PHYS-3301

Lecture 17

Oct. 22, 2024

Chapter. 7
QM in 3-dims & Hydrogen Atom

Outline:

- The Schrödinger Eq. in 3-Dimensions
- The 3D Infinite Well
- Energy Quantization & Spectral Lines in Hydrogen
- The Schrödinger Eq. for a Central Force
- Angular Behavior in a Central Force
- The Hydrogen Atom
- Radial Probability
- Hydrogen-like Atoms

Stationary States in a 3-D Box

Solution

$$\psi_{n_x,n_y,n_z}(x,\ y,\ z) = A \sin\frac{n_x \pi x}{L_x} \sin\frac{n_y \pi y}{L_y} \sin\frac{n_z \pi z}{L_z}$$

$$E_{n_x,n_y,n_z} = \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)\frac{\pi^2\hbar^2}{2m}$$

Angular Momentum Operator

$$\hat{L}_z^2 \Phi_{m_\ell}(\phi) = (m_\ell \hbar)^2 \Phi_{m_\ell}(\phi)$$

$$L_z = m_\ell \hbar \qquad (m_\ell = 0,\ \pm 1,\ \pm 2,\ \pm 3,\ .\ .\ .\ )$$

Toward the Hydrogen Atom

We break it into pieces.

$$\psi(r,\,\theta,\,\phi) = R(r)\Theta(\theta)\Phi(\phi)$$

i.e. separation variables for a central force (see p247)

$$\frac{\Theta\Phi\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + R\Phi\csc\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + R\Theta\csc^2\theta\frac{\partial^2\Phi}{\partial\phi^2}}{R\Theta\Phi} = \frac{-r^2\frac{2m(E-U(r))}{\hbar^2}R\Theta\Phi}{R\Theta\Phi}$$

After canceling, we find that one of the variables is separate

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{1}{\Theta}\csc\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \csc^2\theta\underbrace{\boxed{\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}}}_{\phi\text{—separate}} = -r^2\frac{2m(E-U(r))}{\hbar^2} \qquad (6\text{-}11)$$

$-m_l^2$

Toward the Hydrogen Atom - Separation of θ

Polar Equation

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \underbrace{\left[\frac{1}{\Theta}\csc\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \csc^2\theta\,(-m_\ell^2)\right]}_{\theta\text{—separate}} = -r^2\frac{2m(E-U(r))}{\hbar^2} \qquad (6\text{-}16)$$

$$\frac{1}{\Theta}\csc\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - m_\ell^2\csc^2\theta = \boxed{C_\theta}$$

or

$$\csc\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta(\theta)}{d\theta}\right) - m_\ell^2\csc^2\theta\,\Theta(\theta) = \boxed{C_\theta\Theta(\theta)}$$

$$\frac{1}{\Theta}\csc\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - m_\ell^2\csc^2\theta = C_\theta$$

or (7-26)

or

$$\csc\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta(\theta)}{d\theta}\right) - m_\ell^2\csc^2\theta\,\Theta(\theta) = C_\theta\Theta(\theta)$$

far more challenging equation than others we have seen ;) and we won't go into the analytical solution; you will see this in the advanced QM textbook

m_l^2

Solution is possible (non-divergent) only if:

C_θ	0	-2	-6	...	$-\ell(\ell+1)$	$(\ell = 0,1,2,\ldots)$
m_ℓ	0	$0,\pm1$	$0,\pm1,\pm2$	...	$0,\pm1,\pm2,\ldots,\pm\ell$	

***m* and *l* are related!**

C_θ	0	-2	-6	...	$\boxed{-\ell(\ell+1)}$	$(\ell = 0,1,2,\ldots)$
m_ℓ	0	$0,\pm1$	$0,\pm1,\pm2$	...	$0,\pm1,\pm2,\ldots,\pm\ell$	

***l* = *a* new quantum number**

$$\frac{1}{\Theta}\csc\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - m_\ell^2\csc^2\theta = C_\theta$$

or

$$\csc\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta(\theta)}{d\theta}\right) - m_\ell^2\csc^2\theta\,\Theta(\theta) = \boxed{C_\theta}\Theta(\theta)$$

Polar Equation

$$\csc\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta(\theta)}{d\theta}\right) - m_\ell^2\csc^2\theta\,\Theta(\theta) = -\ell(\ell+1)\Theta(\theta)$$

C_θ	0	-2	-6	...	$-\ell(\ell+1)$	$(\ell = 0,1,2,\dots)$
m_ℓ	0	$0,\pm1$	$0,\pm1,\pm2$	...	$0,\pm1,\pm2,\dots,\pm\ell$	

l = new quantum number

$$\csc\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta(\theta)}{d\theta}\right)-m_\ell^2\csc^2\theta\,\Theta(\theta)=\boxed{-\ell(\ell+1)}\Theta(\theta)$$

$$\Theta_{\ell,m_\ell}(\theta)=\boxed{P_{\ell,|m_\ell|}(\cos\theta)}\quad\begin{pmatrix}\ell=0,1,2,\dots\\ m_\ell=0,\pm1,\pm2,\dots,\pm\ell\end{pmatrix}$$

Legendre Polynomials

Legendre Polynomials

ℓ, m_ℓ	$P_{\ell,m_\ell}(\cos\theta)$
0, 0	1
1, 0	$\cos\theta$
1, 1	$\sin\theta$
2, 0	$\frac{1}{2}(3\cos^2\theta-1)$
2, 1	$3\cos\theta\sin\theta$
2, 2	$3\sin^2\theta$
3, 0	$\frac{1}{2}(5\cos^3\theta-3\cos\theta)$
3, 1	$\frac{3}{2}(5\cos^2\theta-1)\sin\theta$
3, 2	$15\cos\theta\sin^2\theta$
3, 3	$15\sin^3\theta$

The meaning of l

$L^2 = L_x^2+L_y^2+L_z^2$

See Appendix G

$$\hat{L^2}=-\hbar^2\left[\csc\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\csc^2\theta\frac{\partial^2}{\partial\phi^2}\right]$$

$$\hat{L^2}(\Theta_{\ell,m_\ell}(\theta)\Phi_{m_\ell}(\phi))$$
$$=-\hbar^2\left[\csc\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\csc^2\theta\frac{\partial^2}{\partial\phi^2}\right](\Theta_{\ell,m_\ell}(\theta)\Phi_{m_\ell}(\phi))$$
$$=-\hbar^2\Phi_{m_\ell}(\phi)\csc\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta_{\ell,m_\ell}(\theta)}{\partial\theta}\right)-\hbar^2\Theta_{\ell,m_\ell}(\theta)\csc^2\theta\frac{\partial^2\Phi_{m_\ell}(\phi)}{\partial\phi^2}$$

The meaning of l

$$-\hbar^2\Phi_{m_\ell}(\phi)\csc\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta_{\ell,m_\ell}(\theta)}{\partial\theta}\right)-\hbar^2\Theta_{\ell,m_\ell}(\theta)\csc^2\theta[(-m_\ell^2)\Phi_{m_\ell}(\phi)]$$

$$\hat{L^2}(\Theta_{\ell,m_\ell}(\theta)\Phi_{m_\ell}(\phi))$$
$$=-\hbar^2\Phi_{m_\ell}(\phi)\boxed{\left[\csc\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta_{\ell,m_\ell}(\theta)}{\partial\theta}\right)-m_\ell^2\csc^2\theta\,\Theta_{\ell,m_\ell}(\theta)\right]}$$

$$\hat{L^2}(\Theta_{\ell,m_\ell}(\theta)\Phi_{m_\ell}(\phi))=\hbar^2\boxed{\ell(\ell+1)}(\Theta_{\ell,m_\ell}(\theta)\Phi_{m_\ell}(\phi))$$

Angular part of Schrodinger Eq.

$$|L|=\sqrt{L^2}=\sqrt{\ell(\ell+1)}\,\hbar\qquad(\ell=0,1,2,\dots)$$

l = Orbital Quantum number

$$\begin{array}{llllll} C_\theta & 0 & -2 & -6 & \ldots & -\ell(\ell+1) \quad (\ell = 0,1,2,\ldots) \\ m_\ell & 0 & 0,\pm1 & 0,\pm1,\pm2 & \ldots & 0,\pm1,\pm2,\ldots,\pm\ell \end{array}$$

***l* = *n*ew quantum number**

$$\csc\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta(\theta)}{d\theta}\right) - m_\ell^2 \csc^2\theta\, \Theta(\theta) = \boxed{-\ell(\ell+1)}\Theta(\theta)$$

$$\Theta_{\ell,m_\ell}(\theta) = \boxed{P_{\ell,|m_\ell|}(\cos\theta)} \quad \begin{pmatrix} \ell = 0, 1, 2, \ldots \\ m_\ell = 0, \pm1, \pm2, \ldots, \pm\ell \end{pmatrix}$$

Legendre Polynomials

The meaning of *l*

Angular part of Schrodinger Eq.

$$\hat{L}^2(\Theta_{\ell,m_\ell}(\theta)\Phi_{m_\ell}(\phi)) = \boxed{\hbar}^2\ell(\ell+1)(\Theta_{\ell,m_\ell}(\theta)\Phi_{m_\ell}(\phi))$$

Units of angular momentum

$$|L| = \sqrt{L^2} = \sqrt{\ell(\ell+1)}\,\hbar \qquad (\ell = 0, 1, 2, \ldots)$$

L ~ Magnitude of Angular Momentum

Quantized so far:

$$L_z = m_\ell \hbar \qquad (m_\ell = 0, \pm1, \pm2, \ldots, \pm\ell)$$

The projection of angular momentum to z- axis

m_l = MAGNETIC QUANTUM NUMBER

$$|L| = \sqrt{L^2} = \sqrt{\ell(\ell+1)}\,\hbar \qquad (\ell = 0, 1, 2, \ldots)$$

The magnitude of (orbital) angular momentum

***l* = ORBITAL QUANTUM NUMBER**

Summary

Time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + U(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Hydrogen atom potential energy

$$U(r) = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{r} \qquad (6\text{-}9)$$

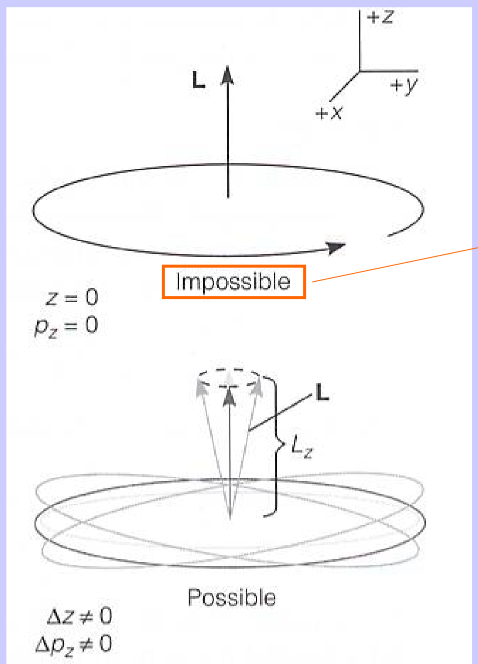
Hydrogen atom wave function

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

$$E = -\frac{me^4}{2(4\pi\epsilon_0)^2\hbar^2}\frac{1}{n^2} \qquad (n = 1, 2, 3, \ldots)$$

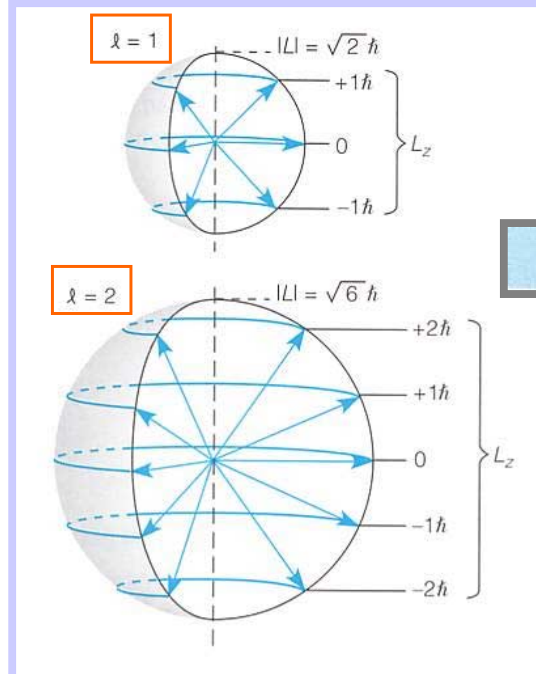
$$|L| = \sqrt{\ell(\ell+1)}\,\hbar \qquad (\ell = 0, 1, 2, \ldots, n-1)$$

$$L_z = m_\ell\hbar \qquad (m_\ell = 0, \pm1, \pm2, \ldots, \pm\ell)$$



The Uncertainty Principle

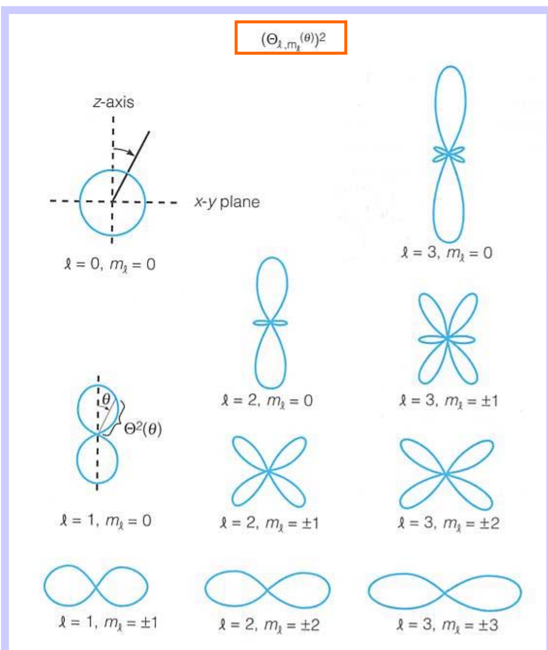
Planar motion violates the uncertainty Principle !!



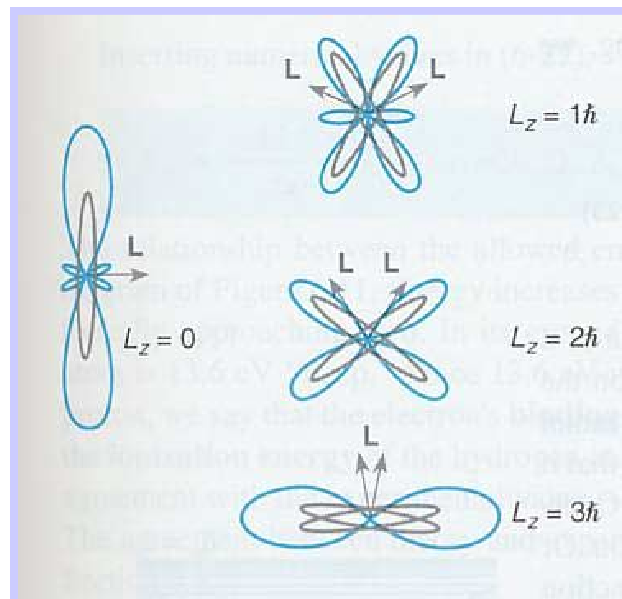
Angular Momentum Quantization

$$|L| = \sqrt{L^2} = \sqrt{\ell(\ell+1)}\,\hbar$$

$$L_z = m_\ell \hbar$$



Angular probability densities for a central force



The Radial Part of Schrodinger Equation for Hydrogen Atom

$$\boxed{\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)} + \left[\frac{1}{\Theta}\csc\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \csc^2\theta\,(-m_\ell^2)\right] = \boxed{-r^2\frac{2m(E-U(r))}{\hbar^2}} \quad (6\text{-}16)$$

θ—separate

$$\csc\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta(\theta)}{d\theta}\right) - m_\ell^2\csc^2\theta\,\Theta(\theta) = -\ell(\ell+1)\Theta(\theta)$$

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \ell(\ell+1) = -r^2\frac{2m(E-U(r))}{\hbar^2}$$

The Radial Part of Schrodinger Equation for Hydrogen Atom

$$\underbrace{\frac{-\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r)}_{KE_{radial}} + \underbrace{\frac{\hbar^2\ell(\ell+1)}{2mr^2}R(r)}_{KE_{rotational}} + \underbrace{\boxed{U(r)}R(r)}_{\text{Potential energy}} = \underbrace{ER(r)}_{\text{Total energy}}$$

Hydrogen P.E.

$$\frac{-\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r) + \left[\frac{\hbar^2\ell(\ell+1)}{2mr^2} - \frac{1}{4\pi\epsilon_0}\frac{e^2}{r}\right]R(r) = ER(r)$$

The radial equation is called the **associated Laguerre equation** and the *solutions R* that satisfy the appropriate boundary conditions are called *associated Laguerre functions*.

The Radial Part of Schrodinger Equation for Hydrogen Atom

$$\underbrace{\frac{-\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r)}_{KE_{radial}} + \underbrace{\frac{\hbar^2\ell(\ell+1)}{2mr^2}R(r)}_{KE_{rotational}} + \underbrace{\boxed{U(r)}R(r)}_{\text{Potential energy}} = \underbrace{ER(r)}_{\text{Total energy}}$$

Hydrogen P.E.

$$\frac{-\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r) + \left[\frac{\hbar^2\ell(\ell+1)}{2mr^2} - \frac{1}{4\pi\epsilon_0}\frac{e^2}{r}\right]R(r) = ER(r)$$

Try a solution $\boxed{R = Ae^{-r/a_0}}$

A is a normalization constant.

a_0 is a constant with the dimension of length.

Take derivatives of *R* and insert them into Eq

Energy quantization

The *principal* quantum number n

$$E = -\frac{me^4}{2(4\pi\epsilon_0)^2\hbar^2}\frac{1}{n^2} \quad (\text{where } n = 1, 2, 3, \ldots)$$

and *l* must obey

$$\ell = 0, 1, 2, \ldots, n-1$$

Quantum number *l* is limited to (n-1)

Bohr Radius

$$E = -\frac{\hbar^2}{2ma_0^2}\frac{1}{n^2}$$

$$a_0 \equiv \frac{(4\pi\epsilon_0)\hbar^2}{me^2} = 0.0529 \text{ nm}$$

How Small is "Small"?

Quantum numbers

$$\ell = 0, 1, 2, \ldots, n-1$$
$$m_\ell = 0, \pm 1, \pm 2, \ldots, \pm\ell$$

$\ell = 0, 1, 2, 3, \ldots$
$m_\ell = -\ell, -\ell + 1, \ldots, -2, -1, 0, 1, 2, . \ell . , \ell - 1, \ell$
$|m_\ell| \le \ell$ and $\ell < 0$

Energy

n	1	2				3									…	n
ℓ	0	0	1			0	1			2					…	$0, \ldots, n-1$
m_ℓ	0	0	−1	0	+1	0	−1	0	+1	−2	−1	0	+1	+2	…	$-\ell, \ldots, +\ell$

Degeneracy

	1	4	9	…	n^2

$$\frac{-\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r) + \frac{\hbar^2\boxed{\ell(\ell+1)}}{2mr^2}R(r) + U(r)R(r) = \boxed{E}R(r)$$

Because of 1/r

"accidental" degeneracy

Probability Density and Normalization

$$|\Psi(\mathbf{r}, t)|^2 = |\psi(r, \theta, \phi)\phi(t)|^2 = (R(r)\Theta(\theta)\Phi(\phi)\phi(t))^*(R(r)\Theta(\theta)\Phi(\phi)\phi(t))$$

$$|\psi(r, \theta, \phi)|^2 = (R(r)\Theta(\theta))^2$$

Total Prob. of finding electron somewhere in space must be "1". Using the volume element in spherical polar coordinate (see 7-4), normalization condition becomes…

Hydrogen Atom Radial Wave Functions

Table 6.5 Radial Solutions of (6-26)

First few radial wave functions $R_{n\ell}$

$$\boxed{R = Ae^{-r/a_0}}$$

n, ℓ	$R_{n,\ell}(r)$
1, 0	$\frac{1}{(1a_0)^{3/2}}2e^{-r/a_0}$
2, 0	$\frac{1}{(2a_0)^{3/2}}2\left(1-\frac{r}{2a_0}\right)e^{-r/2a_0}$
2, 1	$\frac{1}{(2a_0)^{3/2}}\frac{r}{\sqrt{3}\,a_0}e^{-r/2a_0}$
3, 0	$\frac{1}{(3a_0)^{3/2}}\left(2-\frac{4r}{3} \ldots \frac{4r^2}{\ldots}\right)$
3, 1	$1 \quad 4\sqrt{2}r$ …

n	1	2				3									…	n
ℓ	0	0	1			0	1			2					…	$0, \ldots, n-1$
m_ℓ	0	0	−1	0	+1	0	−1	0	+1	−2	−1	0	+1	+2	…	$-\ell, \ldots, +\ell$

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \ell(\ell+1) = -r^2\frac{2m(E-U(r))}{\hbar^2}$$

Associated Leguerre Equation; $R(r) = Ae^{-r/a0}$, $d^2R/dr^2 = R/a_0^2$

Table 6.6 Angular Solutions (Spherical Harmonics)*

ℓ, m_ℓ	$\Theta_{\ell, m_\ell}(\theta)\, \Phi_{m_\ell}(\phi)$
0, 0	$\sqrt{\frac{1}{4\pi}}$
1, 0	$\sqrt{\frac{3}{4\pi}} \cos\theta$
1, ±1	$\sqrt{\frac{3}{8\pi}} \sin\theta\, e^{\pm i\phi}$
2, 0	$\sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1)$
2, ±1	$\sqrt{\frac{15}{8\pi}} \cos\theta \sin\theta\, e^{\pm i\phi}$
2, ±2	$\sqrt{\frac{15}{32\pi}} \sin^2\theta\, e^{\pm 2i\phi}$
3, 0	$\sqrt{\frac{7}{16\pi}} (5\cos^3\theta - 3\cos\theta)$
3, ±1	$\sqrt{\frac{21}{64\pi}} (5\cos^2\theta - 1)\sin\theta\, e^{\pm i\phi}$
3, ±2	$\sqrt{\frac{105}{32\pi}} \cos\theta \sin^2\theta\, e^{\pm 2i\phi}$
3, ±3	$\sqrt{\frac{35}{64\pi}} \sin^3\theta\, e^{\pm 3i\phi}$

$$\csc\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta(\theta)}{d\theta}\right) - m_\ell^2 \csc^2\theta\, \Theta(\theta) = -\ell(\ell+1)\Theta(\theta)$$

Now, we can discuss where hydrogen's e might be found

Traditional naming scheme

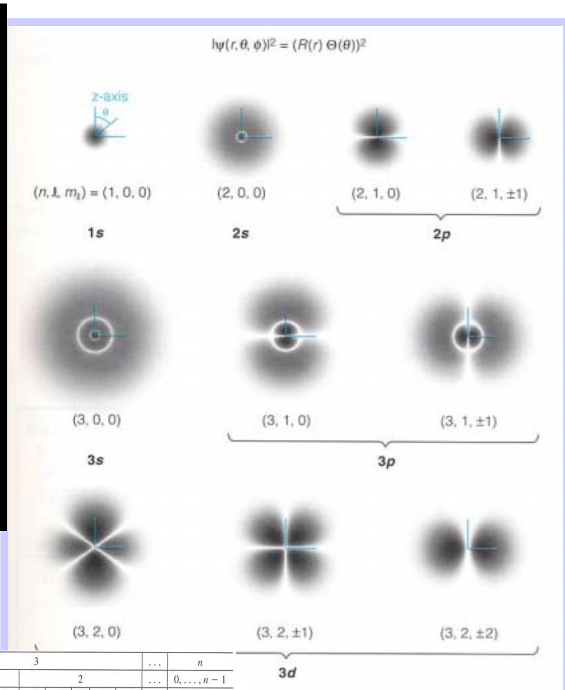
Spectroscopic notation

Letter	s	p	d	f	g	h
Value of ℓ	0	1	2	3	4	5

s: sharp, p: principle, d: diffuse, f: fundamental…
3d state: n=3 & l = 2
2p state: n=2 & l = 1

Electron Prob. Densities in the Hydrogen atom, through n = 3

State are labeled using spectroscopic notation; n, l



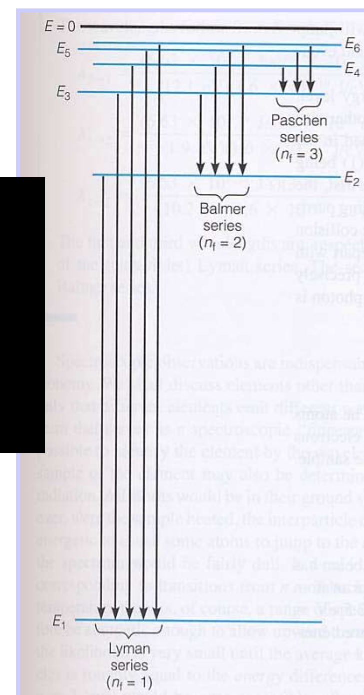
n	1	2				3									…	n
ℓ	0	0	1			0	1			2					…	$0, \ldots, n-1$
m_ℓ	0	0	−1	0	+1	0	−1	0	+1	−2	−1	0	+1	+2	…	$-\ell, \ldots, +\ell$

2d state is possible? -- No!! Because, here, n=2, d =2; Remember n > d

Spectral Lines

Hydrogen' energies & specral lines;

A photon is emitted when the electron jumps downward.



$$
\begin{aligned}
E &= E_{\mathrm{i}} - E_{\mathrm{f}} \\
&= \left[-\frac{me^4}{2(4\pi\epsilon_0)^2\hbar^2}\frac{1}{n_{\mathrm{i}}^2} \right] - \left[-\frac{me^4}{2(4\pi\epsilon_0)^2\hbar^2}\frac{1}{n_{\mathrm{f}}^2} \right] \\
&= \frac{me^4}{2(4\pi\epsilon_0)^2\hbar^2}\left(\frac{1}{n_{\mathrm{f}}^2} - \frac{1}{n_{\mathrm{i}}^2} \right)
\end{aligned}
$$

For a photon, $E = hf = hc/\lambda$. Therefore,

$$
\frac{hc}{\lambda} = \frac{me^4}{2(4\pi\epsilon_0)^2\hbar^2}\left(\frac{1}{n_{\mathrm{f}}^2} - \frac{1}{n_{\mathrm{i}}^2} \right)
$$

or

$$
\begin{aligned}
\frac{1}{\lambda} &= \frac{me^4}{2(4\pi\epsilon_0)^2\hbar^2 hc}\left(\frac{1}{n_{\mathrm{f}}^2} - \frac{1}{n_{\mathrm{i}}^2} \right) \\
&= 1.097 \times 10^7\ \mathrm{m}^{-1}\left(\frac{1}{n_{\mathrm{f}}^2} - \frac{1}{n_{\mathrm{i}}^2} \right)
\end{aligned}
$$