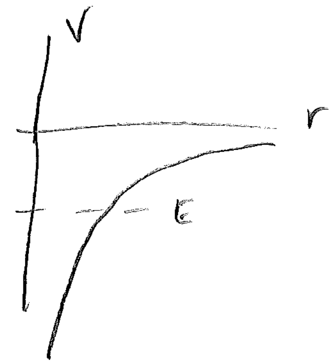
Hydrogen atom

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

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



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

$$\frac{d^2w}{dr^2} - \frac{\ell(\ell+1)}{r^2}w = \underbrace{\left(-\frac{2mE}{\hbar^2}\right)}_{}w - \left(\frac{2m\alpha c}{\hbar}\right)\frac{w}{r}$$

positive quantity (for bound states)
w/ units of (length)$^{-2}$

Consider bound states: $E < 0$

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

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

$$\underbrace{\sqrt{\frac{m\alpha^2c^2}{-2E}}}_{\substack{\text{dimensionless}\\ \to \text{ call it } \lambda}} \Rightarrow E = -\frac{m\alpha^2c^2}{2\lambda^2}$$

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

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

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

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

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

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

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

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

~~More generally, w(ρ) = ρ ... subject this~~

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

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

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

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

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

Look at $\rho \to 0$ limit: $y'' - \cancel{2y'} - \frac{\ell(\ell+1)}{\rho^2} y = 0$

try neglecting

What are some simple fcns? $\rho, \rho^2, \rho^n \ldots$ try ρ^a

$a(a-1)\rho^{a-2} - \ell(\ell+1)\rho^{a-2} = 0$

$a(a-1) = \ell(\ell+1) \Rightarrow a = \ell+1$ (also $-\ell$ but not normalizable)

So $y \to \rho^{\ell+1}$ as $\rho \to 0$;

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

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)

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

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

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

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

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

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

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

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

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

[argument by taking derivative + 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 nonvanishing coefficient

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

leads to non normalizable wavefn

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

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

Also

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

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

e.g. $$a_{l+2} = \frac{-2(\lambda - l - 1)}{2(l+1)} a_{l+1}$$

$$a_{l+3} = \frac{-2(\lambda - l - 2)}{2(2l+3)} a_{l+2}$$

etc.

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

Consider recursion relation for large i

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

~~If~~ 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 if 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 $\{a_{l+1}, \ldots, a_n\}$

$$y(\rho) = \rho^{l+1}\Big[\underbrace{a_{l+1} + a_{l+2}\rho + \ldots + a_n \rho^{n-l-1}}_{\text{called associated Laguerre polynomial } L^{2l+1}_{n-l-1}(2\rho)}\Big]$$

see below

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

$$a_{l+3} = -\frac{(n-l-2)}{(2l+3)}\, a_{l+2}$$

$\vdots$

For example

$n = l+1$: $L^{2l+1}_0 = a_{l+1}$

$n = l+2$: $L^{2l+1}_1 = a_{l+1}\left[1 - \frac{\rho}{l+1}\right]$

$n = l+3$: $L^{2l+1}_2 = a_{l+1}\left[1 - \frac{2\rho}{l+1} + \frac{2\rho^2}{(2l+3)(l+1)}\right]$

Griffiths

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

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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

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

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

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

$$= (2l+1)!$$

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

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

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

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

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

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

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

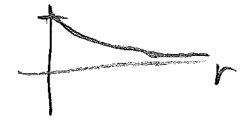
So we require

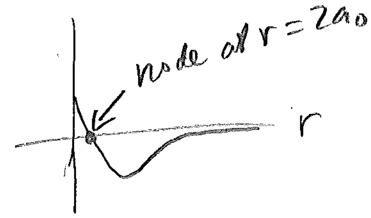
$$\int_0^\infty r^2 |R_{nl}(r)|^2 dr = 1$$

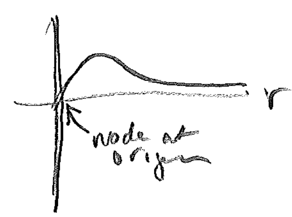
Units $\Rightarrow R_{nl} \sim \dfrac{1}{a_0^{3/2}}$

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

$n\,l\,m$	$\rho = \frac{r}{na_0}$	$u_{nlm}(r,\theta,\phi)$
1 0 0	$\frac{r}{a_0}$	$\sim \rho^0 L_0^1(2\rho)e^{-\rho}\, Y_{00}(\theta,\phi) = \left(\frac{2}{a_0^{3/2}}\right)\frac{1}{\sqrt{4\pi}} e^{-\frac{r}{a_0}}$
2 0 0	$\frac{r}{2a_0}$	$\sim \rho^0 \underbrace{L_1^1(2\rho)}_{a_1(1-\rho)} e^{-\rho}\, Y_{00}(\theta,\phi) = \frac{1}{\sqrt{2}\,a_0^{3/2}}\frac{1}{\sqrt{4\pi}}\left(1-\frac{r}{2a_0}\right)e^{-\frac{r}{2a_0}}$
2 1 m	$\frac{r}{2a_0}$	$\sim \rho^1 L_0^3(2\rho)e^{-\rho}\, Y_{1m}(\theta,\phi) = \frac{1}{\sqrt{24}\,a_0^{3/2}}\left(\frac{r}{a_0}\right)e^{-\frac{r}{2a_0}} \begin{cases} -\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i\phi} \\ \sqrt{\frac{3}{4\pi}}\cos\theta \\ \sqrt{\frac{3}{8\pi}}\sin\theta\, e^{-i\phi} \end{cases}$







$$K = \left(\frac{r}{a_0}\right)^k e^{-\frac{r}{na_0}}$$

$$\int_0^\infty dr\, r^{2+2k} e^{-\frac{2r}{na_0}} dr = (2+2k)!\, a_0^3 \left(\frac{n}{2}\right)$$

$$k = 0 \Rightarrow 2!\left(\frac{1}{2}\right)$$