The Hydrogen Atom

Consider a two particle system consisting a negatively charged particle near a positively charged object such as a lepton (e.g., electron of mass m_e and charge –e) around a nucleus (mass m_N and charge Ze).

First, convert from individual coordinates to CM coordinates:

$$\vec{p_1},\ \vec{p_2},\ \vec{r_1},\ \ \vec{r_2}\quad \Rightarrow \quad \vec{P}=\vec{p_1}+\vec{p_2}=M\dot{\vec{R}},\quad \vec{p}=\mu\dot{\vec{r}}$$

$$\vec{R}=\frac{m_1\vec{r_1}+m_2\vec{r_2}}{m_1+m_2},\qquad \vec{r}=\vec{r_1}-\vec{r_2}$$

$$\mu=\frac{m_1 m_2}{m_1+m_2},\qquad M=m_1+m_2$$

We can write Hamiltonian

$$H=\frac{\vec{p_1}^2}{2m_1}+\frac{\vec{p_2}^2}{2m_2}+V(\vec{r_1},\vec{r_2})$$

Particularly we know

$$V=-\frac{Ze^2}{|\vec{r_1}-\vec{r_2}|}$$

The potential depends on the difference between $\vec{r_1}$ and $\vec{r_2}$ so it reduces to one variable $\vec{r}$.

$$H=\frac{\vec{P}^2}{2M}+\frac{\vec{p}^2}{2\mu}-\frac{Ze^2}{r}$$

Now the system can be separated into free-particle motion of the center of mass (describing $\vec{P}$ and $\vec{R}$) and an equivalent single particle system with mass μ and a central potential.

We can describe the system with already developed method.

$$R_{E,l}(r)=\frac{u_{E,l}(r)}{r}$$

The Schroedinger equation is

$$u''-\frac{l(l+1)}{r^2}u+\frac{2\mu E}{\hbar^2}u+\frac{2\mu}{\hbar^2}\frac{Ze^2}{r}u=0$$

We want to get possible eigenvalues of E. We'll focus only a solution E<0, i.e., the bound state only.

As $r\rightarrow\infty$ this equation converges to

$$u''=\kappa^2 u\qquad where\ \kappa^2=-\frac{2\mu E}{\hbar^2}$$

$$u(r\rightarrow\infty)=c\cdot e^{-\kappa\cdot r}$$

c is a constant. +κ leads to an un-normalizable function so it's discarded.

As $r \to 0 \qquad u \sim r^{l+1}$

Consider our Ansatz ;

$$u(r) = v(\rho)e^{-\rho} \quad \textit{where } \rho = \kappa r$$

$$u' = \kappa v' e^{-\rho} - \kappa v e^{-\rho}$$

$$u'' = \kappa^2 v'' e^{-\rho} - \kappa^2 v' e^{-\rho} - \kappa^2 v' e^{-\rho} + \kappa^2 v e^{-\rho}$$

The Schroedinger equation becomes

$$\kappa^2 v''(\rho)e^{-\rho} - 2\kappa^2 v'(\rho)e^{-\rho} + \kappa^2 v(\rho)e^{-\rho} - \kappa^2 \frac{l(l+1)}{\rho^2} v(\rho)e^{-\rho} - \kappa^2 v(\rho)e^{-\rho} + \frac{2\mu}{\hbar^2}\kappa \frac{Ze^2}{\rho} v(\rho)e^{-\rho} = 0$$

Divide both sides by $\kappa^2 e^{-\rho}$

$$v''(\rho) - 2v'(\rho) - \frac{l(l+1)}{\rho^2} v(\rho) + \frac{2\mu}{\hbar^2 \kappa} \frac{Ze^2}{\rho} v(\rho) = 0$$

$$\frac{2\mu}{\hbar^2 \kappa} = \frac{2\mu}{\hbar^2} \sqrt{\frac{\hbar^2}{2\mu|E|}} = \frac{1}{\hbar} \sqrt{\frac{2\mu}{|E|}}$$

$$v = \rho^{l+1} \sum_{k=0}^{\infty} c_k \rho^k$$

$$v' = \sum_{k=0}^{\infty} c_k \rho^{l+k} (l + k + 1)$$

$$v'' = \sum_{k=1}^{\infty} c_k \rho^{l+k-1} (l + k + 1)(l + k) = \sum_{k\prime=0}^{\infty} c_{k'+1} \rho^{l+k'} (l + k' + 2)(l + k' + 1)$$

$$-\frac{l(l+1)}{\rho^2} v(\rho) = -l(l+1) \sum_{k=1}^{\infty} c_k \rho^{l+k-1} = \sum_{k\prime=0}^{\infty} c_{k'+1} \rho^{l+k\prime}$$

Combine all terms

$$[(l + k + 2)(l + k + 1) - l(l + 1)]c_{k+1} = \left[2(l + k + 1) - \frac{2\mu}{\hbar^2 \kappa} Ze^2\right] c_k$$

Solutions: Laguerre polynomials

They should terminate at k_{max} so that the wave function falls off exponentially at large r as required:

$$c_{kmax+1} = 0$$

This puts a requirement

$$(l + k_{max} + 1) = \frac{\mu Z e^2}{\hbar^2 \kappa}$$

$$(l + k_{max} + 1)^2 = \frac{\mu^2 Z^2 e^4}{\hbar^4 \frac{2\mu|E|}{\hbar^2}} = \frac{\mu Z^2 e^4}{2\hbar^2|E|}$$

Let $l + k_{max} + 1 = n$

$$|E| = \frac{\mu Z^2 e^4}{2\hbar^2 n^2}$$

Since E<0

$$E = -\frac{\mu Z^2 e^4}{2\hbar^2 n^2} \quad : \text{Binding energy of hydrogen-like atoms}$$

$$\Psi_{n,l,m} = \rho^l L_{k_{max}}^{2l+1}(2\rho) Y_l^m(\theta,\varphi) e^{-\rho}$$

Since $l + k_{max} + 1 = n$ n is at least $l+1$.

The lowest possible bound state is

$$\Psi_{1,0,0} = C \cdot Y_0^0(\theta,\varphi) e^{-\rho}$$

The normalization constant $C = \sqrt{4\kappa^3}$ and

$$E_0 = -\frac{\mu Z^2 e^4}{2\hbar^2} = -Ry$$

$$\frac{e^2}{\hbar c} = \frac{1}{137} = \alpha_{EM} \quad : \text{unit-less}$$

$E_{1,0,0} = \frac{\mu c^2 Z^2 \alpha^2}{2}$, $\kappa_0 = \sqrt{\frac{2\mu E_{1,0,0}}{\hbar^2}} \stackrel{\text{def}}{=} \frac{1}{a_0}$

When n=1, l=0, m=0 : 1s $\Psi_{1,0,0} = \sqrt{\frac{1}{a_0^3 \pi}} e^{-r/a_0}$

n=2, l=0, m=0 : 2s $\Psi_{2,0,0} = \sqrt{\frac{1}{32 a_0^3 \pi}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$

l=1 m=0, ±1 : 2p $\Psi_{2,1,0} = \sqrt{\frac{1}{32 a_0^3 \pi}} \frac{r}{a_0} \cos\theta \, e^{-r/2a_0}$, $\Psi_{2,1,\pm1} = \mp\sqrt{\frac{1}{64 a_0^3 \pi}} \frac{r}{a_0} \sin\theta \, e^{\pm i\varphi} e^{-r/2a_0}$

For Hydrogen atom, μc^2=510,700 eV and $E_{1,0,0}$=13.6 eV : binding energy of Hydrogen atom

$$\Delta E_{m\to n} = 13.6eV\left(\frac{1}{m^2} - \frac{1}{n^2}\right) \quad where\ m,n\text{: any integers}$$

Any transition → $m = 1$ ΔE > 10 eV : corresponds to ultraviolet light and called Lyman series.

m→2 $\frac{13.6}{m^2} - 3.4\ eV$ ~less than 3.4 eV and corresponds to visible light and called Balmer series.

In case Z=10 (neon), it emits 100 times more energy (X-ray). For Deuterium the energy is slightly higher since $m_D = 2\ m_N$ and μc^2=510,850 eV. For muonic atoms μc^2=95 MeV and the corresponding energies are 186 times higher (keV's).

From $\rho = \kappa r$, the average radius (more precisely, the radius of maximum probability) is deduced as

$$a = \frac{1}{\kappa} = \frac{\hbar}{\sqrt{2\mu|E|}} = \frac{\hbar}{\sqrt{\mu^2c^2Z^2\alpha^2\frac{1}{n^2}}} = \frac{\hbar n}{\mu c Z\alpha} = a_0\frac{n}{Z}$$

$$a_0 = \frac{\hbar}{\mu c\alpha} \quad : \quad Bohr\ radius$$

$$a_0 = 5\times10^{-11}\ \text{m} = 0.5\ \text{Å}\ \text{ for an ordinary Hydrogen atom}$$

$$\langle X^2\rangle_{1,0,0} = \langle Y^2\rangle = \langle Z^2\rangle = {a_0}^2$$

Again, for higher Z atoms, the radius shrinks like 1/Z (so a Helium atom is a lot smaller than a hydrogen atom although it has more electrons). For muonic atoms, the average radius is smaller by a factor 186 smaller, or about 270 fm (meaning the muon probes the interior of the nucleus to much larger extent than the electron).