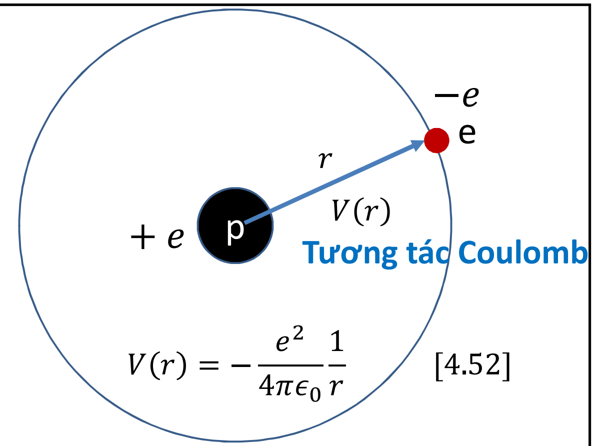
Nguyên tử hydro



$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} \qquad [4.52]$$

$m_p \gg m_e$ → proton đứng yên so với electron.
Chọn gốc tọa độ tại proton

Tọa độ cầu – Ph. trình bán kính

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

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

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

PT cho nguyên tử hydro

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

Tìm $u(r)$ và năng lượng E

Xét trạng thái liên kết ($E < 0$)

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

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

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

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

Giải PT – xét tiệm cận

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

$\boxed{\rho \to \infty}$ $\Rightarrow 1 \gg \dfrac{\rho_0}{\rho} \gg \dfrac{l(l+1)}{\rho^2} \Rightarrow \dfrac{d^2u}{d\rho^2} = u$

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

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

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

Giải PT – xét tiệm cận

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

$\boxed{\rho \to 0}$

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

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

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

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

$\rho \to \infty \quad u(\rho) \sim Ae^{-\rho}$ [4.58]
$\rho \to 0 \quad u(\rho) \sim C\rho^{l+1}$ [4.59]

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

Cần tìm $v(\rho)$.

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

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

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

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

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

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

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

Cần xác định các hệ số c_j

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

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

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

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

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

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

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

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

Tìm "dáng điệu" của $v(\rho)$ khi $\rho\to\infty$.

$\rho\to\infty$ thì ρ^j (j lớn) có đóng góp quyết định.

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

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

$c_j = \frac{2^j}{j!} c_0$ [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: $\sum_{j=0}^{\infty} \frac{x^j}{j!} = e^x$

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

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

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

Nhận xét: $\rho \to \infty$ $u(\rho) \to \infty$!!!

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

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

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

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

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

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

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

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

$\rho_0 = 2n$ [4.68]

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

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

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

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

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

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

Bán kính Bohr

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

Hàm sóng

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

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

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

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

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

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

Trạng thái nền (ground state) $n = 1$

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

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

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

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

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

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

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

Trạng thái nền (ground state) $n = 1$

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

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

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

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

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

Trạng thái kích thích I $n = 2$

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

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

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

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

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

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

Trạng thái kích thích n

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

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

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

n cho trước: $l = 0, 1, 2, \ldots, n-1$ [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?

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

Trạng thái kích thích n

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

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

Đa thức Laguerre liên kết

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

Đa thức Laguerre

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

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

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

[4.90]

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

Nghiệm: Đa thức Laguerre

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

Nghiệm: Đa thức Laguerre liên kết

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

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

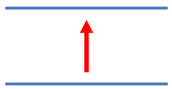
Nghiệm: Đa thức Legendre

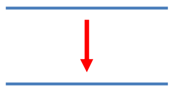
Phổ nguyên tử hydro

Nguyên tử hydro ↔ 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

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

Phổ nguyên tử hydro

Chuyển dời → trạng thái cơ bản (n=1): dãy Lyman

Cực tím

Chuyển dời → trạng thái KT I (n=2): dãy Balmer.

Khả kiến

Chuyển dời → trạng thái KT II (n=3): dãy Paschen.

Hồng ngoại