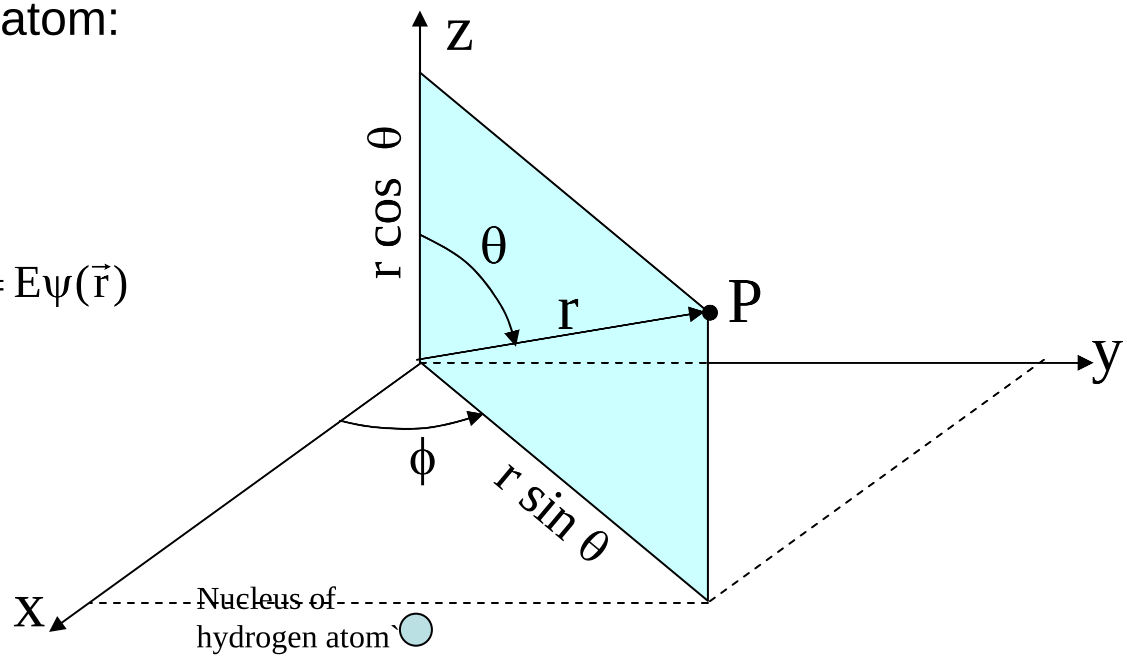
Schrödinger Equation for the hydrogen atom

Potential for hydrogen atom:

$$V(\vec{r}) = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$$

$$\therefore -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E\psi(\vec{r})$$



Use polar coordinates:

$$x = r\cos\phi\sin\theta$$

$$y = r\sin\phi\sin\theta$$

$$z = r\cos\theta$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial^2\phi}$$

$$\text{But } L^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

$$\therefore\ \nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{L^2}{\hbar^2 r^2}$$

Schrödinger Equation for central force field:

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\psi(\vec{r}) + \underbrace{\left[\frac{L^2}{2mr^2} + V(\vec{r})\right]}_{\text{Effective potential}}\psi(\vec{r}) = E\psi(\vec{r})$$

Radial equation for central force field

Schrödinger Equation for central force field :

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\psi(r)+\left[\frac{L^2}{2mr^2}+V(r)\right]\psi(r)=E(\vec{r})$$

$$\Rightarrow\underbrace{\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+V(r)\right]}_{\text{Radial part}}\psi(r)+\underbrace{\frac{L^2}{2mr^2}}_{\text{Angular part}}\psi(r)=E\psi(r)$$

L^2 is a constant of motion in a central force field.

$$\therefore\quad \boxed{\psi(\vec{r})=R(r)\,Y_{\ell m}(\theta,\phi)}$$

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+V(r)\right]R(r)+\frac{\ell(\ell+1)\hbar^2}{2mr^2}R(r)=ER(r)$$

$$\Rightarrow\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}[V-E]R=\ell(\ell+1)R$$

(Write R(r) as R and V(r) as V)

Reduction of radial equation

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}[V(r)-E]R=\ell(\ell+1)R$$

Change variable $u(r)=rR(r)\Rightarrow\ R=\frac{u}{r},\ \frac{dR}{dr}=-\frac{u}{r^2}+\frac{1}{r}\frac{du}{dr}$

$$\frac{d^2}{dr^2}\left(r^2\frac{dR}{dr}\right)=\frac{d}{dr}\left(-u+r\frac{du}{dr}\right)=-\frac{du}{dr}+\frac{du}{dr}+r\frac{d^2u}{dr^2}=r\frac{d^2u}{dr^2}$$

The Radial equation is reduced to :

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}[V(r)-E]R=\ell(\ell+1)R$$

$$\Rightarrow\quad r\frac{d^2u}{dr^2}-\frac{2mr^2}{\hbar^2}[V(r)-E]\frac{u}{r}=\ell(\ell+1)\frac{u}{r}$$

$$\Rightarrow-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2}+\left[V+\frac{\hbar^2}{2mr^2}\ell(\ell+1)\right]u=Eu$$

Boundary conditions of u(r)

Normalization condition of $R(r)$:

$$\int_0^\infty |R|^2 r^2 dr = 1$$

With $u = Rr$

$$\therefore \int_0^\infty |u|^2 dr = 1$$

Also, since $u = rR$, we have $u(0) = 0$.

For the normalization to be possible, we also know $R \to 0$ at least as fast as $\frac{1}{r}$ as $r \to \infty$

$$\therefore u(\infty) = 0$$

In summary:

$$\boxed{\begin{aligned} u(0) &= 0 \\ u(\infty) &= 0 \end{aligned}}$$

Simplification of differential equation

$$V = -\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r}$$

Substitute this into the Schroedinger equation :

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2mr^2}\ell(\ell+1)\right]u = Eu \Rightarrow -\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left(-\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r} + \frac{\ell(\ell+1)\hbar^2}{2m}\frac{1}{r^2}\right)u = Eu$$

For bound state in hydrogen atom, $E < 0$

$$\therefore \text{Let } \kappa = \frac{\sqrt{-2mE}}{\hbar} \text{ or } \kappa = \frac{\sqrt{2m|E|}}{\hbar}$$

Above equation becomes

$$\frac{1}{\kappa^2}\frac{d^2u}{dr^2} = \left[1 + \frac{1}{E}\left(\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r} - \frac{\ell(\ell+1)\hbar^2}{2m}\frac{1}{r^2}\right)\right]u \Rightarrow \frac{1}{\kappa^2}\frac{d^2u}{dr^2} = \left[1 + \left(-\frac{Ze^2}{4\pi\varepsilon_0}\cdot\frac{2m}{\kappa^2\hbar^2}\frac{1}{r} + \frac{\ell(\ell+1)}{(\kappa r)^2}\right)\right]u$$

$$\Rightarrow \frac{1}{\kappa^2}\frac{d^2u}{dr^2} = \left[1 + \left(-\frac{Zme^2}{2\pi\varepsilon_0\kappa\hbar^2}\cdot\frac{1}{\kappa r} + \frac{\ell(\ell+1)}{(\kappa r)^2}\right)\right]u$$

$$\text{Let } \rho = \kappa r \text{ and } \rho_0 = \frac{Zme^2}{2\pi\varepsilon_0\kappa\hbar^2}$$

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

Asymptotic properties

As $\rho \to \infty$, the differential equation becomes

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

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

For finite u as $\rho \to \infty$, $A = 0$.

i.e. $u(r) \sim e^{\rho}$ as $\rho \to \infty$.

Now consider $\rho \to 0$, the differential equation becomes

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

Solution :

$u = C\rho^{\ell+1} + D\rho^{-\ell}$

For finite u as $\rho \to 0$, $D = 0$.

i.e. $u(r) \sim \rho^{\ell+1}$ as $\rho \to 0$.

$\therefore$ The general solution must be in the form

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

Extraction of asymptotic properties

Substitute $u(r) = \rho^{\ell+1} e^{-\rho}\ v(\rho)$ into

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

Equation reduces to:

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

Series solution

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

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

$$\Rightarrow c_{j+1} = \frac{2(\ell+1+j) - \rho_0}{(j+2\ell+2)(j+1)} c_j$$

Higher order terms: $c_{j+1} = \dfrac{2(\ell+1+j) - \rho_0}{(j+2\ell+2)(j+1)} c_j \approx \dfrac{2j}{j^2} c_j = \dfrac{2}{j} c_j$

This is the same recurrence relationship for $e^{2\rho}$. $\therefore u = e^{-\rho}\rho^{\ell+1}v \sim e^{\rho}\rho^{\ell+1}$ at higher order tems and this is not square integrable.

Termination of series

$$c_{j+1} = \frac{2(\ell+1+j)-\rho_0}{(j+2\ell+2)(j+1)} c_j$$

To make $v(\rho)$ a finite series, we let $c_j = 0$ at some $j = j_{max}$:

$$2(\ell+1+j_{max})-\rho_0 = 0 \qquad \text{so } c_{j_{max}+1} = c_{j_{max}+2} = \cdots = c_\infty = 0$$

Let $n = \ell + 1 + j_{max}$ $\qquad n = 1, 2, 3, ...$

$$2n - \rho_0 = 0 \quad \Rightarrow \quad \rho_0 = 2n$$

But $\rho_0 = \dfrac{Zme^2}{2\pi\varepsilon_0 \kappa \hbar^2}$

$$\therefore \ \frac{Zme^2}{2\pi\varepsilon_0 \kappa \hbar^2} = 2n \ \Rightarrow \ \kappa = \frac{Zme^2}{4\pi n \varepsilon_0 \hbar^2}$$

$$\kappa = \frac{\sqrt{-2mE}}{\hbar} \ \Rightarrow E = -\frac{\hbar^2\kappa^2}{2m} = -\frac{\hbar^2}{2m}\left(\frac{Zme^2}{4\pi n\varepsilon_0\hbar^2}\right)^2$$

$$\Rightarrow E = -\frac{Z^2me^4}{32\pi^2\varepsilon_0{}^2\hbar^2}\cdot\frac{1}{n^2} \ = \ -\frac{13.6\text{eV}}{n^2} \ \text{for } Z = 1 \longleftarrow$$

Quantization of energy level

Degeneracy

Since $n = j_{max} + \ell + 1 \Rightarrow j_{max} = n - \ell - 1$

$j_{max} \geq 0 \Rightarrow n - \ell - 1 \geq 0$

$\Rightarrow \boxed{\ell \leq n - 1}$

So we now have three quantum numbers, n, ℓ, and m to label the orbital of an atom.

n	l	Degeneracy
1	0(s)	1
2	0(s), 1(p)	1+3=4
3	0(s), 1(p), 2(d)	1+3+5=9
4	0(s), 1(p), 2(d),3(f)	1+3+5+7 =16

In general, the degeneracy of principal quantum number n is:

degeneracy = 1 + 3 + 5 + ...+ [2(n-1))1]

$= n^2$