Hydrogen

$$V(r) = \frac{-e^2}{4\pi\varepsilon_0 r}$$

e = charge of electron

$$\varepsilon_0 = 8.85 \times 10^{-12} \frac{C^2}{Nm^2}$$

Radial Eqn

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[\frac{-e^2}{4\pi\varepsilon_0 r} + \frac{\hbar^2 l(l+1)}{2mr^2}\right]u = Eu$$

Strategy

1. Work down to a dimensionless differential eqn.
2. Examine $\rho \to 0$, $\rho \to \infty$ limits.
3. Construct power series solution.

Work Down to Dimensionless Eqn

Consider bound states, $E<0$. You can do scattering states in grad school.

Define

$$\kappa = \sqrt{\frac{-2mE}{\hbar^2}} \implies E = \frac{-\hbar^2 \kappa^2}{2m}$$

Divide by E

$$\frac{-\hbar^2}{2mE} \frac{d^2u}{dr^2} = \left[1 + \frac{e^2}{4\pi\varepsilon_0 E r} - \frac{\hbar^2 \ell(\ell+1)}{2mr^2 E}\right] u$$

$$\frac{1}{\kappa^2} \frac{d^2u}{dr^2} = \left[1 - \frac{2me^2}{4\pi\varepsilon_0 \hbar^2 \kappa^2 r} + \frac{\ell(\ell+1)}{\kappa^2 r^2}\right] u$$

Dimensionless variables + constants

$$\rho \equiv \kappa r \qquad \rho_0 = \frac{me^2}{2\pi\varepsilon_0 \hbar^2 \kappa}$$

Note, we expect the energy to be quantized, so we are trying to find a condition restricting ρ_0.

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

Consider $\rho \to 0$, $\rho \to \infty$ limits

$\rho \to \infty$ Limit

$$\frac{d^2u}{d\rho^2} = u$$

$$u = Ae^{-\rho} + Be^{+\rho}$$

$B = 0$ because u not normalizable as $\rho \to \infty$.

As $\rho \to \infty$, $u = Ae^{-\rho}$

$\rho \to 0$ limit $\qquad \frac{1}{\rho^2}$ term dominates

$$\frac{d^2 u}{d\rho^2} = \frac{l(l+1)}{\rho^2} u$$

Let $u = \rho^\alpha$, $\frac{du}{d\rho} = \alpha \rho^{\alpha-1}$, $\frac{d^2 u}{d\rho^2} = \alpha(\alpha-1)\rho^{\alpha-2}$

$$\alpha(\alpha-1)\rho^{\alpha-2} = l(l+1)\frac{\rho^\alpha}{\rho^2}$$

$$\alpha(\alpha-1) = l(l+1)$$

Solutions $\quad \alpha = l+1, \quad \alpha = -l \qquad l \geq 0$

So as $\rho \to 0$, $\quad u = A\rho^{l+1} + B\rho^{-l}$

$B = 0$ since $\rho^{-l} \to 0$ as $\rho \to 0$

$$u = A\rho^{l+1}$$

Putting the two limits together

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

$\Rightarrow$ Normalization constant buried in $v(\rho)$

Find differential equation for $v(\rho)$

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

$$\cancel{= e^{-\rho} \rho^{l+1} \Big[(l+1}$$

$$\cancel{\frac{d^2 u}{d\rho^2} =}$$

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

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

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

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

Collect terms in $v(\rho)$

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

$$+ e^{-\rho}\rho^{l}\left[-\rho + l + l+1-\rho+1\right]\frac{dv}{d\rho}$$

$$+ e^{-\rho}\rho^{l}\left[\rho\frac{d^2v}{d\rho^2}\right]$$

$$= \rho^{l}e^{-\rho}\left[\left(\frac{l(l+1)}{\rho} - 2l - 2 + \rho\right)v(\rho)\right.$$

$$+ 2(l+1-\rho)\frac{dv}{d\rho}$$

$$\left. + \rho\frac{d^2v}{d\rho^2}\right]$$

Substitute into dimensionless radial eqn

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

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

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

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

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

Collect terms

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

Propose a power series solution

$$v(\rho) = \sum_{j=0}^{\infty} a_j \rho^j$$

$$\frac{dv}{d\rho} = \sum_{j=1}^{\infty} j a_j \rho^{j-1} = \sum_{j'=0}^{\infty} (j'+1) a_{j'+1} \rho^{j'}$$

Let $j' = j-1$, $j = j'+1$

$$\frac{d^2v}{d\rho^2} = \sum_{j=1}^{\infty} (j+1) j \, a_{j+1} \rho^{j-1}$$

$$= \sum_{j=0}^{\infty} (j+1) j \, a_{j+1} \rho^{j-1}$$ since $j=0$ kills $j=0$ term

$$\rho \frac{d^2v}{d\rho^2} = \sum_{j=0}^{\infty} (j+1) j \, a_{j+1} \rho^j$$

$$2(l+1)\frac{dv}{d\rho} - 2\rho\frac{dv}{d\rho} = 2(l+1)\sum_{j=0}^{\infty} (j+1) a_{j+1} \rho^j$$

$$- 2 \sum_{j=0}^{\infty} j a_j \rho^j$$

where I used both forms of the $\frac{dv}{d\rho}$ expansion

$$(\rho_0 - 2\ell - 2)\, v(\rho) = \sum_{j=0}^{\infty} a_j (\rho_0 - 2\ell - 2)\, \rho^j$$

Substitute expansions into modified radial eqn

$$\sum_{j=0}^{\infty} (j+1)\, j\, a_{j+1} \rho^j + 2(\ell+1) \sum (j+1)\, a_{j+1}\, \rho^j$$

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

Collect Like powers

$$j(j+1)\, a_{j+1} + 2(\ell+1)(j+1)\, a_{j+1}$$

$$- 2 j a_j + (\rho_0 - 2\ell - 2)\, a_j = 0$$

Recurrence Relation

$$a_{j+1} = \frac{2j - (\rho_0 - 2\ell - 2)}{(j+1)(j + 2\ell + 2)}\, a_j$$

$$a_{j+1} = \frac{(2j + 2l + 2) - \rho_0}{(j+1)(j + 2l + 2)} a_j$$

This allows us to build all coefficients of the series if we choose a_0.

Two possibilities

1. There are a finite number of non-zero $a_j \Rightarrow$ the series defines a polynomial.

2. The series is infinite.

See what the series does as $j \to \infty$.

$$j \to \infty \Rightarrow a_{j+1} = \frac{2j}{j^2} a_j = \frac{2}{j} a_j$$

$$\Rightarrow a_j \sim \frac{2^j}{j!}$$

This gives $v(\rho)$ as

$$v(\rho) = \sum a_j \rho^j = \sum \frac{2^j}{j!} \rho^j$$

$$= e^{2\rho}$$ recognizing the power series of the exponential.

This gives $u(\rho)$ as

$$u(\rho) = e^{-\rho} \rho^{l+1} e^{2\rho} = e^{\rho} \rho^{l+1}$$

$\Rightarrow$ Not normalizable as $\rho \to \infty$

$\Rightarrow$ There must be largest $j \equiv j_{max}$ such that $a_{j_{max}+1} = 0 \Rightarrow$ The series truncates at some point.

What does this imply?

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

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

$\Rightarrow$ ρ_0 is an integer and therefore energy is quantized.

Define Principle Quantum Number

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

$\Rightarrow$ Note, $j_{max} \geq 0$, $l \geq 0$

$\Rightarrow$ $n \geq 1$, $n = 1, 2, 3, \ldots$

For the power series to truncate,

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

$$2n = \rho_0$$

Dig back through our definitions

$$E = \frac{-\kappa^2 \hbar^2}{2m}$$

$$\kappa = \frac{me^2}{2\pi\varepsilon_0 \hbar^2 \rho_0}$$

Bohr Formula

$$E_n = -\left(\frac{me^2}{2\pi\varepsilon_0 \hbar^2 \rho_0}\right)^2 \frac{\hbar^2}{2m}$$

$$= -\left(\frac{m}{2\hbar^2}\right)\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{n^2}$$

Collect a characteristic length

Bohr Radius

$$a = \frac{4\pi\varepsilon_0 \hbar^2}{me^2} = 0.529 \times 10^{-10} m \approx \frac{1}{2} \mathring{A}$$

$$\kappa = \frac{1}{an} \qquad E = \frac{-\hbar^2}{2ma^2} \frac{1}{n^2}$$

Full Hydrogen Wave Function

$$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho) = r R_{nl}(r)$$

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

$n = 1, 2, 3 \ldots$

$l = n-1, n-2 \ldots 0$

$m = l, l-1 \ldots -l$

$$u(\rho) = r R(r) = \rho^{\ell+1} e^{-\rho} v(\rho)$$

$$\kappa r R(r) = \rho R(r) = \kappa \rho^{\ell+1} e^{-\rho} v(\rho)$$

$$R_{n\ell}(r) = \kappa \rho^{\ell} e^{-\rho} v_{n\ell}(\rho)$$

$$= \kappa (r\kappa)^{\ell \cancel{+1}} e^{-\rho} v_{n\ell}(\rho)$$

$$= \kappa^{\ell+1} r^{\ell} e^{-\kappa r} v_{n\ell}(\kappa r)$$

$$= \left(\frac{1}{na}\right)^{\ell+1} r^{\ell} e^{-r/an} v_{n\ell}\left(\frac{r}{an}\right)$$

<u>So to determine $R_{n\ell}$ we need $v_{n\ell}$</u>

Constructing $v_{n\ell}$

Start at the bottom, $v_{10} \Rightarrow n=1, \ell=0$

$$n = j_{max} + \ell + 1$$

$$1 = j_{max} + 0 + 1$$

$$\Rightarrow j_{max} = 0$$

So only a_0 in the expansion is non-zero.

$$v(\rho) = a_0$$

which will be determined by normalization.

$$R_{10} = \left(\frac{1}{1 \cdot a}\right)^{0+1} r^0 e^{-r/1 \cdot a} \underbrace{v_{10}\left(\frac{r}{a \cdot 1}\right)}_{= a_0}$$

$$= \frac{a_0}{a} e^{-r/a}$$

$$\equiv A e^{-r/a}$$

Normalize to find A

$$1 = \int_0^\infty dr\, r^2 R^* R$$

$$= A^2 \int_0^\infty dr\, r^2 e^{-2r/a}$$

$$= A^2 \left(\frac{a^3}{4}\right)$$

$$A = \frac{2}{a^{3/2}}$$

$$R_{10} = \frac{2}{a^{3/2}} e^{-r/a}$$

$$\psi_{100} = R_{10} Y_0^0 = \frac{2}{a^{3/2}} \left(\frac{1}{4\pi}\right)^{1/2} e^{-r/a}$$

Ground State Energy of Hydrogen

$$E_1 = \frac{-\hbar^2}{2ma^2} \cdot \frac{1}{1^2} = -2.16 \times 10^{-18}\,J$$

$$= -13.6\,eV$$

Consider n, ℓ, m more generally. Examine

$$n = j_{max} + \ell + 1$$

The minimum j_{max} is zero, so the maximum ℓ is $n-1$.

Quantum Numbers

Principle Quantum Number $n = 1, 2, \cdots$

Azimuthal Quantum Number $\ell = 0, 1, \cdots n-1$

Magnetic Quantum Number $m = -\ell, -\ell+1 \cdots \ell$

Examine the first excited state, $n=2$

If $\ell = 0$, $j_{max} = 1$

If $\ell = 1$, $j_{max} = 0$ and $v_{21}(\rho) = a_0$

Construct v_{20}

$$a_{j+1} = \frac{2(j+l+1) - \overset{\rho_0}{\overset{\shortparallel}{2n}}}{(j+1)(j+2l+2)}\, a_j \qquad \begin{array}{l} n=2 \\ l=0 \\ j_{max}=1 \end{array}$$

$$a_1 = \frac{2(0+0+1) - 2\cdot 2}{(0+1)(0+2\cdot 0+2)}\, a_0 = -a_0$$

$$v_{20} = a_0 - a_0\rho = a_0(1-\rho)$$

$$R_{nl} = \kappa^{l+1} r^l e^{-\rho} v_{nl}(\rho)$$

$$R_{20} = \kappa^1 r^0 e^{-\rho} a_0 (1-\rho) \qquad \begin{array}{l} l=0 \\ n=2 \end{array}$$

$$= \kappa a_0 (1-\rho) e^{-\rho}$$

$$\rho = \kappa r = \frac{r}{an} = \frac{r}{2a}$$

$$R_{20} = A\left(1 - \frac{r}{2a}\right) e^{-r/2a}$$

Normalize or read out of a table

$$R_{20} = \frac{1}{\sqrt{2}} a^{-3/2} \left(1 - \frac{1}{2}\frac{r}{a}\right) e^{-r/2a}$$

In general, $v_{n\ell}(\rho)$ is a class of special function called the associate Laguerre polynomial.

Dfn Laguerre Polynomial

$$L_q(x) = e^x \left(\frac{d}{dx}\right)^q \left(e^{-x} x^q\right)$$

Dfn Associated Laguerre Polynomial

$$L^p_{q-p}(x) = (-1)^p \left(\frac{d}{dx}\right)^p L_q(x)$$

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

Full Normalized Hydrogen Wave Function

$$\psi_{n\ell m}(r,\theta,\phi) = \left(\sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n\left[(n+\ell)!\right]^3}}\right) \cdot$$

$$e^{-r/na}\left(\frac{2r}{na}\right)^{\ell} L^{2\ell+1}_{n-\ell-1}\left(\frac{2r}{na}\right) Y_{\ell}^{m}(\theta,\phi)$$

Orthogonality

$$\int_{\text{space}} \psi^*_{n\ell m}\, \psi^*_{n'\ell' m'}\, r^2 \sin\theta \, dr\, d\theta\, d\phi$$

$$= \delta_{nn'}\, \delta_{\ell\ell'}\, \delta_{mm'}$$

<u>Completeness</u>

$$\hat{1} = \sum_{n,m,\ell} |\psi_{nm\ell}\rangle \langle \psi_{nm\ell}|$$

Hydrogen Continued

Modified Hydrogen - Replace proton or electron with particle with same charge but different mass.

$\Rightarrow$ If the two particles have near the same mass, replace m with μ the reduced mass.

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Ex Positronium - e^-, e^+

positron

$$E_n = \left[\frac{\mu}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2}$$

Hydrogen-like Atoms Ionized heavier atoms with a single remaining electron like He^+.
Let Z be the atomic number, the number of protons.

$$E_n = \left[\frac{m}{2\hbar^2} \left(\frac{Z e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2}$$

Spectrum of Hydrogen

– Excited hydrogen atoms emit light by making transitions to lower energy levels. The energy of the emitted photon is $E = \hbar\omega = hf$

$$E = hf = \frac{hc}{\lambda} = -13.6\,\text{eV}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$\lambda \equiv$ wavelength $\qquad f \equiv$ frequency

$$\frac{1}{\lambda} = \frac{-13.6\,\text{eV}}{hc}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$= R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

Rydberg Constant

$$R = \frac{m}{4\pi c \hbar^3}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 = 1.097\times10^7\ \text{m}^{-1}$$

Ex Red Line of Hydrogen

$$n_i = 3 \implies n_f = 2$$

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

$$\lambda = 656.3 \text{ nm}$$

Spectral Series

$n_f = 1$ Lyman Series

$n_f = 2$ Balmer Series

$n_f = 3$ Paschen Series