Spherical coordinates

$$x = r\sin\vartheta\cos\varphi \qquad r = \sqrt{x^2 + y^2 + z^2}$$
$$y = r\sin\vartheta\sin\varphi \qquad \vartheta = \cos^{-1}(z/r)$$
$$z = r\cos\vartheta \qquad \varphi = \tan^{-1}(y/x)$$

- Laplace in polar coordinates

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\vartheta^2} + \frac{1}{r^2}\cot\vartheta\frac{\partial}{\partial\vartheta} + \frac{1}{r^2}\frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}$$

- Operator of angular momentum

$$\hat{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\vartheta^2} + \cot\vartheta\frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right)$$

Hydrogen atom

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{1}{\hbar^2 r^2}\hat{L}^2\right)\psi - \frac{e^2}{4\pi\varepsilon_0 r}\psi = \varepsilon\psi$$
$$\psi(r,\vartheta,\varphi) = R(r)Y(\vartheta,\varphi)$$

- Two problems - radial and angular
  - A. Angular part

$$\hat{L}^2 Y(\vartheta,\varphi) = \gamma Y(\vartheta,\varphi)$$

1. *Eigenvalues*

$$\gamma = l(l+1)\hbar^2$$

2. *Eigenfunctions*

Spherical harmonics

$$Y_l^m(\vartheta,\varphi);\ l = 0,1,2,\ldots;\ |m| \le l$$

Spherical harmonics

$$Y_l^m(\vartheta,\varphi) = \frac{(-1)^l}{2^l l!}\sqrt{\frac{2l+1}{4\pi}\frac{(l+m)!}{(l-m)!}}\,\frac{e^{im\varphi}}{\sin^m\vartheta}\,\frac{d^{l-m}}{d(\cos\vartheta)^{l-m}}\left(\sin^{2l}\vartheta\right)$$

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\vartheta$$

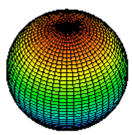
$$Y_1^{\pm1} = \sqrt{\frac{3}{8\pi}}e^{\pm i\varphi}\sin\vartheta$$

$$Y_2^0 = \sqrt{\frac{5}{16\pi}}(3\cos^2\vartheta - 1)$$

$$Y_2^{\pm1} = \sqrt{\frac{15}{8\pi}}\sin\vartheta\cos\vartheta e^{\pm i\varphi}$$

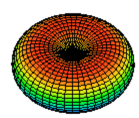
$$Y_2^{\pm2} = \sqrt{\frac{15}{32\pi}}\sin^2\vartheta e^{\pm i2\varphi}$$

Hydrogen Atom - Spherical Harmonics

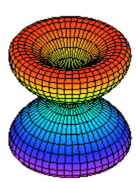


l=0, m=0

l=1, m=0



l=1, m=1



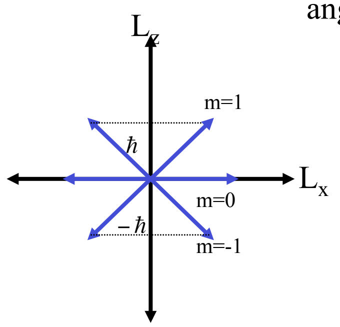
l=2, m=1

l=3, m=1

Hydrogen Atom-Angular Momentum

$L^2 = \hbar^2 l(l+1)$ l=0,1,2,... Magnitude of the orbital angular momentum

$L_z = m\hbar \quad -l \le m \le +l$ z-component of the orbital angular momentum



$|L| = \sqrt{2}\hbar$

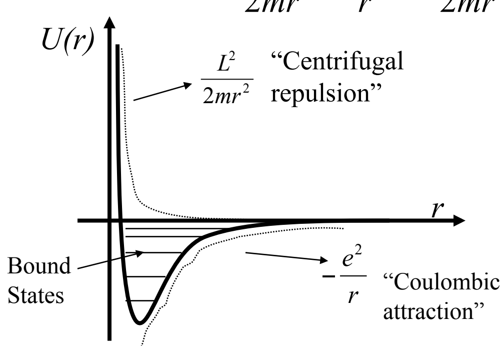
$l = 1$

"Space Quantization"

Hydrogen Atom - Effective Radial Potential

Radial Equation: One dimensional problem with effective potential

$$U(r) = \frac{\hat{L}^2}{2mr^2} - \frac{e^2}{r} = \frac{\hbar^2 l(l+1)}{2mr^2} - \frac{e^2}{r}$$



Bound States

Quantized States

Radial part of the wave function

$$R_{nl} = r^l e^{-\frac{r}{an}} \sum_{j=0}^{n-l-1} b_j r^j$$

$$a = \frac{4\pi\varepsilon_0\hbar^2}{me^2} = 0.53\text{A}$$

$$b_{j+1} = \frac{2}{na}\frac{j+l+1-n}{(j+1)(j+2l+2)} b_j$$

- For each R_{nl}, b_0 is determined by normalization

Radial part of the wave function

$$R_{10} = \frac{2}{\sqrt{a^3}} e^{-\frac{r}{a}}$$

$$R_{20} = \frac{1}{\sqrt{2a^3}}\left(1 - \frac{r}{2a}\right) e^{-\frac{r}{2a}}$$

$$R_{21} = \frac{1}{2\sqrt{6a^3}}\frac{r}{a} e^{-\frac{r}{2a}}$$

$$R_{30} = \frac{2}{3\sqrt{3a^3}}\left(1 - \frac{2r}{3a} + \frac{2r^2}{27a^2}\right) e^{-\frac{r}{3a}}$$

Hydrogen atom

$$\boxed{E = -\frac{me^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2} = -\frac{13.6}{n^2}\,\mathrm{eV}}$$

- For bound energy states, E depends on n only
- The wave function depends on all quantum numbers

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

allowed values :

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

$l = 0,1,2,3,\ldots.(n-1)$

$m = 0,\pm1,\pm2,\pm3,\ldots.\pm l$

Degeneracy

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

Hydrogenlike wavefunctions

$$\Psi_{100} = \frac{1}{\sqrt{\pi a^3}}e^{-\frac{r}{a}}$$

$$\Psi_{200} = \frac{1}{2\sqrt{2\pi a^3}}\left(1-\frac{r}{2a}\right)e^{-\frac{r}{2a}}$$

$$\Psi_{210} = \frac{1}{4\sqrt{2\pi a^3}}\frac{r}{a}e^{-\frac{r}{2a}}\cos\theta$$

$$\Psi_{300} = \frac{1}{3\sqrt{3\pi a^3}}\left(1-\frac{2r}{3a}+\frac{2r^2}{27a^2}\right)e^{-\frac{r}{3a}}$$

Ground state

- *n=1, l=0*

$$R_{10} = e^{-\frac{r}{a}} b_0$$

b_0 *obtained by normalization*

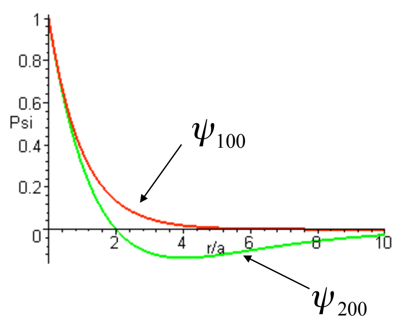
$$|b_0|^2 \int_0^\infty e^{-\frac{2r}{a}} r^2 dr = 1 = |b_0|^2 \frac{a^3}{4}$$

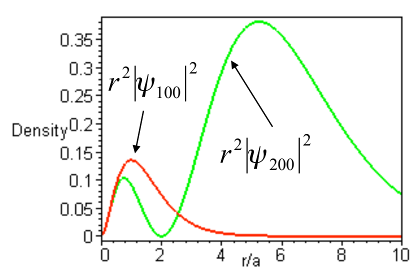
$$R_{10} = \frac{2}{a^{3/2}} e^{-\frac{r}{a}}$$

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}$$

$$\psi_{100} = \frac{1}{\sqrt{\pi a^3}} e^{-\frac{r}{a}}$$

Ground State & First Excited State





Orbitals

- Approximation: use orbitals for a single electron atom

***l* = 0**	***s***	**sharp**
***l* = 1**	***p***	**principal**
***l* = 2**	***d***	**diffuse**
***l* = 3**	***f***	**fundamental**

- Quantum numbers

n	***principal***	**1, 2, 3, …**
l	***angular/orbital***	**0, 1, 2, … (*n-1*)**
m	***magnetic***	**0, ±1, ±2, … *l***
s	***spin***	**±1/2**

Orbital Density

Hydrogen Orbitals
http://webphysics.davidson.edu/Applets/Hydrogenic/