$$\frac{d^2}{dr^2}u(r) + 2\left(\frac{l+1}{r} - \kappa\right)\frac{d}{dr}u(r) - \left[\frac{2(l+1)\kappa}{r} + \frac{2m}{\hbar^2}V(r)\right]u(r) = 0$$

3.5. The Hydrogen Atom

The hydrogen atom is a two body bound state composed of a proton of mass $m_1 = 1.7 \times 10^{-27}$ Kg ($m_1c^2 = 935$ MeV) and an electron of mass $m_2 = 0.91 \times 10^{-30}$ Kg ($m_2c^2 = 0.511$ MeV). The proton carries a positive charge $e > 0$ while the electron has the opposite charge $-e$. The 2 particles are bound by the Coulomb potential

$$V(|\vec{r}_1 - \vec{r}_2|) = \frac{-e^2}{|\vec{r}_1 - \vec{r}_2|}.$$

Hence the hydrogen atom potential is the form of the 2-body central potential we have been analyzing.

The reduced mass of the system is

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

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

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

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

In the CM coordinate system the hydrogen atom 2 body problem reduces to the atom moving as a free particle, with the reduced particle of mass m moving in the

central potential $V = V(r) = \frac{-e^2}{r}$.

We concentrate on the central Coulomb potential problem. The Hamiltonian becomes

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r}.$$

The bound state energy eigenfunctions take the form

$$\psi_{lm}(r,\theta,\varphi) = R(r)\,Y_l^m(\theta,\varphi)$$
$$= u(r)\,r^l e^{-kr}\,Y_l^m(\theta,\varphi)$$

with $l = 0, 1, 2, \ldots$; $m = -l, -l+1, \ldots, l-1, l$.
The spherical harmonics Y_l^m are eigenfunctions of $\vec{L}^2$ and L_z recall

$$\vec{L}^2 Y_l^m = \hbar^2 l(l+1)\,Y_l^m$$

$$L_z Y_l^m = m\hbar\, Y_l^m.$$

The radial equation for $u(r)$ has the form

$$\frac{d^2}{dr^2}u(r) + 2\left(\frac{l+1}{r} - \kappa\right)\frac{d}{dr}u(r) + \frac{2\kappa\eta}{r}u(r) = 0$$

with

$$\eta \equiv \frac{me^2}{\kappa\hbar^2} - l - 1$$

and

$$\kappa = \sqrt{\frac{-2mE}{\hbar^2}} \quad .$$

As stated earlier, we desire a solution that is square-integrable, hence, $u(0)$ is finited and $u(r)$ grows like a power as $r \to \infty$ at most. In general we try a solution in the form of a power series, as we have argued we will find the conditions on κ so that this series will terminate to be a polynomial.

Let $$u(r) = \sum_{\nu=0}^{\infty} a_\nu r^\nu \quad .$$

Substituting into the radial equation implies

$$\sum_{N=2}^{\infty} N(N-1)a_N r^{N-2} - 2\kappa \sum_{N=1}^{\infty} N a_N r^{N-1} + 2(\ell+1)\sum_{N=1}^{\infty} a_N r^{N-2} + \sum_{N=0}^{\infty} 2\kappa\eta a_N r^{N-1} = 0.$$

Isolating the $\frac{1}{r}$ terms and re-labelling the dummy summation indices as usual yields

$$\left(2(\ell+1)a_1 + 2\kappa\eta a_0\right)\frac{1}{r}$$

$$+\sum_{N=2}^{\infty}\Big[N(N-1)a_N - 2(N-1)\kappa a_{N-1} + 2N(\ell+1)a_N + 2\kappa\eta a_{N-1}\Big] r^{N-2}$$

$$= 0.$$

Since the r^M are independent functions, their coefficients must vanish

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

2) $$[N(N-1) + 2N(\ell+1)] a_N = [2(N-1)K - 2K\eta] a_{N-1}$$

$N = 2, 3, \ldots$.

Combining these we have the single formula

$$(N+1)(N+2\ell+2) a_{N+1} = 2K(N-\eta) a_N$$

$N = 0, 1, 2, 3, \ldots$

(where we let $N \to N+1$ in the equation 2 above).

If $(N-\eta)$ never vanishes for all N, then a_N never vanishes and as N gets large

$$\frac{a_{N+1}}{a_N} \xrightarrow{N\to\infty} \frac{2K}{N}$$ which

implies $a_N \to \frac{(2K)^N}{N!}$ as $N \to \infty$.

So with this behavior for large N, say when $N \geq M$, the radial function $u(r)$ has the form

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

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

Thus for large r, $u(r) \xrightarrow[r\to\infty]{} e^{+2\kappa r}$.

But this implies

$$R(r) = u(r) r^l e^{-\kappa r}$$

$$\xrightarrow[r\to\infty]{} r^l e^{+\kappa r}, \text{ which}$$

is not square-integrable!

Hence, to avoid this we require $N - \eta = 0$ for some integer $N = n' = 0, 1, 2, \ldots$, that is $\eta = n'$.

Hence, if $u(r)$ is to grow like a power as $r \to \infty$; η must be equal to some integer n', $\eta = n'$, with $n' = 0, 1, 2, \ldots$. Then $u(r)$ is a polynomial in r of degree n', i.e. $a_{N+1} = 0$ for $N \geq n'$. Further

$$\eta = \frac{me^2}{\chi\hbar^2} - l - 1 = n'$$

$$\Rightarrow \quad \frac{me^2}{\chi\hbar^2} = n' + l + 1 \equiv n = \text{integer}.$$

Note that $n = 1, 2, 3, \ldots$ and $n - 1 \geq l \geq 0$.

Since the bound state energy is related to χ, it is quantized

$$E_n = -\frac{\hbar^2\chi^2}{2m}$$

$$= -\frac{me^4}{2\hbar^2 n^2} \quad ,$$

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

The n'-order polynomials $u(r)$ are known as associated Laguerre polynomials. Setting

$\eta = n' = n-\ell-1$, the recursion relation becomes

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

with

$$K_n = \frac{me^2}{\hbar^2 n} = \sqrt{\frac{-2mE_n}{\hbar^2}} .$$

The solution can be found by noting

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

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

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

$$\vdots$$

$\Rightarrow$

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

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

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

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

Hence the coefficients are

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

The $u(r)$ becomes

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

Choosing $a_0 = N_{n\ell}(-1)^{2\ell+1}[(n+\ell)!]^2$, this is just the associated Laguerre polynomial

$$u_{n\ell}(r) = N_{n\ell}\, L^{2\ell+1}_{n+\ell}(2\kappa_n r)$$

with the associated Laguerre polynomial L^p_q.

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

(i.e. $p = 2\ell+1$, $q-p = n' = n-\ell-1$, $z = 2\kappa r$ to find $u(r)$).

Hence the radial wavefunction is found

$$R_{n\ell}(r) = N_{n\ell} \mathcal{L}_{n\ell}(r) r^{\ell} e^{-K_n r}$$

$$= N_{n\ell} r^{\ell} L_{n+\ell}^{2\ell+1}(2K_n r) e^{-K_n r}$$

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

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

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

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

hence let

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

It is convenient to introduce the Bohr radius a_0

$$a_0 \equiv \frac{\hbar^2}{me^2} \quad \left(= 5.29 \times 10^{-9}\,\text{cm}\right).$$

The wavenumber k_n and eigenenergies E_n become

$$k_n = \frac{me^2}{\hbar^2 n} = \frac{1}{a_0 n}$$

$$E_n = -\frac{me^4}{2\hbar^2 n^2} = -\frac{e^2}{2a_0 n^2}$$

$$\left(= -\frac{13.6}{n^2}\ \text{eV}\right).$$

In addition it is useful to define the fine structure constant α as

$$\alpha \equiv \frac{e^2}{\hbar c} \quad \left(\simeq \frac{1}{137}\right).$$

The

$$a_0 = \frac{\hbar}{mc\alpha}$$

and $\boxed{E_n = -\frac{mc^2\alpha^2}{2n^2}}$, $n = 1, 2, 3, \ldots$.

Putting this altogether finally, the hydrogen atom 2-body bound state wave functions are

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

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

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

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

where

$$R_{nl}(r) = -\left[\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right]^{1/2} \times$$

$$\times \left(\frac{2r}{na_0}\right)^l L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right) e^{-\frac{r}{na_0}} .$$

These wavefunctions are normalized to be orthonormal

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

Some low lying radial wavefunctions are

$$R_{10}(r) = a_0^{-3/2}\, 2\, e^{-\frac{r}{a_0}}$$

$$R_{20}(r) = (2a_0)^{-3/2}\left(2 - \frac{r}{a_0}\right) e^{-\frac{r}{2a_0}}$$

$$R_{21}(r) = (2a_0)^{-3/2}\, \frac{r}{\sqrt{3}\, a_0}\, e^{-\frac{r}{2a_0}}$$

$$\vdots$$

The energy eigenfunctions are labelled by 3 quantum numbers

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 $\ell = 0, 1, 2, \ldots n-1$. In spectroscopic notation the ℓ numbers are denoted by letters

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

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

For a given n there correspnds

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

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

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

$$E_1 = -\frac{mc^2\alpha^2}{2} = -\frac{e^2}{2a_0} = -13.6\,eV.$$

The energy eigenfunction for the ground state is

$$\psi_{100}(\vec{r}) = \frac{2}{a_0^{3/2}} e^{-\frac{r}{a_0}} \underbrace{Y_0^0(\theta,\varphi)}_{=\frac{1}{\sqrt{4\pi}}}$$

So

$$\boxed{\psi_{100}(\vec{r}) = \frac{1}{\sqrt{4\pi}} \frac{2}{a_0^{3/2}} e^{-\frac{r}{a_0}}}.$$

This is just a function of r, the distance from the origin and so is spherically symmetric. 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 quantities can be explicitly calculated. For example, the expectation value of the distance the electron is from the proton (actually from the CM) in the ground state is

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

$$= \int_0^\infty dr\, r^2 \int_{4\pi} d\Omega \left(\frac{1}{\sqrt{4\pi}} \frac{2}{a_0^{3/2}} e^{-\frac{r}{a_0}} \right) r \times$$

$$\times \left(\frac{1}{\sqrt{4\pi}} \frac{2}{a_0^{3/2}} e^{-\frac{r}{a_0}} \right)$$

$$= \frac{4}{a_0^3} \underbrace{\left(\frac{1}{4\pi} \int_{4\pi} d\Omega \right)}_{=1} \int_0^\infty dr\, r^3 e^{-\frac{2r}{a_0}}$$

Now $\int_0^\infty d\xi\, \xi^n e^{-a\xi} = (-1)^n \frac{d^n}{da^n} \int_0^\infty d\xi\, e^{-a\xi}$

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

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

Thus we find

$$\langle r \rangle_{100} = \frac{3}{2} a_0 .$$

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

$$4\pi r^2 |\psi_{100}(\vec{r})|^2 \quad \left(\text{i.e. } dP_{100}(r,\theta,\varphi) = |\psi_{100}|^2 \times r^2 dr\, d\Omega \right)$$

So $4\pi r^2 |\psi_{100}|^2 \sim r^2 e^{-\frac{2r}{a_0}}$.

This function has a maximum at $r = r_0$ where

$$\left.\frac{d}{dr}\left(r^2 e^{-\frac{2r}{a_0}}\right)\right|_{r=r_0} = 0$$

and $$\left.\frac{d^2}{dr^2}\left(r^2 e^{-\frac{2r}{a_0}}\right)\right|_{r=r_0} < 0 .$$

Solving for r_0 we find from the 1st derivative

$$0 = \frac{d}{dr}\left(r^2 e^{-\frac{2r}{a_0}}\right) = 2\left(r - \frac{r^2}{a_0}\right) e^{-2r/a_0}\Big|_{r=r_0}$$

$$\Rightarrow \boxed{r_0 = a_0}, \text{ the Bohr radius.}$$

And $$\left.\frac{d^2}{dr^2}\left(r^2 e^{-2r/a_0}\right)\right|_{r=r_0=a_0} = \left[2 - \frac{4r}{a_0} - \frac{4}{a_0}\left(r - \frac{r^2}{a_0}\right)\right] e^{-\frac{2r}{a_0}}\Big|_{\substack{r=r_0 \\ =a_0}}$$

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

The probability density is maximized at the Bohr radius