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# The Hydrogen Atom

We write the ~~attractive~~ Coulomb potential

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

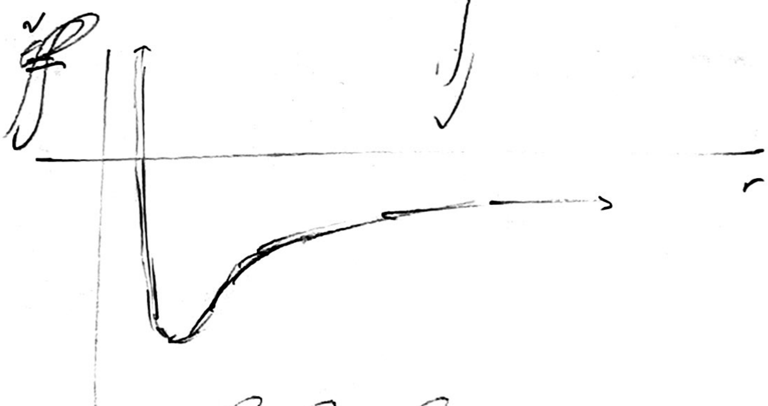
where $\alpha$ is the dimensionless fine structure constant $\alpha \sim \frac{1}{137}$.

Therefore, the TISE

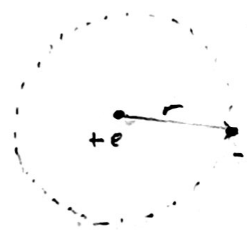
$$\left[-\frac{\hbar^2}{2m_e}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \alpha\frac{\hbar c}{r} + \frac{\hbar^2}{2m_e}\frac{1}{r^2}l(l+1)\right]R_l = E R_l$$

letting $R_l(r) = \frac{u_l(r)}{r}$,

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} \underbrace{- \alpha\frac{\hbar c}{r} + \frac{\hbar^2}{2m}\frac{1}{r^2}l(l+1)}_{V_{eff}}\right]u_l = E u_l$$




$V_{eff}$ for hydrogen




the hydrogen atom.

# Bound State ($E<0$) solutions

Letting $\kappa = \frac{\sqrt{-2mE}}{\hbar}$ & dividing equation by $E$,

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

Letting $\rho = \kappa r$, $\rho_0 = \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa} = \alpha\sqrt{\frac{2mc^2}{|E|}}$,

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

As $\rho \to \infty$, $\frac{d^2u_l}{d\rho^2} \sim u \Longrightarrow u_l(\rho) = Ae^{-\rho} + \cancel{Be^{\rho}}$

As $\rho \to 0$, $\frac{d^2u_l}{d\rho^2} \sim \frac{l(l+1)}{\rho^2}u_l(\rho) \Longrightarrow u_l(\rho) = C\rho^{l+1} + \cancel{D\rho^{-l}}$

$$u_l(\rho) = \begin{cases} Ae^{-\rho} & \text{large } \rho \\ C\rho^{l+1} & \text{small } \rho \end{cases}$$

Let's introduce a new function $v_l(\rho)$, such that

$$u_l(\rho) \sim \rho^{l+1}e^{-\rho}v_l(\rho)$$

Plugging this in,

where

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

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

Therefore,

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

we look for a power series soln

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

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

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

Substituting in,

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

Since all terms carry $\rho^j$ we conclude

$$c_{j+1}\, j(j+1) + 2(l+1)\, c_{j+1}(j+1) - 2c_j\, j + (\rho_0 - 2(l+1))\, c_j = 0$$

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

For large $j$, $c_{j+1} \approx \frac{2j}{j(j+1)} c_j = \frac{2}{j+1} c_j$

$$\Longrightarrow c_{j+1} \sim \frac{2^{j+1}}{(j+1)!} c_0, \quad c_j = \frac{2^j}{j!} c_0$$

Therefore,

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

$$u_l(\rho) \sim \rho^{l+1} e^{-\rho} v_l(\rho) \sim \rho^{l+1} e^{-\rho} c_0 e^{2\rho}$$
$$\sim c_0 \rho^{l+1} e^{\rho}$$

However, this is not normalizable. This means the series must terminate.

There must be some $j_{max}$ such that

$$c_{j_{max}} \neq 0, \quad c_{j_{max}+1} = 0 \Longrightarrow c_{\text{after } j_{max}} = 0$$

Therefore,

$v(\rho)$ must be a finite polynomial, where $c_{j_{max}}$ is some last nonzero coefficient.

In this case, the recursion equation

$$c_{j+1} = \left[\frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)}\right] c_j \Longrightarrow 2(j_{max}+l+1) - \rho_0 = 0$$

Defining $n = j_{max} + l + 1$ we have

$$2n - \rho_0 = 0 \Longrightarrow 2n = \rho_0$$

But since $\rho_0 = \alpha\sqrt{\dfrac{2mc^2}{|\varepsilon|}}$

$$2n = \alpha\sqrt{\frac{2mc^2}{|\varepsilon|}} \Longrightarrow |\varepsilon_n| = \frac{\alpha^2 mc^2}{2n^2} = \frac{-|\varepsilon_1|}{n^2}$$

* Bohr formula

The Energy depends just on $n$.

$$n=1 \quad |\varepsilon_1| = \frac{\alpha^2 mc^2}{2} \quad l=0: \ 1s$$

$$n=2 \quad |\varepsilon_2| = \frac{|\varepsilon_1|}{4} \quad l=0,1: \ 2s,\ 2p$$

$$n=3 \quad |\varepsilon_3| = \frac{|\varepsilon_1|}{9} \quad l=0,1,2: \ 3s,\ 3p,\ 3D$$

As each $l$ has $2m+1$ magnetic ~~substates~~ the ~~total~~ degeneracy for $\mathcal{E}_n$,

$$\# \text{states w/ energy } \mathcal{E}_1 : \sum_{l=0}^{n-1} (2l+1) = \underline{\underline{n^2}}$$

There exists a natural distance scale for the hydrogen atom based on the 1s-wave orbit

Combining Equations

$$\rho_0 = \alpha \sqrt{\frac{2mc^2}{|\mathcal{E}|}} \quad ; \quad \rho_0 = 2n$$

$$1 = a_0 \kappa_1 \equiv a_0 \sqrt{\frac{2m|\mathcal{E}_1|}{\hbar^2}} = a_0 \frac{\alpha mc^2}{\hbar c}$$

$$a_0 \sim \frac{(137)(1973\, eV\, \mathring{A})}{511000\, eV} \sim \underline{\underline{0.529\, \mathring{A}}}$$

Bohr Radius $|\mathcal{E}_1| \sim 13.6\,eV$

distance to 1s $e^-$ orbit

## Basic scale of Hydrogen

1s binding energy $\sim 13.6\,eV$, Bohr Radius $\sim 0.529\,\mathring{A}$, $1\,\mathring{A} = 10^{-10}\,m$

## 3. wave solutions

Angular momenta $l=0$

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

Calling $j_{max}$ the last nonzero term,

$$\rho = \kappa r = \frac{1}{n}\frac{r}{a_0}$$

$j_{max}=0 \quad n=1 \quad v(\rho) = c_0$

$j_{max}=1 \quad n=2 \quad v(\rho) = c_0(1-\rho) = c_0\left(1-\frac{1}{2}\frac{r}{a_0}\right)$

$j_{max}=2 \quad n=3 \quad v(\rho) = c_0\left(1-2\rho+\frac{2}{3}\rho^2\right)$

$$= c_0\left(1-\frac{2}{3}\frac{r}{a_0}+\frac{2}{27}\left(\frac{r}{a_0}\right)^2\right)$$

$\vdots \qquad \vdots \qquad \vdots$

Now since

$$R_l(r) = \frac{1}{r}\rho^{l+1}e^{-\rho}v_l(\rho) \Rightarrow R_0(r) = \frac{1}{r}\rho e^{-\rho}v_0(\rho)$$

Therefore,

$$R_{n=1,\,l=0} \sim c_0 e^{-r/a_0} \qquad R_{n=2,\,l=0} \sim c_0 e^{-r/2a_0}\left(1-\frac{1}{2}\frac{r}{a_0}\right)$$

$$R_{n=3,\,l=0} \sim c_0 e^{-r/3a_0}\left(1-\frac{2}{3}\frac{r}{a_0}+\frac{2}{27}\left(\frac{r}{a_0}\right)^2\right)$$

finally, we ~~determine~~ $c_0$ via normalization,

$$\int_0^\infty r^2 dr \, |R_{n,l=0}(r)|^2 = 1$$

which yields

$$R_{n=1,\, l=0} = \frac{2}{\sqrt{a_0^3}} e^{-r/a_0}$$

$$R_{n=2,\, l=0} = \frac{2}{\sqrt{(2a_0)^3}} e^{-r/2a_0}\left(1 - \frac{1}{2}\frac{r}{a_0}\right)$$

$$R_{n=3,\, l=0} = \frac{2}{\sqrt{(3a_0)^3}} e^{-r/3a_0}\left(1 - \frac{2}{3}\frac{r}{a_0} + \frac{2}{27}\left(\frac{r}{a_0}\right)^2\right)$$

which makes the full 3D normalized ~~stationary states~~

$$\phi_{n=1,\, m=0,\, l=0} = R_{n=1,\, l=0} Y_{00}(\theta,\phi)$$

$$\phi_{n=2,\, m=0,\, l=0} = R_{n=2,\, l=0} Y_{00}(\theta,\phi)$$

$$\phi_{n=3,\, m=0,\, l=0} = R_{n=3,\, l=0} Y_{00}(\theta,\phi)$$

## General Solution

The full recursion relation:

$$c_{j+1} = \frac{2(j+l+1-n)}{(j+1)(j+2l+2)} c_j \Rightarrow v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$$

is a function well-known to mathematicians.

Apart from normalization,

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

where $L^{p}_{q}(x) \equiv (-1)^p \left(\frac{d}{dx}\right)^p L_{p+q}(x)$ Associated Laguerre Poly.

where $L_q(x) \equiv \frac{e^x}{q!} \left(\frac{d}{dx}\right)^q (e^{-x} x^q)$ Laguerre Poly.

$L_0 = 1 \quad L_1 = 1 - x \quad L_2 = 1 - 2x + \frac{1}{2}x^2 + \dots$

Combining Expressions,

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

After normalization, we get

$$\psi_{nlm}(\vec{r}) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}}\, e^{-r/na_0} \left(\frac{2r}{na_0}\right)^l \left[L^{2l+1}_{n-l-1}\left(2r/na_0\right)\right] Y_{lm}(\theta,\phi)$$

$$\int r^2\, dr\, d\Omega\, \psi^*_{n'l'm'}(\vec{r})\, \psi_{nlm}(\vec{r}) = \delta_{n'n}\,\delta_{l'l}\,\delta_{m'm}$$