L29-Hydrogen Atom

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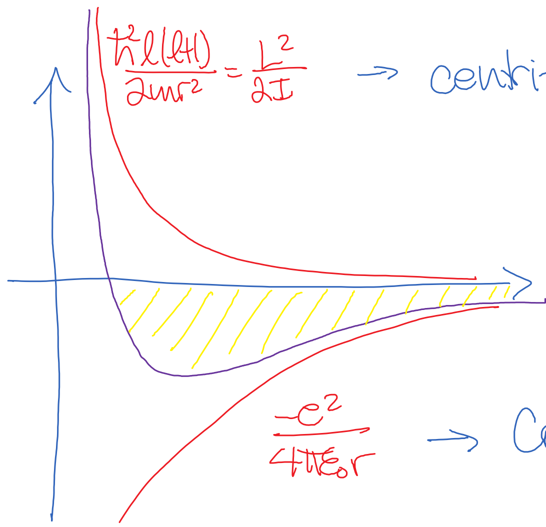
* Radial Equation

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

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

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



$\rightarrow$ centrifugal (inertial force)

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

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

V_{eff} = effective potential.

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

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

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

thus let $u(\rho) = \rho^{\ell} e^{-\rho} v(\rho)$

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

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

$$\rho v'' + 2(\ell+1-\rho) v' + (\rho_0 - 2(\ell+1)) v = 0$$

– 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 $\sum_{j=0}^{\infty} \cdots \rho^j$

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

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

* 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}

ie. $\rho_0 = 2(\ell+1+j_{max})$ where $j_{max} = 0, 1, 2, \ldots$

$$E = \frac{-\hbar^2 \kappa^2}{2m} = \frac{-\hbar^2}{2m}\left(\frac{me^2}{2\pi\varepsilon_0 \hbar^2 \rho_0}\right)^2 = \frac{-me^4}{2(4\pi\varepsilon_0 \hbar)^2 \underbrace{(l+1+j_{max})^2}}$$

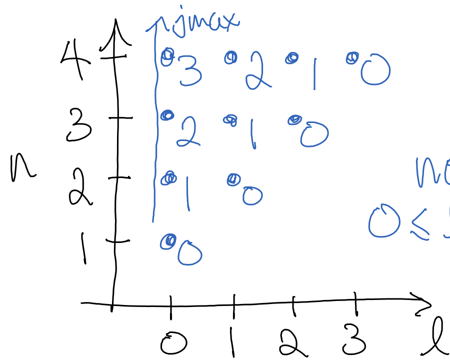
define $n \equiv l+1+j_{max}$

$$E_n = -\frac{1}{2}\underbrace{mc^2}_{\text{rest mass of electron}}\underbrace{\left(\frac{e^2}{4\pi\varepsilon_0 \hbar c}\right)^2}_{\alpha \approx 1/137 = \text{electric quantum}}\frac{1}{n^2}$$

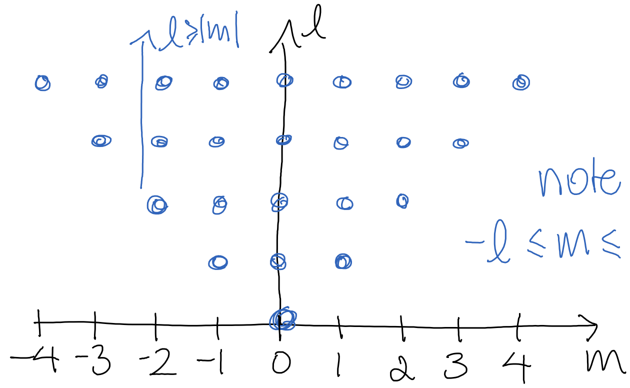
We recovered the Bohr formula "legally"!

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

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



note: $0 \leq l \leq n-1$



note: $-l \leq m \leq l$

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"

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

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

- degeneracy: $g_l = 2l+1$ # of m substates

$g_n = \sum_{l=0}^{n-1} 2l+1 = n^2$ # 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"