa (power series - phương pháp Frobenius, dựa vào định lý Taylor)

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j \quad [4.62]$$

Cần xác định các hệ số c_j

$$\rho \frac{d^2 v}{d\rho^2} + 2(l+1-\rho) \frac{dv}{d\rho} + [\rho_0 - 2(l+1)]v = 0 \quad [4.61]$$

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j \quad [4.62]$$

$$\frac{dv}{d\rho} = \sum_{j=0}^{\infty} j c_j \rho^{j-1} = \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j \quad \frac{d^2 v}{d\rho^2} = \sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^{j-1}$$

$$\sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^j + 2(l+1) \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j - 2 \sum_{j=0}^{\infty} j c_j \rho^j + [\rho_0 - 2(l+1)] \sum_{j=0}^{\infty} c_j \rho^j = 0$$

$$\sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^j + 2(l+1) \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j - 2 \sum_{j=0}^{\infty} j c_j \rho^j + [\rho_0 - 2(l+1)] \sum_{j=0}^{\infty} c_j \rho^j = 0$$

$$\Rightarrow j(j+1) c_{j+1} + 2(l+1)(j+1) c_{j+1} - 2j c_j + [\rho_0 - 2(l+1)] c_j = 0$$

$$\Rightarrow c_{j+1} = \left\{ \frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} \right\} c_j \quad [4.63]$$

$$c_{j+1} = \left\{ \frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} \right\} c_j \quad [4.63]$$

$$\Leftrightarrow c_j = \left\{ \frac{2(j+l) - \rho_0}{j(j+2l+1)} \right\} c_{j-1}$$

Tìm “dáng điệu” của $v(\rho)$ khi $\rho \rightarrow \infty$.
 $\rho \rightarrow \infty$ thì ρ^j (j lớn) có đóng góp quyết định.

$$c_j = \frac{2(j+l) - \rho_0}{j(j+2l+1)} c_{j-1} \xrightarrow{j \text{ lớn}} \frac{2j}{j(j)} c_{j-1} = \frac{2}{j} c_{j-1}$$

$$c_{j+1} \cong \frac{2}{j+1} c_j \Rightarrow c_j = \frac{2^j}{j!} c_0 \quad [4.64]$$

$$c_j = \frac{2^j}{j!} c_0 \quad [4.64]$$

$$\Rightarrow v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = c_0 e^{2\rho}$$

Nhắc lại: $\sum_{j=0}^{\infty} \frac{x^j}{j!} = e^x$

$$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho) \quad [4.60]$$

$$v(\rho) = c_0 e^{2\rho}$$

$$\Rightarrow u(\rho) = c_0 \rho^{l+1} e^{\rho} \quad [4.65]$$

Nhận xét: $\rho \rightarrow \infty \quad u(\rho) \rightarrow \infty !!!$

Sự phân kỳ đến từ chuỗi $v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j \quad [4.62]$$

Những số hạng với j lớn làm cho chuỗi phân kỳ.
Do đó, chuỗi phải bị “ngắt” từ số hạng j lớn nào đó.

$$\Rightarrow \text{Phải tồn tại } j_{\max} \text{ để } c_{(j_{\max}+1)} = 0 \quad [4.66]$$

$$c_{j+1} = \left\{ \frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} \right\} c_j \quad [4.63]$$

$$\Rightarrow 2(j_{\max} + l + 1) - \rho_0 = 0$$

$$\text{Đặt: } n \equiv j_{\max} + l + 1 \quad [4.67]$$

n được gọi là số lượng tử chính. $n \geq 1$

$$\text{Số lượng tử chính: } n \equiv j_{\max} + l + 1 \quad [4.67]$$

$$\rho_0 = 2n \quad [4.68]$$

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar} \quad [4.54] \quad \rho \equiv \kappa r, \rho_0 \equiv \frac{me^2}{2\pi\epsilon_0 \hbar^2 \kappa} \quad [4.55]$$

$$\Rightarrow E = -\frac{\hbar^2 \kappa^2}{2m} = -\frac{me^4}{8\pi^2 \epsilon_0^2 \hbar^2 \rho_0^2} \quad [4.69]$$

Năng lượng

$$E_n = -\left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} = \frac{E_1}{n^2}, n = 1, 2, 3, \dots \quad [4.70]$$

Công thức **Bohr** (đưa ra 1913. QM:1924)

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar} \quad [4.54] \quad \rho \equiv \kappa r, \rho_0 \equiv \frac{me^2}{2\pi\epsilon_0 \hbar^2 \kappa} \quad [4.55]$$

$$E = -\frac{\hbar^2 \kappa^2}{2m} = -\frac{me^4}{8\pi^2 \epsilon_0^2 \hbar^2 \rho_0^2}$$

$$E_n = -\left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} = \frac{E_1}{n^2}, n = 1, 2, 3, \dots$$

$$\kappa = \left(\frac{me^2}{4\pi\epsilon_0 \hbar^2} \right) \frac{1}{n} = \frac{1}{an} \quad [4.71]$$

$$a \equiv \frac{4\pi\epsilon_0 \hbar^2}{me^2} = 0.529 \times 10^{-1} \text{ m} \quad [4.72]$$

Bán kính Bohr

$$\rho = \frac{r}{an} \quad [4.73]$$

Hàm sóng

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_l^m(\theta, \phi) \quad [4.74]$$

$$u(r) = rR(r) \quad [4.36]$$

$$u(\rho) = \rho^{l+1}e^{-\rho}v(\rho) \quad [4.60]$$

$$v(\rho) = \sum_{j=0}^{j_{\max}} c_j \rho^j \quad [4.62]$$

$$R_{nl}(r) = \frac{1}{r} \rho^{l+1} e^{-\rho} v(\rho) \quad [4.75]$$

$$c_{j+1} = \frac{2(j+l+1-n)}{(j+1)(j+2l+2)} c_j \quad [4.76]$$

Trạng thái nền (ground state) $n = 1$

$$E_n = -\left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} = \frac{E_1}{n^2}, n = 1, 2, 3, \dots$$

$$E_1 = -\left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] = -13.6 \text{ eV} \quad [4.77]$$

$$n = j_{\max} + l + 1 \quad [4.67]$$

$$l = 0, 1, 2, \dots; m = -l, -l+1, \dots, -1, 0, 1, \dots, l-1, l \quad [4.29]$$

$$n = 1 \Rightarrow l = 0, m = 0$$

$$\psi_{100}(r, \theta, \phi) = R_{10}(r)Y_0^0(\theta, \phi) \quad [4.78]$$

$$R_{10}(r) = \frac{c_0}{a} e^{-r/a} \quad [4.79]$$

Trạng thái nền (ground state) $n = 1$

$$\psi_{100}(r, \theta, \phi) = R_{10}(r)Y_0^0(\theta, \phi) \quad [4.78]$$

$$R_{10}(r) = \frac{c_0}{a} e^{-r/a} \quad [4.79]$$

$$\int_0^\infty |R_{10}|^2 r^2 dr = |c_0|^2 \frac{a}{4} = 1 \Rightarrow c_0 = \frac{2}{\sqrt{a}}.$$

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}$$

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a} \quad [4.80]$$

Trạng thái kích thích I $n = 2$

$$E_2 = \frac{-13.6 \text{ eV}}{4} = -3.4 \text{ eV} \quad [4.81]$$

$$n = j_{\max} + l + 1 \quad [4.67]$$

$$l = 0, 1, 2, \dots; m = -l, -l+1, \dots, -1, 0, 1, \dots, l-1, l \quad [4.29]$$

$$n = 2 \Rightarrow l = 0 (m = 0), 1 (m = -1, 0, 1)$$

$$R_{20}(r) = \frac{c_0}{2a} \left(1 - \frac{r}{2a} \right) e^{-r/2a} \quad [4.82]$$

$$R_{21}(r) = \frac{c_0}{4a^2} r e^{-r/2a} \quad [4.83]$$

Trạng thái kích thích n

$$E_n = \frac{E_1}{n^2} \quad \psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_l^m(\theta, \phi)$$

$$n = j_{\max} + l + 1 \quad [4.67]$$

$$l = 0, 1, 2, \dots; \quad m = -l, -l+1, \dots, -1, 0, 1, \dots, l-1, l \quad [4.29]$$

n cho trước: $l = 0, 1, 2, \dots, n-1$ [4.84]

mỗi l có $2l+1$ giá trị m

$$E_n \leftrightarrow \psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_l^m(\theta, \phi)$$

1 mức năng lượng ứng với bao nhiêu hàm sóng?

$$\text{Độ suy biến } d(n) = \sum_{l=0}^{n-1} (2l+1) = n^2 \quad [4.85]$$

Trạng thái kích thích n

$$v(\rho) = \sum_{j=0}^{j_{\max}} c_j \rho^j \quad [4.62] \quad c_{j+1} = \frac{2(j+l+1-n)}{(j+1)(j+2l+2)} c_j \quad [4.76]$$

$$v(\rho) = L_{n-l-1}^{2l+1}(2\rho) \quad [4.86]$$

Đa thức Laguerre liên kết

$$L_{q-p}^p(x) \equiv (-1)^p \left(\frac{d}{dx} \right)^p L_q(x) \quad [4.87]$$

Đa thức Laguerre

$$L_q(x) \equiv e^x \left(\frac{d}{dx} \right)^q (e^{-x} x^q) \quad [4.88]$$

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-\frac{r}{na}} \left(\frac{2r}{na} \right)^l \times \left[L_{n-l-1}^{2l+1} \left(\frac{2r}{na} \right) \right] Y_l^m(\theta, \phi) \quad [4.89]$$

$$\int \psi_{nlm}^* \psi_{n'l'm'} r^2 \sin \theta dr d\theta = \delta_{nn'} \delta_{ll'} \delta_{mm'} \quad [4.90]$$

$$x \frac{d^2 y}{dx^2} + (1-x) \frac{dy}{dx} + ny = 0$$

Nghiệm: Đa thức Laguerre

$$x \frac{d^2 y}{dx^2} + (\alpha + 1 - x) \frac{dy}{dx} + ny = 0$$

Nghiệm: Đa thức Laguerre liên kết

$$\rho \frac{d^2 v}{d\rho^2} + 2(l+1-\rho) \frac{dv}{d\rho} + [\rho_0 - 2(l+1)]v = 0$$

$$\frac{d}{dx} \left[(1-x^2) \frac{dy}{dx} \right] + n(n+1)y = 0$$

Nghiệm: Đa thức Legendre

Phổ nguyên tử hydro

Nguyên tử hydro $\leftrightarrow$ trạng thái $\psi_{nlm}(r, \theta, \phi)$

Không lực tác động: NT hydro ở yên trong ψ_{nlm}

Có tác động: NT hydro chuyển dời trạng thái



$$E_\gamma = E_i - E_f = -13.6 \text{ eV} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad [4.91]$$

Planck: $E_\gamma = h\nu = hc/\lambda$ [4.92]

Phổ nguyên tử hydro

Công thức Rydberg

$$\frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad [4.93]$$

Hằng số Rydberg

$$R \equiv \frac{m}{4\pi\hbar^3} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 = 1.097 \times 10^7 \text{ m}^{-1} \quad [4.94]$$

Phổ nguyên tử hydro

Chuyển dời $\rightarrow$ trạng thái cơ bản ($n=1$): dãy Lyman
Cực tím

Chuyển dời $\rightarrow$ trạng thái KT I ($n=2$): dãy Balmer.
Khả kiến

Chuyển dời $\rightarrow$ trạng thái KT II ($n=3$): dãy Paschen.
Hồng ngoại

