L36-Hydrogen Atom

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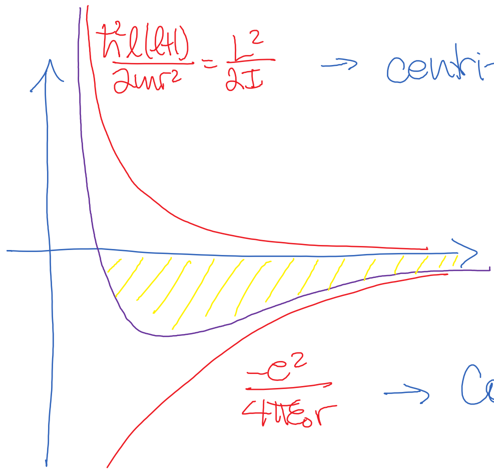
* Radial Equation

$$\hat{H}\psi = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi(r,\theta,\phi) \qquad V(r) = \frac{-e^2}{4\pi\epsilon_0 r}$$

$$= \left[\frac{-\hbar^2}{2m}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{l(l+1)}{r^2}\right) - \frac{e^2}{4\pi\epsilon_0 r}\right] \quad \frac{u(r)}{r} Y_{lm}(\theta,\phi)$$

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



$\frac{\hbar^2 l(l+1)}{2mr^2} = \frac{L^2}{2I}$ → centrifugal (inertial force)

$$F = -\left(\frac{\partial}{\partial r}\frac{L^2}{2I}\right)_{L\,const} = \frac{-\partial}{\partial r}\frac{\hbar^2 l(l+1)}{2mr^2}$$

$$= \frac{\hbar^2 l(l+1)}{mr} = \frac{(mvr)^2}{mr} = \frac{mv^2}{r}$$

V_{eff} = effective potential.

$\frac{-e^2}{4\pi\epsilon_0 r}$ → Coulomb attraction

- effective "wave number" $i\kappa$ (decay const. κ as $r \to \infty$) $\quad E = \frac{-\hbar^2\kappa^2}{2m}$

$$\frac{d^2u}{d(\kappa r)^2} = \left(1 - \frac{e^2}{4\pi\epsilon_0 r}\Big/\frac{\hbar^2\kappa^2}{2m} + \frac{l(l+1)}{(\kappa r)^2}\right)u$$

- normalize coordinates: $\rho = \kappa r \quad V/E = \rho_0/\rho = \frac{2me^2}{4\pi\epsilon_0 r\,\hbar^2\kappa^2} \quad \rho_0 = \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}$

$$\frac{d^2u}{d\rho^2} = \Big(\underbrace{1}_{r\to\infty} - \frac{\rho_0}{\rho} + \underbrace{\frac{l(l+1)}{\rho^2}}_{r\to 0}\Big)u$$

- assymptotic dependence:

as $r \to \infty$: $\quad \frac{d^2u}{d\rho^2} \approx u \quad \longrightarrow \quad u(\rho) \sim e^{-\rho}$ [similar to SHO]

as $r \to 0$: $\quad \frac{d^2u}{d\rho^2} \approx \frac{l(l+1)}{\rho^2}u \quad \longrightarrow \quad u(\rho) \sim \rho^{l+1}$ [like square well]

thus let $u(\rho) = \rho^{l+1}e^{-\rho}v(\rho)$

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

$$u''(\rho) = \Big[\Big(\underbrace{\frac{\ell(\ell+1)}{\rho^2}}_{\text{centrifugal}} - \frac{2(\ell+1)}{\rho} + \underbrace{1}_{\text{coulomb}}\Big)v + \Big(\frac{2(\ell+1)}{\rho} - 2\Big)v' + v''\Big]e^{-\rho}$$

$$\rho v'' + \underbrace{2}_{\text{doesn't match!}}(\ell+1-\rho)v' + (\rho_0 - 2(\ell+1))v = 0 \qquad (*)$$

* Radial Solution: this is very close to Laguerre's eq'n!

$f_n(x)$	index	a	b	wdx	$+p$ / $-p$	$+q$ / $-q$	$-\lambda$ / λ	h_n	wave type
$L_k^{(\alpha)}(x)$	$k=0,1,2\ldots$	$0<x<\infty$		$x^{\alpha}e^{-x}dx$	$x^{\alpha+1}e^{-x}$	0	k	$\frac{\Gamma(\alpha+1+k)}{k!}$	(Harmonic osc. Coulomb potential)

$$\frac{1}{x^\alpha e^{-x}}\Big[-\frac{d}{dx}x^{\alpha+1}e^{-x}\frac{d}{dx}\Big]L_k^{(\alpha)}(x) = k\,L_k^{(\alpha)}(x) \qquad \int_0^\infty x^\alpha e^{-x}L_{k'}^{(\alpha)}(x)\,L_k^{(\alpha)}(x) = \delta_{kk'}\frac{\Gamma(\alpha+1+k)}{k!}$$

$$xL'' + (\alpha+1-x)L' + kL = 0 \qquad k=0,1,2,\ldots \qquad \text{let } v(\rho) = L_k^{(\alpha)}(x=2\rho)$$

$$\frac{(*)}{2} = \frac{1}{2}\Big[\frac{x}{2}\cdot 4L'' + 2\Big(\ell+1-\frac{x}{2}\Big)\cdot 2L' + (\rho_0 - 2(\ell+1))L\Big] = 0 \qquad \alpha = 2\ell+1$$

$$= \Big[x\frac{d^2}{dx^2} + \Big(\underbrace{(2\ell+1)}_{\alpha}+1-x\Big)\frac{d}{dx} + \underbrace{\Big(\rho_0/2 - (\ell+1)\Big)}_{k}\Big]L_k^{(\alpha)}(x) = 0 \qquad \begin{aligned}\rho_0 &= 2(k+\ell+1)\\ &= 2n\end{aligned}$$

$$\psi_{n\ell m} = N\rho^\ell e^{-\rho}L_{n-\ell-1}^{2\ell+1}(2\rho)\,Y_{\ell m}(\theta,\phi) \quad \text{where } \rho = \kappa r \qquad E = -\frac{\hbar^2\kappa^2}{2m}$$

$$-\ell \le m \le \ell\,, \quad 0 \le \ell < n\,, \quad n = 1,2,3\ldots \qquad \kappa = \frac{me^2}{2\pi\varepsilon_0\hbar^2\rho_0} = \frac{me^2}{4\pi\varepsilon_0\hbar^2 n}$$

* series solution: let $v = \sum_{j=0}^{\infty} c_j\rho^j$

$$v' = \sum_{j=1}^{\infty} c_j(j)\rho^{j-1} = \sum_{j=0}^{\infty} c_{j+1}(j+1)\rho^j \qquad \rho v' = \sum_{j=0}^{\infty} c_j(j)\rho^j$$

$$v'' = \sum_{j=2}^{\infty} c_j(j)(j-1)\rho^{j-2} \qquad \rho v'' = \sum_{j=1}^{\infty} c_{j+1}(j+1)(j)\rho^j$$

$$\rho\sum_{j=2}^{\infty} c_j(j)(j-1)\rho^{j-2} + (2(\ell+1)-\rho)\sum_{j=1}^{\infty} c_j(j)\rho^{j-1} + (\rho_0 - 2(\ell+1))\sum_{j=0}^{\infty} c_j\rho^j = 0$$

relabel indices to get all terms like $\sum_{j=0}^{\infty}\cdots\rho^j$

$$\sum_{j=0}^{\infty}\Big[\underbrace{c_{j+1}(j+1)(j)}_{\rho v''} + 2(\ell+1)\underbrace{c_{j+1}(j+1)}_{v'} - 2\underbrace{c_j(j)}_{\rho v'} + (\rho_0 - 2(\ell+1))\underbrace{c_j}_{v}\Big]\rho^j = 0$$

c_{j+1} $\quad -2j + (\rho_0 - 2(\ell+1))$ $\quad 2(\ell+1+j) \to 0$ $\quad$ as $j\to\infty$ $\quad 2$

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

* quantization of energy E_n

This is the series for $v = e^{2\rho} = \sum_{j=0}^{\infty} \frac{(2\rho)^j}{j!} \xrightarrow{\text{as } \rho\to\infty} \infty$

Thus the series must truncate: $c_{j+1} = 0$ for some j_{max}

i.e. $\rho_0 = 2(l+1+j_{max})$ where $j_{max} = 0, 1, 2, \ldots$

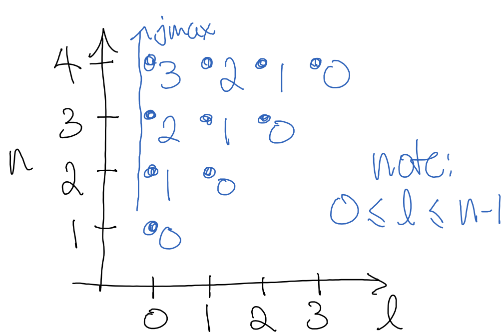
$$E = \frac{-\hbar^2\kappa^2}{2m} = \frac{-\hbar^2}{2m}\left(\frac{me^2}{2\pi\epsilon_0\hbar^2\rho_0}\right)^2 = \frac{-me^4}{2(4\pi\epsilon_0\hbar)^2\underbrace{(l+1+j_{max})^2}_{\text{define } n\equiv l+1+j_{max}}}$$

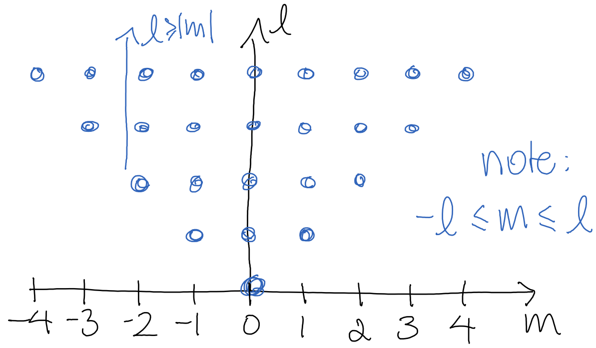
$$E_n = -\frac{1}{2}\underbrace{mc^2}_{\substack{\text{rest mass}\\ \text{of electron}}}\underbrace{\left(\frac{e^2}{4\pi\epsilon_0\hbar c}\right)^2}_{\alpha\approx 1/137 = \text{electric quantum}}\frac{1}{n^2}$$

We recovered the Bohr formula "legally"!

* Quantum numbers of H atom: 3: n, l, m

note: j_{max} = level for l^{th} angular state = # of radial lobes





at a given $l>0$, the first radial mode $R_{nl}(r)$ is already in an excited energy state

at a given $m\neq 0$ the first polar mode $P_l^{|m|}(\cos\theta)$ already has nonzero (azimuthal) ang. momentum.

-switching order of quantum numbers:

$n = 0, 1, 2, \dots \infty$ "shells, energy levels"

$\ell = 0$ "s", 1 "p", 2 "d", 3 "f", 4 "g", $\dots$ $n-1$ "ang. mom. orbitals"

$m = -\ell, -\ell+1, \dots -1, 0, 1, \dots \ell-1, \ell$ "magnetic substates"

- degeneracy: $g_\ell = 2\ell+1$ # of m substates

  $g_n = \sum_{\ell=0}^{n-1} 2\ell+1 = n^2$ # of energy substates

* Spectrum:

$$\frac{hc}{\lambda} = \hbar\nu = E_{if} = -E_0\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$\frac{1}{\lambda} = \frac{E_0}{\hbar c}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \qquad R_\infty = E_0/\hbar c = \frac{mc^2}{2\hbar c}\cdot\alpha^2$$

$$= 10973731\ /m$$

"Rydberg constant"