IIB) Hence our normalization condition reduces to

$$1 = \int_{r=0}^{\infty} dr\, |u(r)|^2$$

Next, the potential must be specified.

c) The Hydrogen Atom

The Hydrogen atom is a two body bound state composed of a proton of mass $m_1 = 1.7\times10^{-28}$ Kg ($m_1c^2 = 935$ (MeV)) and an electron of mass $m_2 = 9.1\times10^{-31}$ Kg ($m_2c^2 = 0.511$ (MeV)). The proton carries positive charge $e>0$ and the electron has opposite charge $-e$. The 2 particles are bound by the Coulomb potential (in SI units)

$$V(|\vec{r}_1-\vec{r}_2|) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\vec{r}_1-\vec{r}_2|}$$

which in spherical polar coordinates is given by

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$$

III C) Note the reduced mass of the system is

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = m_2 \frac{1}{1 + \frac{m_2}{m_1}} \approx m_2 \left(1 - \frac{m_2}{m_1} + \cdots\right)$$

$$\approx m_2 - \frac{m_2^2}{m_1} + \cdots$$

$$\approx m_2 \quad \text{since} \quad \frac{m_2}{m_1} = \frac{m_e}{m_p} \simeq \frac{1}{1836}.$$

The reduced mass is very close to that of the electron.

The position of the center of mass of the system is

$$\vec{R} = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2}$$

$$= \left(\frac{1}{1 + \frac{m_2}{m_1}}\right) \vec{r}_1 + \frac{m_2}{m_1}\left(\frac{1}{1 + \frac{m_2}{m_1}}\right) \vec{r}_2$$

$$\approx \vec{r}_1 - \frac{m_2}{m_1}(\vec{r}_1 - \vec{r}_2) + \cdots$$

$$\approx \vec{r}_1 \quad \text{since} \quad \frac{m_2}{m_1} \approx \frac{1}{1836}.$$

Thus the center of mass is essentially at the location of the proton.

III c) Again, our hydrogen atom wavefunction is the product of the center of mass free particle motion described by the CM plane wave, times the relative particle wavefunction $\psi_{\ell m}(\vec{r})$

$$\psi_{\ell m}(\vec{r}) = R(r)\, Y_\ell^m(\theta,\phi)$$

$$= \frac{1}{r} u(r)\, Y_\ell^m(\theta,\phi) .$$

For the Coulomb potential the radial equation for R, that is u, becomes

$$-\frac{\hbar^2}{2\mu}\frac{d^2u(r)}{dr^2} + \left[\frac{-e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2}{2\mu}\frac{\ell(\ell+1)}{r^2}\right]u(r)$$

$$= E\,u(r) .$$

Note $E>0$ also has solutions describing the e^--p scattering — we will ignore these solutions for now and focus on the bound state solutions $E<0$, the Hydrogen atom.

III c) As usual, since $E<0$, define

$$\kappa \equiv \sqrt{\frac{2m(-E)}{\hbar^2}} > 0, \text{ real.}$$

So $\div E$ the radial equation becomes

$$\frac{1}{\kappa^2}\frac{d^2u}{dr^2} = \left[1 - \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}\frac{1}{(\kappa r)} + \frac{l(l+1)}{(\kappa r)^2}\right]u$$

Hence we define $\boxed{\rho \equiv \kappa r}$, dimensionless

and $\boxed{\rho_0 \equiv \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}}$, dimensionless

Hence, letting $u(r) \to u(\rho)$ we have

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

Step 1: Asymptotic form of solutions

as $\rho \to \infty$ the radial equation becomes

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

III.c) The general solution is

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

but e^{ρ} diverges as $\rho \to \infty \Rightarrow \boxed{B=0}$

Thus, asymptotically

$$\boxed{u(\rho) \sim Ae^{-\rho} \quad \text{for large } \rho}$$

At the other end as $\rho \to 0$ the centrifugal term dominates and the radial equation becomes

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

The general solution is

$$u(\rho) = C\rho^{l+1} + \frac{D}{\rho^l}$$

but $\frac{1}{\rho^l}$ diverges as $\rho \to 0 \Rightarrow \boxed{D=0}$

Thus

$$\boxed{u(\rho) \sim C\rho^{l+1} \quad \text{for small } \rho}$$

III c) Step 2: We factor this asymptotic behaviour from the solution

$$\text{Ansatz:} \quad u(\rho) \equiv \rho^{l+1} e^{-\rho} v(\rho)$$

Substitute this into the radial equation

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

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

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

Now we search for a solution that is square-integrable, hence $v(0)$ is finite and $v(\rho)$ grows like a power as $\rho \to \infty$ at most. In general we try a solution in the form of a power series. We will find that the above conditions impose constraints on K so that the series will terminate and be a finite polynomial.

(c) So Ansatz: $v(\rho) = \sum_{N=0}^{\infty} a_N \rho^N$

Substituting into the radial eq. for v

$\Rightarrow$

$$\sum_{N=2}^{\infty} N(N-1) a_N \rho^{N-1} + 2(l+1) \sum_{N=1}^{\infty} N a_N \rho^{N-1}$$

$(M = N-1)$ $\qquad$ $(M = N-1)$

$$- 2 \sum_{N=1}^{\infty} N a_N \rho^N + (\rho_0 - 2(l+1)) \sum_{N=0}^{\infty} a_N \rho^N = 0$$

Re-labeling the powers and the summation indices $\Rightarrow$

$$\sum_{N=0}^{\infty} \left[N(N+1) a_{N+1} + 2(l+1)(N+1) a_{N+1} - 2N a_N + (\rho_0 - 2(l+1)) a_N \right] \rho^N = 0$$

Setting the coefficient $= 0$ for each power of ρ $\Rightarrow$

$$a_{N+1} = \frac{2(N+l+1) - \rho_0}{(N+1)(N+2l+2)} a_N$$

for $N = 0, 1, 2, \ldots$

IIIc) If $2(N+l+1)-\rho_0 \neq 0$ never vanishes for all N, then a_N never vanishes and as $N \to \infty$

$$\frac{a_{N+1}}{a_N} \xrightarrow[N\to\infty]{} \frac{2}{N}$$

This implies that $a_N \xrightarrow[N\to\infty]{} \frac{2^N}{N!} A$

Hence, after some suitably large integer, M, we have that

$$N(r) = \sum_{N=0}^{M-1} a_N \rho^N + A \sum_{N=M}^{\infty} \frac{(2\rho)^N}{N!}$$

$$= \underbrace{\sum_{N=0}^{M-1} \left[a_N - A\frac{2^N}{N!} \right] \rho^N}_{\text{polynomial in } \rho \text{ of degree } M-1} + \underbrace{\sum_{N=0}^{\infty} A \frac{(2\rho)^N}{N!}}_{= A e^{2\rho}}$$

Thus for large ρ: $N(\rho) \xrightarrow[\rho\to\infty]{} e^{+2\rho}$

But this implies $R \approx \rho^l e^{-\rho} N \to \rho^l e^{+\rho}$

and hence is not square-integrable!

IIC) Hence we must have

$$2(N_{max}+l+1)-\rho_0=0 \text{ for}$$

some integer $N_{max}=0,1,2,\ldots$

The series will then terminate with the N_{max} power; that is $a_{N_{max}+1}=0$

Thus $v(r)$ is a polynomial of degree N_{max}

let

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

n is called the principal quantum number. Since $N_{max}=0,1,2,\ldots$ and $l=0,1,\ldots$ we have that

$$\boxed{n=1,2,3,\ldots}$$

and

$$\boxed{\rho_0=2n}$$

- (c) Recall that $\rho_0 = \frac{me^2}{2\pi\epsilon_0 \hbar^2 \kappa} = 2n$

and $$E = -\frac{\hbar^2\kappa^2}{2m} = -\frac{me^4}{8\pi^2\epsilon_0^2\hbar^2\rho_0^2}$$

Hence the allowed energies are

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

$$= \frac{E_1}{n^2}, \quad n = 1, 2, 3, \ldots$$

This is the Bohr formula with $E_1 = -13.6\,eV$, the ground state energy. (= binding energy of hydrogen)

Further $\kappa \to \kappa_n = \left(\frac{me^2}{\hbar^2 4\pi\epsilon_0}\right)\frac{1}{n} \equiv \frac{1}{an}$

$$a \equiv \frac{\hbar^2}{m\frac{e^2}{4\pi\epsilon_0}} = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529\times10^{-10}\,m$$

the Bohr radius a

Note also that $\rho = \kappa_n r = \frac{r}{a}\frac{1}{n}$;

So that the radial solutions will depend on

- III C) the integers n as well:

$$\psi_{n\ell m}(r,\theta,\varphi) = R_{n\ell}(r)\, Y_\ell^m(\theta,\varphi)$$

with $R_{n\ell}(r) = \frac{1}{r}\rho^{\ell+1}e^{-\rho}\nu(\rho)$.

where $\nu(\rho)$ is a polynomial of degree $N_{max} = n-\ell-1$ in ρ.

Since $N_{max} \geq 0 \Rightarrow \ell \leq n-1$, i.e. $\ell = 0, 1, \ldots, n-1$

Indeed these polynomials are known as the associated Laguerre polynomials. Setting $\rho_0 = 2n$ in the recursion formula yields

$$a_{N+1} = -2\frac{(n-\ell-1-N)}{(N+1)(N+2\ell+2)}a_N$$

The solution can be found by noting

$$a_1 = -2\frac{(n-\ell-1)}{1(2\ell+2)}a_0$$

$$a_2 = -2\frac{(n-\ell-1-1)}{2(2\ell+2+1)}a_1$$

$$a_3 = -2\frac{(n-\ell-1-2)}{3(2\ell+2+2)}a_2$$

$$\vdots$$

III c) $\Rightarrow$

$$a_N = (-2)^N \frac{(n-\ell-1)(n-\ell-2)\cdots(n-\ell-N)}{N!\,(2\ell+N+1)(2\ell+N)\cdots(2\ell+2)}\, a_0$$

$$a_N = (-2)^N \frac{(2\ell+1)!\,(n-\ell-1)!}{N!\,(2\ell+N+1)!\,(n-\ell-1-N)!}\, a_0$$

Since $(2\ell+1)!\,(n-\ell-1)!$ is independent of N, we can absorb it into the definition of a_0

$$(2\ell+1)!\,(n-\ell-1)!\,a_0 \longrightarrow a_0$$

Hence the coefficients are

$$\boxed{a_N = (-1)^N \frac{2^N}{N!\,(2\ell+N+1)!\,(n-\ell-1-N)!}\, a_0}$$

Thus $v(\rho)$ becomes

$$v_{n\ell}(\rho) = a_0 \sum_{N=0}^{n-\ell-1} \frac{(-1)^N}{(n-\ell-1-N)!} \frac{(2\kappa_n r)^N}{(2\ell+N+1)!\,N!}$$

III c) Choosing $a_0 \equiv N_{n\ell} \frac{(-1)^{2\ell+1}}{Z_n^{\ell+1}} [(n+\ell)!]^2$,

this is just the associated Laguerre polynomial

$$\boxed{\psi_{n\ell}(\rho) = \frac{N_{n\ell}}{Z_n^{\ell+1}} L_{n+\ell}^{2\ell+1}(2Z_n r)}$$

with the associated Laguerre polynomial L_q^p defined as

$$L_q^p(z) \equiv (q!)^2 \sum_{N=0}^{q+p+1} \frac{(-1)^{p+N} z^N}{(q-p-N)!\,(p+N)!\,N!}$$

(For $\psi_{n\ell}$ above: $z = 2Z_n r$, $p = 2\ell+1$, $q-p = n-\ell-1 = N_{max}$);

Hence the Radial Wavefunction is

$$R_{n\ell}(r) = \frac{N_{n\ell}}{Z_n^{\ell+1}} \frac{1}{r} (Z_n r)^{\ell+1} e^{-Z_n r} \times L_{n+\ell}^{2\ell+1}(2Z_n r)$$

- III c) Thus

$$R_{n\ell}(r) = N_{n\ell} r^{\ell} e^{-Z_n r} L^{2\ell+1}_{n+\ell}(2Z_n r)$$

for $n = 1, 2, 3,$ and $\ell = 0, 1, 2, \ldots, n-1$

The normalization factor $N_{n\ell}$ for the radial wavefunction can be defined by appealing to the associated Laguerre polynomial normalization

$$\int_0^\infty dz \left[e^{-z} z^{2(\ell+1)} \right] \left[L^{2\ell+1}_{n+\ell}(z) \right]^2$$

$$= \frac{2n[(n+\ell)!]^3}{(n-\ell-1)!} .$$

Hence define

$$N_{n\ell} = -(2Z_n)^{\ell} \left[\frac{(2Z_n)^3 (n-\ell-1)!}{2n[(n+\ell)!]^3} \right]^{1/2}$$

Recall $\rho = Z_n r = \frac{r}{na}$; $Z_n = \frac{1}{na}$

III C) So finally bringing all this together, the hydrogen atom 2-body bound state wavefunctions are

$$\psi_{n\ell m}(\vec{r}) = R_{n\ell}(r)\, Y_\ell^m(\theta,\phi)$$

with $n = 1, 2, 3, \ldots$

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

$m = -\ell, -\ell+1, \ldots, \ell-1, +\ell$

where

$$R_{n\ell}(r) = -\left[\left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}\right]^{1/2} \times$$

$$\times \left(\frac{2r}{na}\right)^\ell L_{n+\ell}^{2\ell+1}\left(\frac{2r}{na}\right) e^{-\frac{r}{na}}$$

The $\psi_{n\ell m}(\vec{r})$ are <u>orthonormal</u>

$$\int d^3r\, \psi^*_{n\ell m}(\vec{r})\, \psi_{n'\ell'm'}(\vec{r}) = \delta_{nn'}\delta_{\ell\ell'}\delta_{mm'}$$

III C) The Low lying radial wavefunctions are

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

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

$$R_{21}(r) = \frac{1}{(2a)^{3/2}} \frac{r}{\sqrt{3}\, a} e^{-r/2a}$$

$$\vdots$$

The energy eigenfunctions are labeled by 3 quantum numbers — n, l, m

1) n is called the principal quantum number and $n = 1, 2, 3, \ldots$. The bound state energy depends only on n, the principal quantum number.

2) l is called the orbital angular momentum quantum number and $l = 0, 1, 2, \ldots, n-1$. In spectroscopic notation, the l numbers are denoted by letters

-IV.C.

$l=0 \leftrightarrow$ S state (sharp)
$l=1 \leftrightarrow$ P state (principal)
$l=2 \leftrightarrow$ D state (diffuse)
$l=3 \leftrightarrow$ F state (fundamental), and so on.

3) m is called the magnetic quantum number and $m = -l, -l+1, \ldots, l-1, +l$, it has $2l+1$ posible values.

For a given n there corresponds

$$d_n \equiv \sum_{l=0}^{n-1} \sum_{m=-l}^{+l} = \sum_{l=0}^{n-1} (2l+1) = n^2$$

different (l, m) states. Hence the n^{th} energy level, E_n, is n^2-fold degenerate.

The lowest energy state is for $n=1$ hence $\Rightarrow l=0, m=0$, the ground state

$$E_1 = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 = -\frac{1}{2}\frac{e^2}{4\pi\epsilon_0 a}$$

$$= -13.6\ eV.$$

III C) The energy eigenfunction for the ground state is

$$\psi_{100}(\vec{r}) = \frac{2}{a^{3/2}} e^{-r/a} \underbrace{Y_0^0(\theta,\varphi)}_{= \frac{1}{\sqrt{4\pi}}}$$

So

$$\boxed{\psi_{100}(\vec{r}) = \frac{1}{\sqrt{4\pi}} \frac{2}{a^{3/2}} e^{-\frac{r}{a}}}$$

This is just a function of r, the distance from the origin (i.e. CM) and so is spherically symmetric (i.e. it does not depend on θ, φ only r). Indeed all S-states have $l = m = 0$ and since $Y_0^0(\theta,\varphi) = \frac{1}{\sqrt{4\pi}}$, they have spherically symmetric wavefunctions:

$$\psi_{n00}(\vec{r}) = \frac{1}{\sqrt{4\pi}} R_{n0}(r) .$$

With the knowledge of the wavefunctions all (measurable) quantities can be explicitly calculated.

-III C) For example, the expectation value of the distance the electron is from the proton (actually from the CM) in the ground state is

$$\langle r \rangle_{100} = \int d^3r\, \psi^*_{100}(\vec{r})\, r\, \psi_{100}(\vec{r})$$

$$= \int_0^\infty dr\, r^2 \int_{4\pi} d\Omega \left(\frac{1}{\sqrt{4\pi}} \frac{2}{a^{3/2}} e^{-\frac{r}{a}}\right)^* r \times$$

$$\times \left(\frac{1}{\sqrt{4\pi}} \frac{2}{a^{3/2}} e^{-\frac{r}{a}}\right)$$

$$= \frac{4}{a^3} \underbrace{\left(\frac{1}{4\pi}\int_{4\pi} d\Omega\right)}_{=1} \int_0^\infty dr\, r^3 e^{-\frac{2r}{a}}$$

Recall $\int_0^\infty d\xi\, \xi^n e^{-a\xi} = (-1)^n \frac{d^n}{d\xi^n} \underbrace{\int_0^\infty d\xi\, e^{-a\xi}}_{=\frac{1}{a}}$

$$= (-1)^n \frac{d^n}{da^n} \frac{1}{a} = n! \frac{1}{a^{n+1}}$$

$$\Rightarrow \int_0^\infty d\xi\, \xi^3 e^{-a\xi} = \frac{6}{a^4} .$$

- IIIC) Thus we found

$$\boxed{\langle r \rangle_{100} = \frac{3}{2} a}$$

Further, the probability density for finding the electron in the spherical shell between r and r+dr is

$$4\pi r^2 |\psi_{100}(\vec{r})|^2 \propto r^2 e^{-\frac{2r}{a}}$$

(i.e. $dP_{100}(r,\theta,\varphi) = |\psi_{100}|^2 r^2 dr\, d\Omega$

$$dP_{100}(r) \equiv \sum_{\text{all angles}} \left(dP_{100}(r,\theta,\varphi) \right)$$

$$= \int_{4\pi} d\Omega\, |\psi_{100}|^2 r^2 dr$$

$$= 4\pi r^2 |\psi_{100}|^2 dr \quad)$$

III C) This function has maximum at $r = r_0$ where

$$\left.\frac{d}{dr}\left(r^2 e^{-\frac{2r}{a}}\right)\right|_{r=r_0} = 0$$

and $$\left.\frac{d^2}{dr^2}\left(r^2 e^{-\frac{2r}{a}}\right)\right|_{r=r_0} < 0.$$

Solving for r_0 from the first derivative:

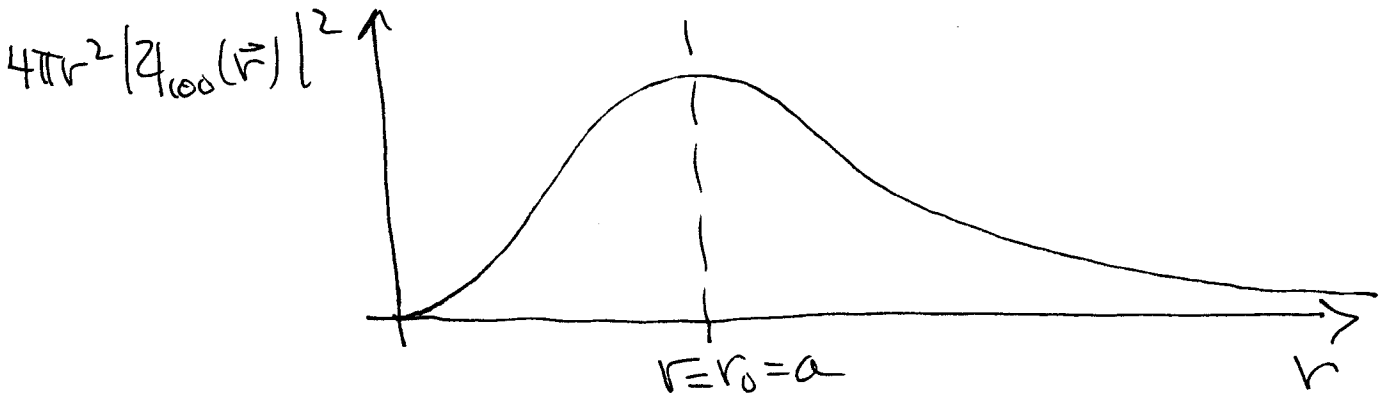
$$0 = \left.\frac{d}{dr}\left(r^2 e^{-\frac{2r}{a}}\right)\right|_{r=r_0} = 2\left(r - \frac{r^2}{a}\right) e^{-2r/a}\Big|_{r=r_0}$$

$$\Rightarrow \boxed{r_0 = a, \text{ the Bohr radius!}}$$

And $$\left.\frac{d^2}{dr^2}\left(r^2 e^{-\frac{2r}{a}}\right)\right|_{r=r_0=a} = \left[2 - \frac{4r}{a} - \frac{4}{a}\left(r - \frac{r^2}{a}\right)\right] \times e^{-\frac{2r}{a}}\Big|_{r=r_0=a}$$

$$= -2e^{-2} < 0.$$

III.C) The probability density is maximized at the Bohr radius



III.D) Orbital Angular Momentum:

In classical mechanics the Hamiltonian for the central potential problem can be written as

$$H = \frac{p_r^2}{2m} + \frac{\vec{L}^2}{2mr^2} + V(r)$$

with p_r the momentum conjugate to r, $p_r = \frac{\partial L}{\partial \dot{r}} = m\dot{r}$, while $\vec{L} = \vec{r} \times \vec{p}$ is the orbital angular momentum. Comparing this to the QM Hamiltonian