Chapter 1
INTRODUCTION

The Hydrogen Atom consists of a heavy, essentially motionless proton, of charge e, together with a much lighter elecron From Coulomb's law potential enrgy is

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

The radial equation is

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

Our problem is to solve this equation for $u(r)$, and determine the allowed energies, E. The coulomb potential admit continuum states ($E > 0$). describing electron-proton scattering, as well as discrete bound states, representing the hydrogen atom.

1 The Radial Wave function

Let $\kappa \equiv \frac{-2mE}{h}$ for bound states E is negative and real

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

This suggests that we introduce

$\rho \equiv \kappa r$, and $\rho_0 \equiv \frac{me^2}{2\pi\epsilon_0 h^2 \kappa}$ so that

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

Next we examine the asymptotic form of th solutions as $\rho \to \infty$, the constnants term in the bracket dominates,so(approx.)

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

The general solution is

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

but e^{ρ} blows up (as $\rho \to \infty$), so $B = 0$. Evidently

$$u(\rho) \approx Ae^{-\rho}$$

for large ρ. On the other hand as $\rho \to 0$ the centrifugal term dominates approximately then:

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

The general solution is

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

but ρ^{-l} blows up (as $\rho \to 0$), so $D = 0$. Thus

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

for small ρ. The next step is to peel off the asymptotic behaviour introducing the new function $v(\rho)$:

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

Differentiating:

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

and

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

In terms of $v(\rho)$, then the radial equation reads

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

Finally, we assume the solution$v(\rho)$can be expressed as a power series in ρ :

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

Differentiating term by term to detemine the coefficients:

$$\frac{dv}{d\rho} = \sum_{j=0}^{\infty} j c_j \rho^{j-1} = \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j$$

Differentiating again and adjusting the dummy index j;

$$\frac{d^2u}{d\rho^2} = \sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^{j-1}$$

Solving;

$$\sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^j + \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j - 2 \sum_{j=0}^{\infty} j c_j \rho^j + [\rho_0 - 2(l+1)] \sum_{j=0}^{\infty} c_j \rho^j = 0$$

Equating the coefficients of like power yields

$$c_{j+1} = \left[\frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} \right] c_j$$

This recursion formula determines the coefficients and hence the function.

For large j the recursion formula can be approximated to

$$c_{j+1} \cong \frac{2j}{j(j+1)} c_j = \frac{2}{j+1} c_j$$

Suppose for a moment that this were exact.Then

$$c_j = \frac{2^j}{j!} c_0$$

so

$$v(\rho) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = c_0 e^{2\rho}$$

and hence

$$u(\rho) = c_0 \rho^{l+1} e^{\rho}$$

which blows up at large ρ because of exponential factor
For finding solution that we are interested in the series must terminate such that

$$c_{(j_{max}+1)} = 0$$

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

$$n \equiv j_m ax + l + 1$$

n = principal quantum number
$\rho_0 = 2n$

so the allowed energies

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

this is the bohr formula.

Above equations give

$$\kappa = \left[\frac{me^2}{4\pi\epsilon_0 \hbar^2} \right] \frac{1}{an} = \frac{1}{an}$$

where

$$\text{Bohr's Radius} = a \equiv \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \times 10^{-10}$$

It follows that $\rho = \frac{r}{an}$ and the spatial wave function for hydrogen are labelled by three quantum numbers (n,l,m)

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

where

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

and $v(\rho)$ is a polynomial of degree $j_{max} = n - l - 1$ whose coefficeints are determined by the recursion formula.

$$c_{j+1} = \left[\frac{2(j + l + 1 - n)}{(j + 1)(j + 2l + 2)}\right] c_j$$

The ground state (n=1) is $E_1 = -13.6eV$. Evidently the binding energy is 13.6 eV.

For hydrogen, after limitaions l=0,m=0 ,so, $\psi_{100}(r, \theta, \phi) = R_{10}(r)Y_0^0(\theta, \phi)$
The recursion formula truncates after the first term so $v(\rho)$is a constant(c_0), and

$$R_{10}(r) = \frac{c_0}{a}e^{-r/a}$$

After normalizing it we get $c_0 = 2 \times \sqrt{a}$ and $Y_0^0 = 1/\sqrt{4\pi}$
Therefore, the ground state of hydrogen is

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi}}e^{-r/a}$$

For arbitray n, the possible values of l are $l = 0, 1, 2, \ldots, n-1$ and for each l there are $(2l + 1)$ possible values of m,so the total degeneracy of the energy level E_n is $d(n) = \sum_{l=0} n - 1 = n^2$. The formula for $v(\rho)$ is a function well known to applied mathematician; apart from normalization ,it can be written as

$$v(\rho) = L_{n-l-1}^{2l+1}(2\rho)$$

where

$$L_{q-p}^{p}(x) \equiv (-1)^p \frac{d}{dx}^{P} L_q(x)$$

is an associated Laguerre polynomial, and

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

is the q^{th} Laguerre Polynomial.The normalized hydrogen wavefunctions are

$$\psi = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n - l - 1)!}{2n((n + 1)!)^3}} \times e^{-r/na} \times \frac{2r}{na}^{l} \times \left(L_{n-l-1}^{2l+1} \times \frac{2r}{na}\right) \times Y_l^m(\theta, \phi)$$

This is one of the very few realistic systems that can be solved at all in exact closed form.The wave function depend on all three quantum numbers whereas the energies are determined by n alone.