Review Bohr model

$$\alpha = \frac{Ke^2}{\hbar c}$$

skip?

Skip

mea

$\cancel{ma} = F$

$$\mu \frac{v^2}{r} = \frac{Ke^2}{r^2} = \frac{\alpha \hbar c}{r^2}$$

$$v^2 = \frac{\alpha \hbar c}{\mu r}$$

$$l = \mu v r$$

$$l^2 = \mu^2 r^2 \left(\frac{\alpha \hbar c}{\mu r}\right) = \alpha \mu \hbar c r$$

$$r = \frac{l^2}{\alpha \mu \hbar c}$$

Bohr: $l = n\hbar \implies r = \frac{n^2 \hbar}{\alpha \mu c}$

$$n = 1 \implies a_0 = \frac{\hbar}{\alpha \mu c} \approx 0.529\ \text{Å}$$

$$E = \frac{1}{2}\mu v^2 - \frac{Ke^2}{r}$$

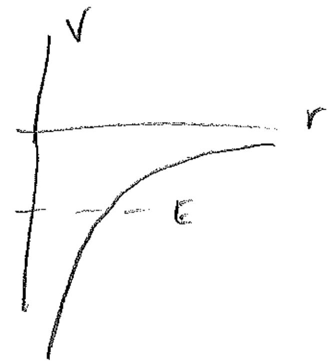
$$= -\frac{1}{2}\frac{Ke^2}{r} = -\frac{1}{2}\frac{\alpha \hbar c}{r} = -\frac{1}{2}\alpha \hbar c \left(\frac{\alpha \mu c}{n^2 \hbar}\right)$$

$$= -\frac{1}{2}\frac{\alpha^2 \mu c^2}{n^2}$$

$$= -\frac{\left(\frac{1}{2}\alpha^2 \mu c^2\right)}{n^2} = -\frac{(13.6\ \text{eV})}{n^2}$$

Hydrogen atom

$$-\frac{\hbar^2}{2m}\nabla^2 u + V u = E u$$



$$V(r) = -\frac{Ke^2}{r} = -\frac{\alpha\hbar c}{r}$$

Bound states $E<0$ (discrete)

"Free" states $E>0$ (continuum)

Spherical symmetry $\Rightarrow u(r,\theta,\phi) = R_{E\ell}(r)\, Y_{\ell m}(\theta,\phi)$

$$\frac{d^2}{dr^2}(rR_{E\ell}) - \frac{\ell(\ell+1)}{r^2}(rR_{E\ell}) = -\frac{2m}{\hbar^2}\left(E + \frac{\alpha\hbar c}{r}\right)(rR_{E\ell})$$

Define $w(r) = r R_{E\ell}(r)$

$$\frac{d^2 w}{dr^2} - \frac{\ell(\ell+1)}{r^2} w = \underbrace{\left(-\frac{2mE}{\hbar^2}\right)}_{\substack{\text{positive quantity (for bound states)} \\ \text{w/ units of (length)}^{-2}}} w - \left(\frac{2m\alpha c}{\hbar}\right)\frac{w}{r}$$

Consider bound states : $E < 0$

Multiply by $\frac{\hbar^2}{-2mE} > 0$ which has units of $(\text{length})^2$

$$\underbrace{\frac{\hbar^2}{-2mE}\frac{d^2}{dr^2}}_{\frac{d^2}{d\rho^2}} w - \ell(\ell+1)\underbrace{\left(\frac{\hbar^2}{-2mEr^2}\right)}_{\substack{\text{positive, dimensionless} \\ \to \text{call it } \frac{1}{\rho^2}}} w = w - 2\underbrace{\frac{m\alpha c}{\hbar}\sqrt{\frac{\hbar^2}{-2mE}}}_{\underbrace{\sqrt{\frac{m\alpha^2c^2}{-2E}}}_{\substack{\text{dimensionless} \\ \to \text{call it } \lambda}}}\underbrace{\sqrt{\frac{\hbar^2}{-2mE}}\frac{1}{r}}_{\frac{1}{\rho}} w$$

$$\Rightarrow \boxed{E = -\frac{m\alpha^2c^2}{2\lambda^2}}$$

$$\frac{d^2w}{d\rho^2} - \frac{\ell(\ell+1)}{\rho^2}w = w - \frac{2\lambda}{\rho}w$$

$$E = -\left(\frac{1}{2}mc^2\alpha^2\right)\frac{1}{\lambda^2} = -\frac{(Ryd)}{\lambda^2} \qquad (Ryd = 13.6\text{ eV})$$

$$\rho = \sqrt{\frac{-2mE}{\hbar^2}}\,r = \sqrt{\frac{-2m}{\hbar^2}\left(-\frac{m\alpha^2c^2}{2\lambda^2}\right)}\,r = \frac{m\alpha c}{\hbar\lambda}r = \frac{r}{\lambda a_0}$$

where $a_0 = \frac{\hbar}{m\alpha c}$ = Bohr = 0.529 Å

$$\Rightarrow \boxed{\rho = \frac{r}{\lambda a_0}}$$

$$\frac{d^2w}{d\rho^2} + \left[-\frac{l(l+1)}{\rho^2} + \frac{2\lambda}{\rho} - 1 \right] w = 0$$

We will solve to eqn & will find that its solutions are "well behaved" (i.e. normalizable) if λ is an integer $> l$.

- Solve this eqn by looking at $\rho \to 0$ and $\rho \to \infty$ limits
- Asymptotic behavior as $\rho \to \infty$

$$\frac{d^2w}{d\rho^2} - w = 0 \quad \Rightarrow \quad w(\rho) \cong \cancel{e^{\rho}},\ e^{-\rho}$$

- Let $w(\rho) = y(\rho)\, e^{-\rho}$ for $y(\rho)$ some polynomial

$$w' = y' e^{-\rho} - y e^{-\rho}$$

$$w'' = y'' e^{-\rho} - 2y' e^{-\rho} + y e^{-\rho}$$

$$\left[y'' - 2y' + \cancel{y} \right] + \left[-\frac{l(l+1)}{\rho^2} + \frac{2\lambda}{\rho} - \cancel{1} \right] y = 0$$

$$y'' - 2y' + \left(\frac{2\lambda}{\rho} - \frac{l(l+1)}{\rho^2} \right) y = 0$$

$$y'' - 2y' + \frac{2\lambda}{\rho} y - \frac{l(l+1)}{\rho^2} y = 0$$

Try power series ansatz: $y = a_k \rho^k + a_{k+1} \rho^{k+1} + a_{k+2} \rho^{k+2} + \dots$

where a_k is the first nonvanishing coefficient $(a_0 = a_1 = \dots = a_{k-1} = 0)$
(k to be determined later)

$$y = \sum_{i=k}^{\infty} a_i \rho^i$$

$$y' = \sum i a_i \rho^{i-1}$$

$$y'' = \sum i(i-1) a_i \rho^{i-2}$$

$$\underbrace{\sum_{i=k} i(i-1) a_i \rho^{i-2}}_{\text{let } i = i'+1} - \sum_{i=k} 2 i a_i \rho^{i-1} + \sum_{i=k} 2\lambda a_i \rho^{i-1} - \underbrace{\sum_{i=k} l(l+1) a_i \rho^{i-2}}_{i = i'+1} = 0$$

$$\sum_{i'=k-1} (i'+1) i' a_{i'+1} \rho^{i'-1} \qquad \sum_{i'=k-1} l(l+1) a_{i'+1} \rho^{i'-1}$$

Relabel $i' \to i$ and combine the sums

$$\sum_{i=k} \left[(i+1) i a_{i+1} - 2 i a_i + 2\lambda a_i - l(l+1) a_{i+1} \right] \rho^{i-1}$$

$$+ \left[k(k-1) a_k - l(l+1) a_k \right] \rho^{k-2} = 0$$

If $b(\rho) = \sum b_i \rho^i = 0$ (for all ρ), then $b_i = 0$ for all i

[argument by taking derivatives + setting to zero]

$$[k(k-1) - l(l+1)]\, a_k = 0$$

If $k(k-1) \neq l(l+1)$ then $a_k = 0$

but a_k is the first ~~non~~vanishing coefficient

so $k^2 - k - l(l+1) = 0 \Rightarrow k = l+1,\ -l$

leads to nonnormalizable wavefn for $l \geq 1$

i.e. a_{l+1} is the first nonvanishing coefficient.

[$k = -l \Rightarrow y \sim \frac{1}{\rho^l} \Rightarrow R \sim \frac{1}{\rho^{l+1}} \Rightarrow \int \rho^2 d\rho\, |R|^2 \sim \int \frac{d\rho}{(\rho^{2l})} = \infty$ if $l \geq 1$]

For $l = 0$ need to look at recursion rel.

$$y(\rho) = a_{l+1}\rho^{l+1} + a_{l+2}\rho^{l+2} + a_{l+3}\rho^{l+3} + \ldots$$

For $l = 0$, $k = 0$ $\Rightarrow a_0 = 0$ from

Also

$$[i(i+1) - l(l+1)]\, a_{i+1} + 2[\lambda - i]\, a_i = 0 \quad \text{for } i \geq k$$

from

For $i \geq k$, $$a_{i+1} = \frac{-2(\lambda - i)}{[i(i+1) - l(l+1)]} a_i$$ (recursion relation)

e.g. $$\left[a_{l+2} = \frac{-2(\lambda - l - 1)}{2(l+1)} a_{l+1} \right]$$ omit

$$\left[a_{l+3} = \frac{-2(\lambda - l - 2)}{2(2l+3)} a_{l+2} \right]$$ omit

(these are given later)

etc.

So recursion relation determines all the coefficients in terms of a_{l+1}, which is determined by normalization condition

Backing

$\ell = 0$ is a special case

$k=0$ is a soln of $[k(k-1) - \ell(\ell+1)]a_k = 0$ for $\ell = 0$

But then the $i=k$ eqn gives: $2\lambda a_0 = 0$

Let's go back to (setting $\ell=0$)

$$\underbrace{\sum_k i(i-1)a_i\rho^{i-2}}_{\text{vanishes for } i=0,1} - \underbrace{\sum_k 2ia_i\rho^{i-1}}_{\text{vanishes for } i=0} + \sum 2\lambda a_i\rho^{i-1} = 0$$

so the ρ^{-1} term is just $2\lambda a_0 = 0$ ✓

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go back to $y'' - 2y' + \frac{2\lambda}{\rho}y = 0$

Can see that $y \sim$ const $+ a\rho + \ldots$
can't solve this unless $\lambda = 0$

so we need to start w/ $k \neq 0 \ldots$

this would be normalizable $\int r^2 dr \left(\frac{1}{r}\right)^2 \sim$ const

go back even further to $\nabla^2 u = -\frac{2m}{\hbar^2}(E - V(r))u$

$\ell = 0 \Rightarrow$ $\frac{\partial^2}{\partial r^2}(ru) = -\frac{2m}{\hbar^2}\left(E - \frac{\alpha\hbar c}{r}\right)(ru)$

Now as $r \to 0$: $ru = C + Dr \Rightarrow u = \frac{C}{r} + D$

$u \sim \frac{1}{r} \Rightarrow \nabla^2 u = \delta^{(3)}(\rho)$ not $\left(\frac{1}{r^2}\right)$ ← $\frac{\partial^2}{\partial r^2}(C) = -\frac{2m}{\hbar^2}\left(\cancel{E} - \frac{\alpha\hbar c}{r}\right)C$ ← can't satisfy

Backup

$$0 = [k(k-1) - \ell(\ell+1)]\, a_k\, \rho^{k-2}$$

$$+ \sum_{i=k} \Big([\, i(i+1) - \ell(\ell+1)]\, a_{i+1} + 2(\lambda - i)\, a_i \Big) \rho^{i-1}$$

Look at $i=k$ term

$$\Big([\, k(k+1) - \ell(\ell+1)]\, a_{k+1} + 2[\lambda - k]\, a_k \Big) \rho^{k-1}$$

$k = \ell+1, -\ell$ solve first eqn

Plug $k = -\ell$ into 2nd

$$[\underbrace{(-\ell)(-\ell+1) - \ell(\ell+1)}_{-2\ell}]\, a_{-\ell+1} + 2(\lambda + \ell)\, a_{-\ell}$$

If $\ell = 0$ $\Rightarrow$ $\boxed{\lambda a_0 = 0}$ $\longrightarrow$ if $\lambda = 0$ and $\ell = 0$

then

$$\frac{d^2 w}{d\rho^2} - w = 0$$

$$\boxed{e^{-\rho}}$$

$\ell = 0$

$$y'' - 2y' + \frac{2\lambda}{\rho} y = 0$$

Consider recursion relation for large i

$$a_{i+1} \approx \frac{2i}{i(i+1)} a_i = \frac{2}{i+1} a_i$$

<u>If</u> this were valid for all i, then we could write

$$a_i = \frac{2^i}{i!} a_0 \quad \Rightarrow \quad a_{i+1} = \frac{2^{i+1}}{(i+1)!} a_0 = \frac{2}{i+1} a_i \checkmark$$

(not Bohr!)

Large i behavior determines large ρ behavior

$$y(\rho) \xrightarrow[\text{large } \rho]{} \sum_{i=0}^{\infty} \frac{2^i}{i!} \rho^i a_0 = a_0 \sum \frac{(2\rho)^i}{i!} = a_0 e^{2\rho}$$

Then $w(\rho) = y(\rho) e^{-\rho} \approx e^{\rho}$! nonnormalizable

Loophole: this behavior can be avoided only if the series terminates at finite i

Series will terminate <u>if</u> λ is some integer $\geq l+1$.

Call this integer n = principal quantum number

$$\Rightarrow E_n = -\frac{(Ryd)}{n^2}, \quad n \geq l+1$$

(Bohr model prediction!)

Recursion relation: $$a_{i+1} = \frac{-2(n-i)}{i(i+1)-l(l+1)}\, a_i$$

$$\Rightarrow a_{n+1} = 0$$

The only nonvanishing coeffs are $\{a_{l+1}, \dots, a_n\}$

$$y(\rho) = \rho^{l+1}\Big[\underbrace{a_{l+1} + a_{l+2}\rho + \dots + a_n \rho^{n-l-1}}\Big]$$

called associated Laguerre polynomial $L^{2l+1}_{n-l-1}(2\rho)$

see below

$$a_{l+2} = -\frac{(n-l-1)}{(l+1)}\, a_{l+1}$$

$$\left[\; a_{l+3} = -\frac{(n-l-2)}{(2l+3)}\, a_{l+2} \;\right]$$ omit

⋮

For example

$n=l+1$: $$L_0^{2l+1} = a_{l+1}$$

$n=l+2$: $$L_1^{2l+1} = a_{l+1}\left[1 - \frac{\rho}{l+1}\right]$$

$n=l+3$: $$\left[\; L_2^{2l+1} = a_{l+1}\left[1 - \frac{2\rho}{l+1} + \frac{2\rho^2}{(2l+3)(l+1)}\right] \;\right]$$ omit

Griffiths

$$L^{2l+1}_{n-l-1}(x) \equiv -\left(\frac{d}{dx}\right)^{2l+1}\left[e^{x}\left(\frac{d}{dx}\right)^{n+l}\left[e^{-x}x^{n+l}\right]\right], \quad x = 2\rho$$

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associated Laguerre =  - D[  Exp[x] D[ Exp[-x] x^(n+L), {x,n+L} ], {x, 2L+1} ]
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Background

$$L^{2\ell+1}_{n-\ell-1}(x) = -\left(\frac{d}{dx}\right)^{2\ell+1}\left[e^{x}\left(\frac{d}{dx}\right)^{n+\ell}\left(e^{-x}x^{n+\ell}\right)\right]$$

$$L^{2\ell+1}_{0}(x) = -\left(\frac{d}{dx}\right)^{2\ell+1}\left[e^{x}\underbrace{\left(\frac{d}{dx}\right)^{2\ell+1}\left(e^{-x}x^{2\ell+1}\right)}_{(-1)^{2\ell+1}e^{-x}\left(x^{2\ell+1}+\text{lower powers}\right)}\right]$$

$$= \left(\frac{d}{dx}\right)^{2\ell+1}\left[x^{2\ell+1} + \text{lower powers}\right]$$

$$= (2\ell+1)!$$

	$\ell=0$	$\ell=1$	$\ell=2$	$\ell=3$
$n=1$	$L_0^1 = 1$			
$n=2$	$L_1^1 = -2(x-2)$	$L_0^3 = 6$		
$n=3$	$L_2^1 = 3(x^2-6x+6)$	$L_1^3 = -24(x-4)$	$L_0^5 = 120$	
$n=4$	$L_3^1 = -4(x^3-12x^2+36x-24)$	$L_2^3 = 60(x^2-10x+20)$	$L_1^5 = -720(x-6)$	$L_0^7 = 5040$

$$y(\rho) = \rho^{l+1} L^{2l+1}_{n-l-1}(2\rho)$$

$$w(\rho) = y(\rho)\, e^{-\rho}$$

But $W = rR_{El}(r) \propto \rho R_{El}$ n

$$\begin{cases} R_{nl}(r) \sim \rho^{l} L^{2l+1}_{n-l-1}(2\rho)\, e^{-\rho} \\ u_{nlm}(r,\theta,\phi) = R_{nl}(r)\, Y_{lm}(\theta,\phi) \\ E_n = -\dfrac{\left(\frac{1}{2}mc^2\alpha^2\right)}{n^2} \end{cases}$$

where $\rho = \dfrac{r}{na_0}$

$a_0 = \dfrac{\hbar}{mc\alpha}$ = Bohr radius

$\frac{1}{2}mc^2\alpha^2 = \text{Ryd} = 13.6\ \text{eV}$

Since $n \geq l+1 \Rightarrow \begin{cases} n = 1, 2, 3, \dots \\ l = 0, \dots, n-1 \\ m = l, \dots, l \end{cases}$

Normalization $\Rightarrow 1 = \int |u_{nlm}|^2\, r^2 dr\, d\Omega = \int |R_{nl}|^2 r^2 dr \underbrace{\int |Y_{lm}|^2 d\Omega}_{1}$

So we require

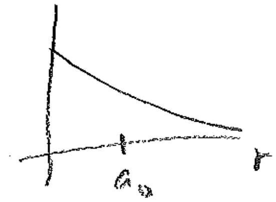
$$\int_0^\infty r^2 |R_{nl}(r)|^2\, dr = 1$$

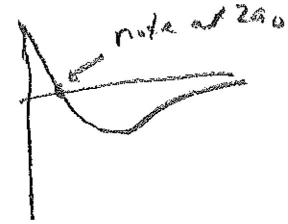
Units $\Rightarrow R_{nl} \sim \dfrac{1}{a_0^{3/2}}$

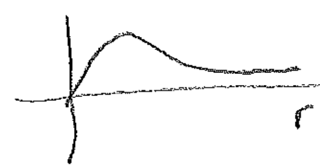
$\boxed{\text{useful} \quad \int_0^\infty x^n e^{-x}\, dx = n!}$

Hydrogen atom energy eigenfunctions

	n	ℓ	m	$u_{n\ell m}(r,\theta,\phi)$
1s	1	0	0	$\left(\frac{2}{a_0^{3/2}}\right)\frac{1}{\sqrt{4\pi}}e^{-\frac{r}{a_0}}$
2s	2	0	0	$\frac{1}{\sqrt{2}\,a_0^{3/2}}\frac{1}{\sqrt{4\pi}}\left(1-\frac{r}{2a_0}\right)e^{-\frac{r}{2a_0}}$
2p	2	1	m	$\frac{1}{\sqrt{24}\,a_0^{3/2}}\left(\frac{r}{a_0}\right)e^{-\frac{r}{2a_0}}\begin{cases}-\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i\phi}\\ \sqrt{\frac{3}{4\pi}}\cos\theta\\ +\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{-i\phi}\end{cases}$







end of course
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