

Announcements

- Homework #1 Question 2
- Homework #1 Question 8 from the textbook
- Homework #2 will be handed out on Tuesday (22nd) and due Monday noon (28th)
- Schedule a review time before the first exam on 29th

PH102: Interactive Lecture 4

- Topics
 - 3d Schrodinger Equation for Hydrogen atom
 - $(x,y,z) \leftrightarrow (r,\theta,\phi)$
 - Separation of variables $R\Theta\Phi$
 - Three equations
 - Three quantum numbers
 - Wave functions
 - Quantization of angular momentum (L)
 - Degeneracies
 - Normalization
 - Electron whereabouts

Schrodinger Equation

$$\left\{ \begin{array}{ll} \frac{\partial^2 \Phi}{\partial \phi^2} = -m_l^2 \Phi & \text{Azimuthal Equation} \\ \sin\theta \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial \Theta}{\partial \theta} \right) + [l(l+1)\sin^2\theta - m_l^2]\Theta = 0 & \text{Polar Equation} \\ \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{2mr^2}{\hbar^2} (E - U(r))R - l(l+1)R = 0 & \text{Radial Equation} \end{array} \right.$$

Schrodinger Equation: Hydrogen Atom

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

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

$$\underline{\left[\frac{-\hbar^2}{2m} \nabla^2 + U(\vec{x}) \right] \psi(\vec{x}) = E \psi(\vec{x})}$$

$$\mathbf{H}\psi_{n,l,m_l} = E_n \psi_{n,l,m_l}$$

Hamiltonian (H) = T (kinetic) + U (Potential)

Kinetic energy w.r.t. r + Kinetic energy w.r.t. rotation

$$\left\{ \begin{array}{l} -\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U(r)) = C = -l(l+1) - \\ \frac{1}{\Theta} \csc\theta \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{1}{\Phi} \csc^2\theta \frac{\partial^2 \Phi}{\partial \phi^2} = C = -l(l+1) \end{array} \right.$$

$$\mathbf{L}^2 \psi_{n,l,m_l} = l(l+1) \hbar^2 \psi_{n,l,m_l}$$

$$\frac{\partial^2 \Phi}{\partial \phi^2} = -m_l^2 \Phi$$

$$\mathbf{L}_z \psi_{n,l,m_l} = m_l \hbar \psi_{n,l,m_l}$$

n	l	m_l	$\Phi(\phi)$	$\Theta(\theta)$	$R(r)$	$\psi(r, \theta, \phi)$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-r/a_0}$
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \cos \theta$
2	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{+i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{+i\phi}$
3	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3} a_0^{3/2}} \left(27 - 18 \frac{r}{a_0} + 2 \frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi} a_0^{3/2}} \left(27 - 18 \frac{r}{a_0} + 2 \frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \cos \theta$
3	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{+i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \sin \theta e^{+i\phi}$
3	2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4} (3 \cos^2 \theta - 1)$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} (3 \cos^2 \theta - 1)$
3	2	± 1	$\frac{1}{\sqrt{2\pi}} e^{+i\phi}$	$\frac{\sqrt{15}}{2} \sin \theta \cos \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin \theta \cos \theta e^{+i\phi}$
3	2	± 2	$\frac{1}{\sqrt{2\pi}} e^{+2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2 \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2 \theta e^{+2i\phi}$

Three quantum numbers

- Principal quantum number: n

$$E_n = -\frac{m e^4}{32 \pi^2 \epsilon_0^2 \hbar^2} \left(\frac{1}{n^2}\right) = -\left(\frac{e^2}{8 \pi \epsilon_0}\right) \left(\frac{m e^2}{4 \pi \epsilon_0 \hbar^2}\right) \left(\frac{1}{n^2}\right) =$$
$$-\left(\frac{e^2}{8 \pi \epsilon_0 a_0}\right) \left(\frac{1}{n^2}\right) = -13.6 \text{ eV} \left(\frac{1}{n^2}\right)$$

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

$$L_z = m_l \hbar$$

- Orbital quantum number: $l = 0, 1, 2, \dots, (n-1)$
- Magnetic quantum number: $m_l = 0, \pm 1, \pm 2, \dots, \pm l$

Degeneracies

$$\psi(r, \theta, \phi) = \psi_{n,l,m_l} = R(r)\Theta(\theta)\Phi(\phi) = R_{n,l}\Theta_{l,m_l}\Phi_{m_l} = R_{n,l}Y_l^{m_l}$$

where $\Theta_{l,m_l}\Phi_{m_l} = Y_l^{m_l}$ (Spherical harmonics)

n	l	m_l	E_n (eV)	$ L $	L_z	$\psi_{n,l,m_l} = R_{n,l}Y_l^{m_l}$	degeneracies	Orbital name	
1	0	0	-13.6	0	0	ψ_{100}	Non-degenerate	1s	
2	0	0	-3.40	0	0	ψ_{200}	4 (=2 ²)	2s	
	1	-1		$\sqrt{2}\hbar$	$-\hbar$	ψ_{21-1}		$R_{21}Y_1^{-1}$	2p
		0			0	ψ_{210}		$R_{21}Y_1^0$	
		1			$+\hbar$	ψ_{211}		$R_{21}Y_1^{+1}$	

n	l	m_l	$E_n(\text{eV})$	$ L $	L_z	$\psi_{n,l,m_l} =$	$R_{n,l} Y_l^{m_l}$	<u>degeneracies</u>	Orbital name	
1	0	0	-13.6	0	0	ψ_{100}	$R_{10} Y_0^0$	Non-degenerate	1s	
2	1	0	-3.40	$\sqrt{2}\hbar$	0	ψ_{200}	$R_{20} Y_0^0$	4 ($=2^2$)	2s	
		-1			$-\hbar$	ψ_{21-1}	$R_{21} Y_1^{-1}$			2p
		0			0	ψ_{210}	$R_{21} Y_1^0$			
		1			$+\hbar$	ψ_{211}	$R_{21} Y_1^{+1}$			
3	1	0	-1.51	$\sqrt{2}\hbar$	0	ψ_{300}	$R_{30} Y_0^0$	9 ($=3^2$)	3s	
		-1			$-\hbar$	ψ_{31-1}	$R_{31} Y_1^{-1}$			3p
		0			0	ψ_{310}	$R_{31} Y_1^0$			
	1	$+\hbar$		ψ_{311}	$R_{31} Y_1^1$					
	2	-2		-2	$\sqrt{6}\hbar$	$-2\hbar$	ψ_{32-2}		$R_{32} Y_2^{-2}$	3d
				-1		$-\hbar$	ψ_{32-1}		$R_{32} Y_2^{-1}$	
				0		0	ψ_{320}		$R_{32} Y_2^0$	
				1		$+\hbar$	ψ_{321}		$R_{32} Y_2^1$	
				2		$+2\hbar$	ψ_{322}		$R_{32} Y_2^2$	

Normalization

$$|\psi_{n,l,m_l}|^2 = R(r)^2 \Theta(\theta)^2 \Phi(\phi)^2$$

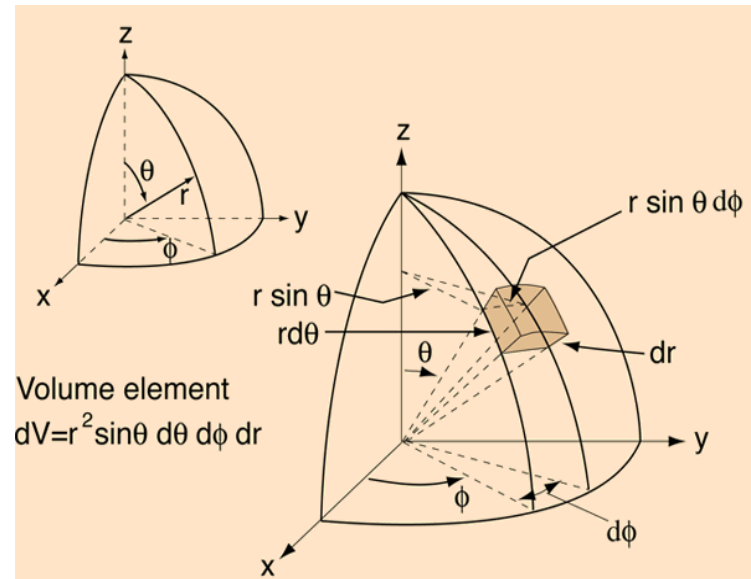
$$(x, y, z) \leftrightarrow (r, \theta, \phi)$$

$$\begin{cases} r = \sqrt{x^2 + y^2 + z^2} \\ \phi = \tan^{-1} \frac{y}{x} \\ \theta = \cos^{-1} \frac{z}{r} \end{cases}$$

$$\begin{cases} x = r \sin \theta \cos \phi \\ y = r \sin \theta \sin \phi \\ z = r \cos \theta \end{cases}$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\begin{aligned} \nabla^2 &= \frac{1}{r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \csc \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \csc^2 \theta \frac{\partial}{\partial \phi^2} \right] & dV &= r^2 \sin \theta \, dr d\theta d\phi \\ &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial}{\partial \phi^2} \end{aligned}$$



Normalization

$$|\psi_{n,l,m_l}|^2 = R(r)^2 \Theta(\theta)^2 \Phi(\phi)^2$$

$$\begin{aligned} \int |\psi_{n,l,m_l}|^2 dV &= \int |\psi_{n,l,m_l}|^2 r^2 \sin\theta \, dr d\theta d\phi \\ &= \int_0^\infty R(r)^2 r^2 \, dr \int_0^\pi \Theta(\theta)^2 \sin\theta \, d\theta \int_0^{2\pi} \Phi(\phi)^2 d\phi \end{aligned}$$

Normalization

$$|\psi_{n,l,m_l}|^2 = R(r)^2 \Theta(\theta)^2 \Phi(\phi)^2$$

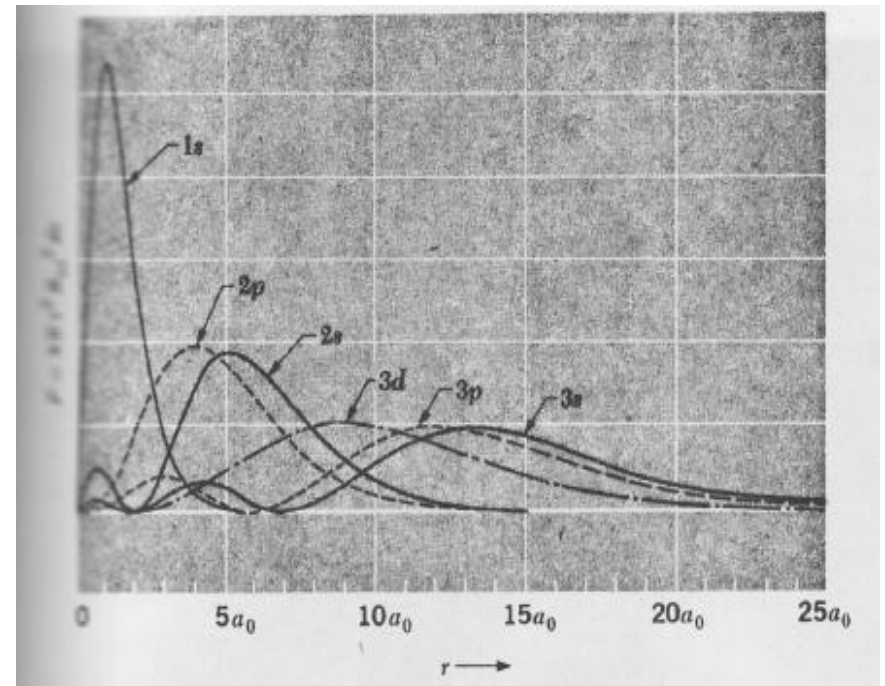
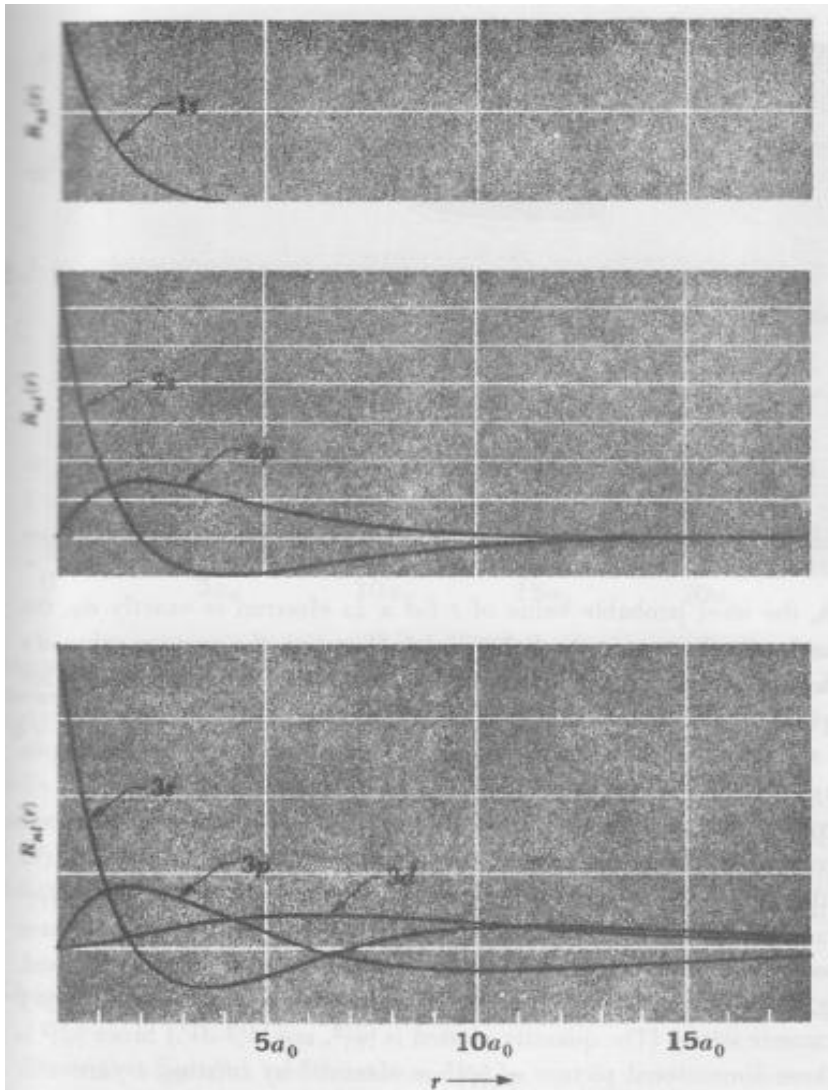
$$\begin{aligned} \int |\psi_{n,l,m_l}|^2 dV &= \int |\psi_{n,l,m_l}|^2 r^2 \sin\theta dr d\theta d\phi \\ &= \int_0^\infty R(r)^2 r^2 dr \int_0^\pi \Theta(\theta)^2 \sin\theta d\theta \int_0^{2\pi} \Phi(\phi)^2 d\phi \end{aligned}$$

$$\begin{cases} \int_0^\infty R(r)^2 r^2 dr = 1 \\ \int_0^\pi \Theta(\theta)^2 \sin\theta d\theta \int_0^{2\pi} \Phi(\phi)^2 d\phi = 2\pi \int_0^\pi \Theta(\theta)^2 \sin\theta d\theta = 1 \end{cases}$$

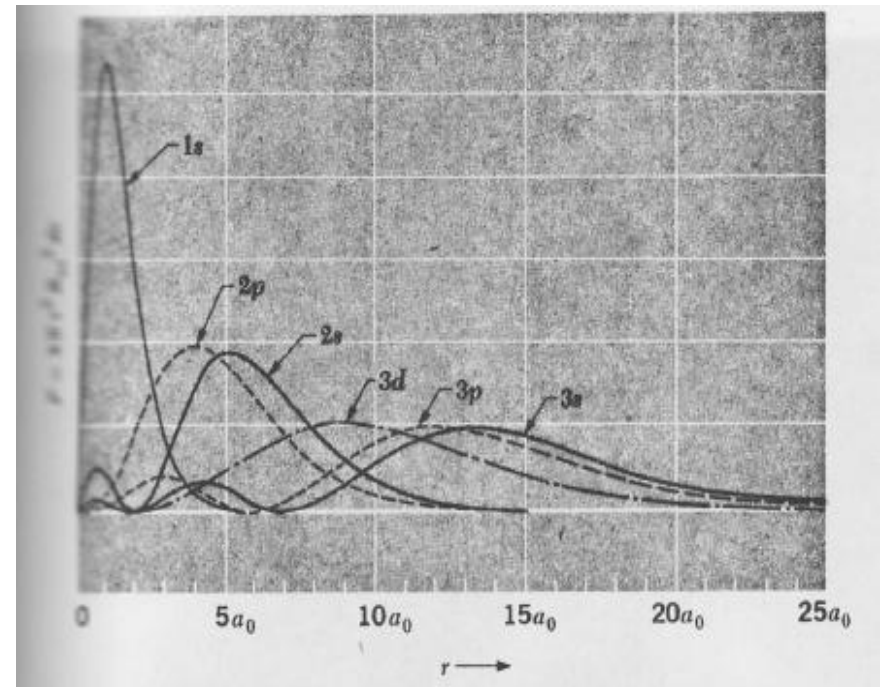
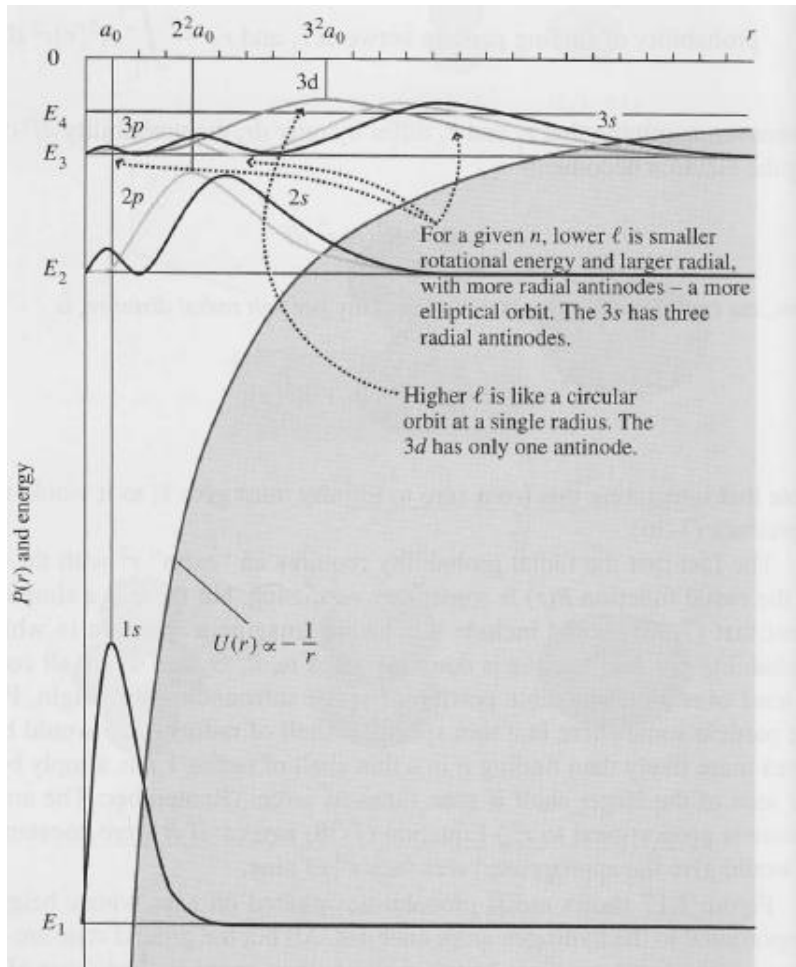
R(r) vs. r² R²(r)

n	l	m_l	$\Phi(\phi)$	$\Theta(\theta)$	$R(r)$	$\psi(r, \theta, \phi)$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-r/a_0}$
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \cos \theta$
2	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{+i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{+i\phi}$
3	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3} a_0^{3/2}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi} a_0^{3/2}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \cos \theta$
3	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{+i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \sin \theta e^{+i\phi}$
3	2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4} (3 \cos^2 \theta - 1)$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} (3 \cos^2 \theta - 1)$
3	2	± 1	$\frac{1}{\sqrt{2\pi}} e^{+i\phi}$	$\frac{\sqrt{15}}{2} \sin \theta \cos \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin \theta \cos \theta e^{+i\phi}$
3	2	± 2	$\frac{1}{\sqrt{2\pi}} e^{+2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2 \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2 \theta e^{+2i\phi}$

$R(r)$ vs. $r^2 R^2(r)$



$$P(r) = r^2 R^2(r)$$



Most probable vs. expectation value

the expected r value is obtained when $\langle r \rangle = \int_0^{\infty} r \cdot r^2 R_{n,l}(r)^2 dr$

The most probable r value is obtained when $\frac{dP(r)}{dr} = \frac{dr^2 R_{n,l}(r)^2}{dr} = 0$

$$r_{n, l=n-1} \text{ (most probable)} = n^2 a_0$$

That is,

$$r_{10} \text{ (1s, most probable)} = a_0$$

$$r_{21} \text{ (2p, most probable)} = 4a_0$$

$$r_{32} \text{ (3d, most probable)} = 9a_0$$

Most probable vs. expectation value

Expectation Value r $\langle r \rangle = \int_0^{\infty} r \cdot r^2 R_{n,l}(r)^2 dr$

Most probable r Value $\frac{dP(r)}{dr} = \frac{dr^2 R_{n,l}(r)^2}{dr} = 0$

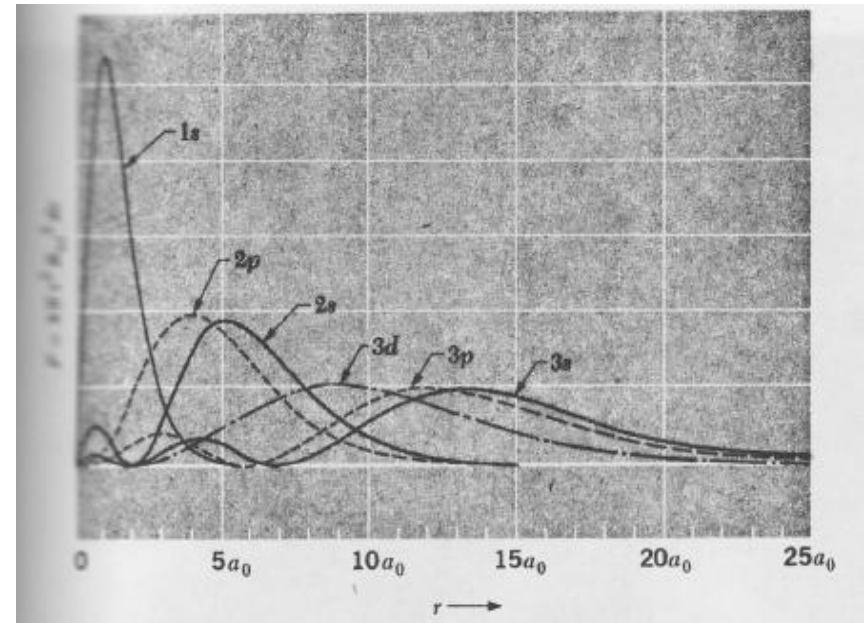
Most probable vs. expectation value

Expectation Value r

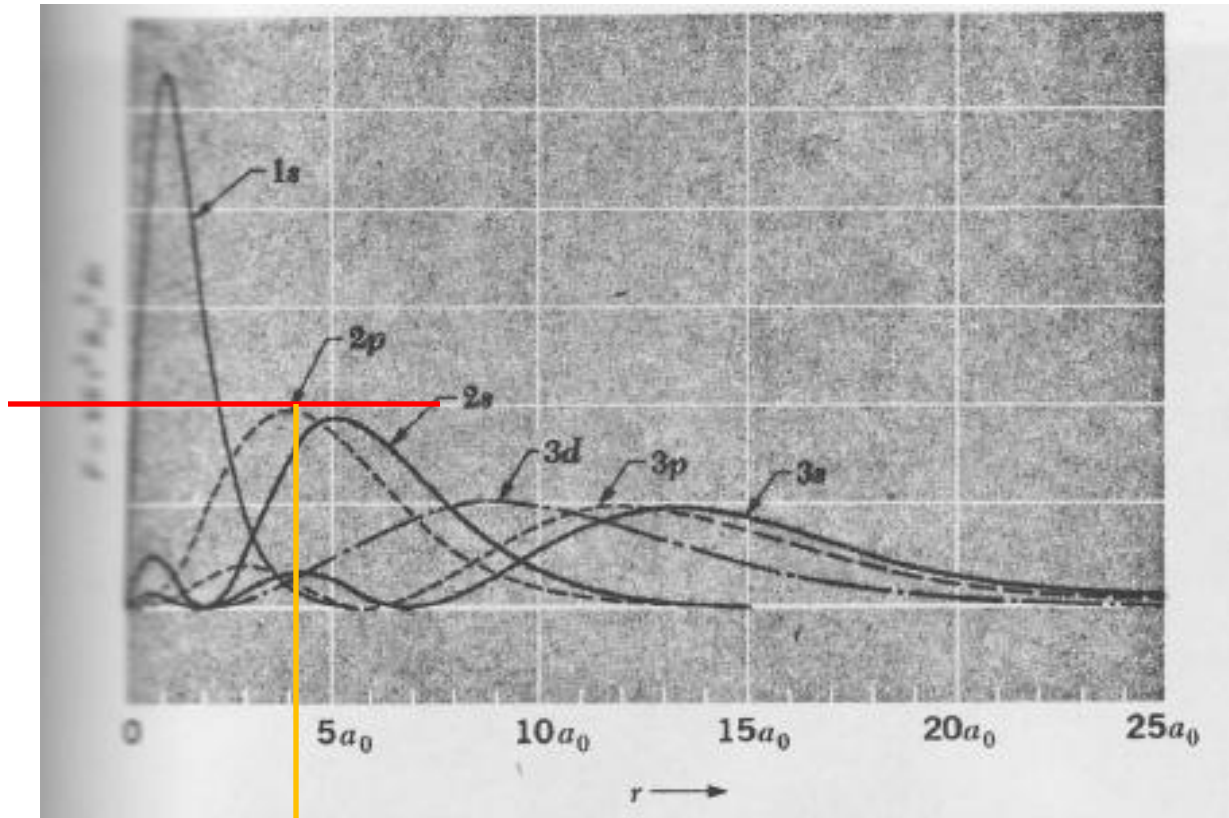
$$\langle r \rangle = \int_0^{\infty} r \cdot r^2 R_{n,l}(r)^2 dr$$

Most probable r Value

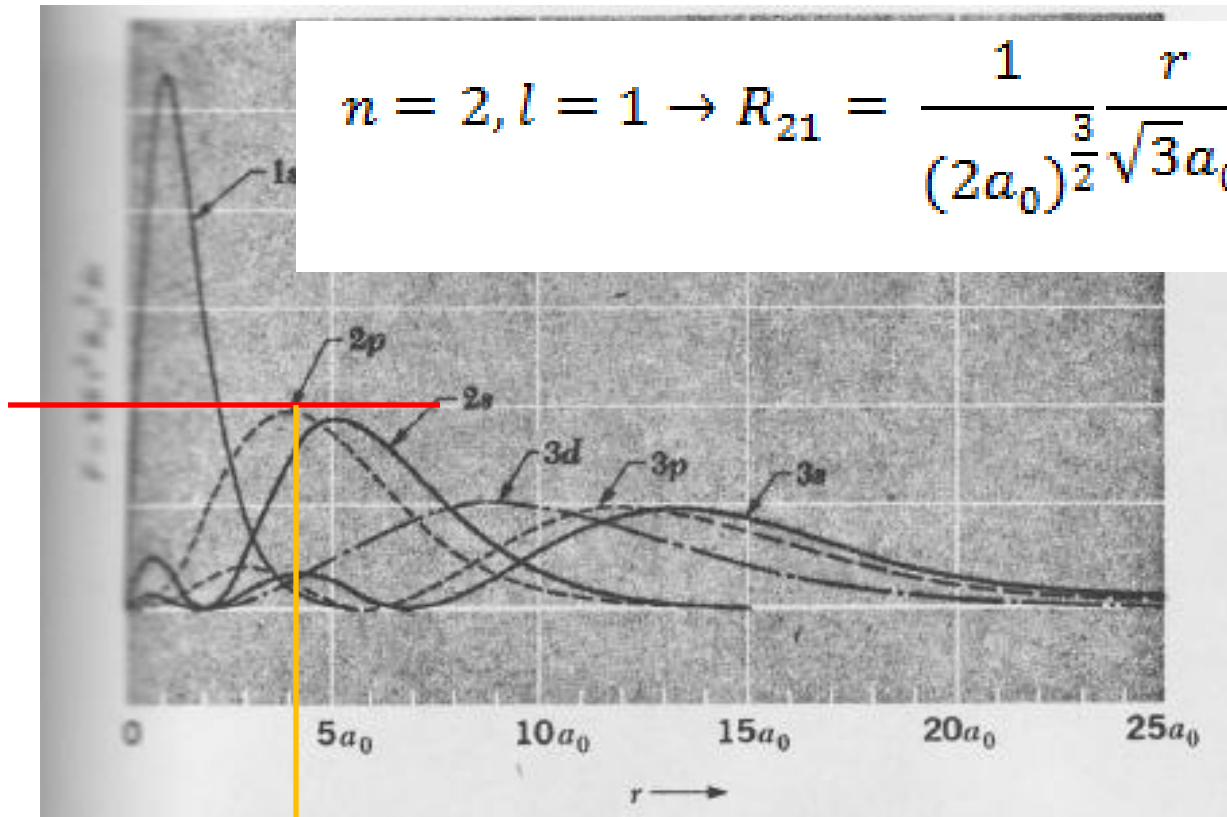
$$\frac{dP(r)}{dr} = \frac{dr^2 R_{n,l}(r)^2}{dr} = 0$$



$$P(r) \sim r^2 R^2(r)$$



$$P(r) \sim r^2 R^2(r)$$



Expected value

$$\langle r \rangle = \int_0^{\infty} r \cdot r^2 R_{n,l}(r)^2 dr$$

$$\int_0^{\infty} r \cdot r^2 \cdot \frac{1}{(2a_0)^3} \frac{r^2}{3a_0^2} e^{-\frac{r}{a_0}} dr$$

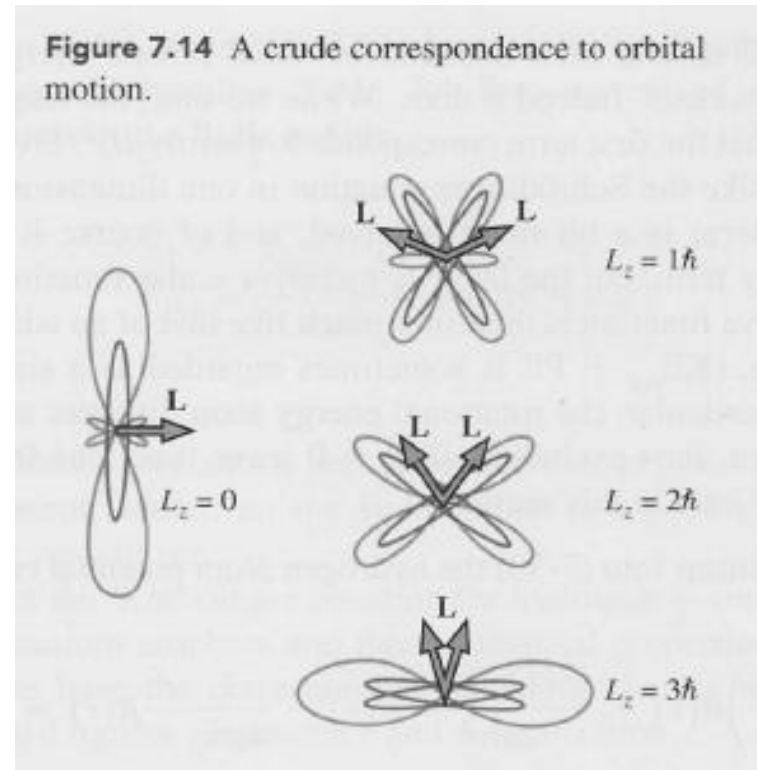
$$\int_0^{\infty} x^m e^{-bx} dx = \frac{m!}{b^{m+1}}$$

$$\frac{1}{3 \cdot 2^3 a_0^5} \int_0^{\infty} r^5 e^{-\frac{r}{a_0}} dr = \frac{1}{3 \cdot 2^3 a_0^5} 5! a_0^6 = 5 a_0$$

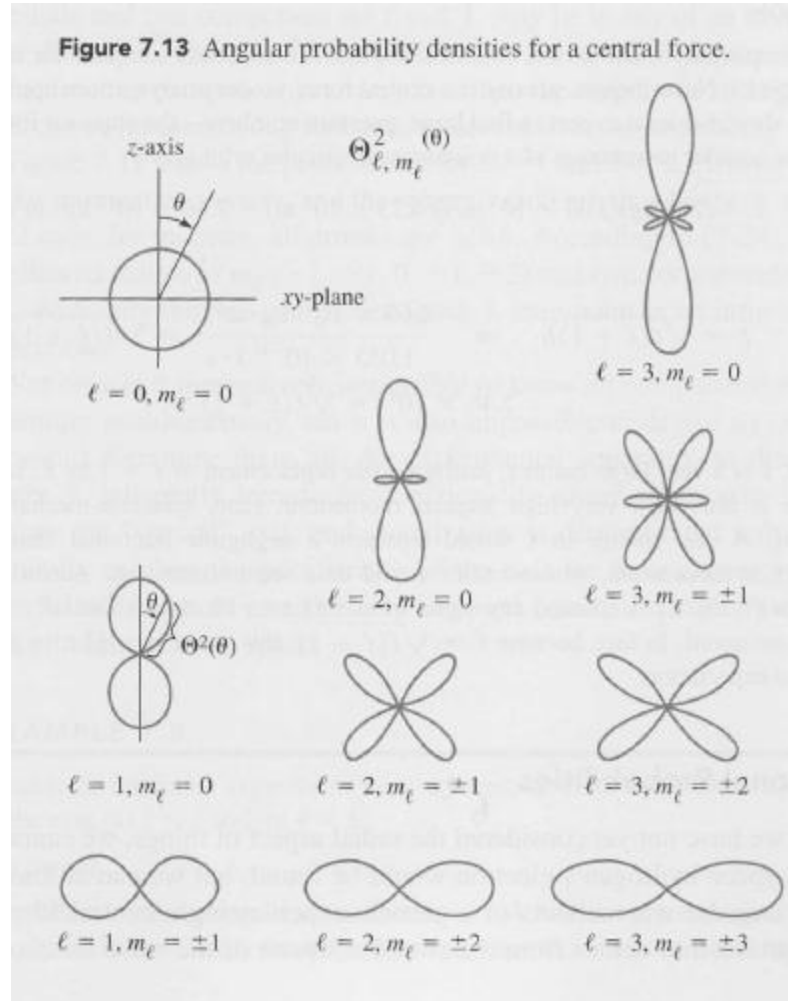
Angular Probability Density

$$\Theta(\theta)^2 \Phi(\phi)^2 \equiv Y_l^{m_l} Y_l^{m_l}$$

l	m_l	$\Phi(\phi)$	$\Theta(\theta)$
0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$
0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$
1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$
1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$
0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$
1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$
1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$
2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4} (3 \cos^2 \theta - 1)$
2	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{15}}{2} \sin \theta \cos \theta$
2	± 2	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2 \theta$



Angular Probability Density



Angular Probability Density

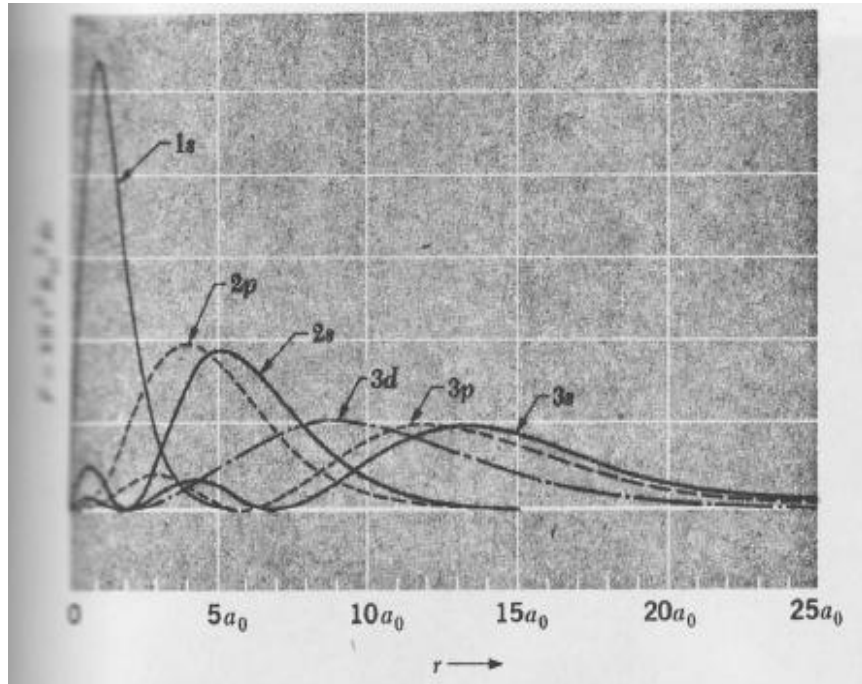
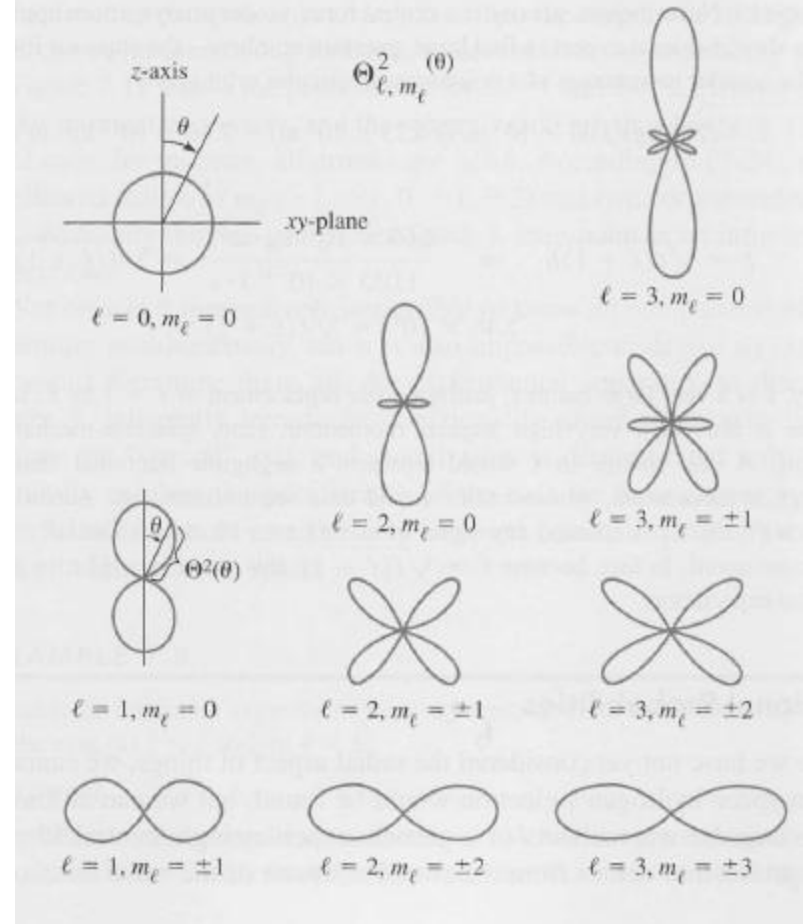
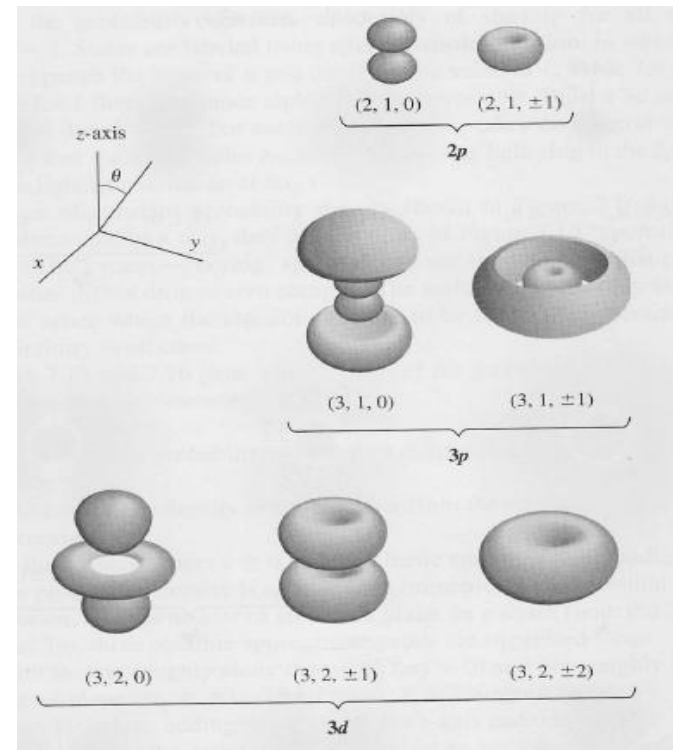
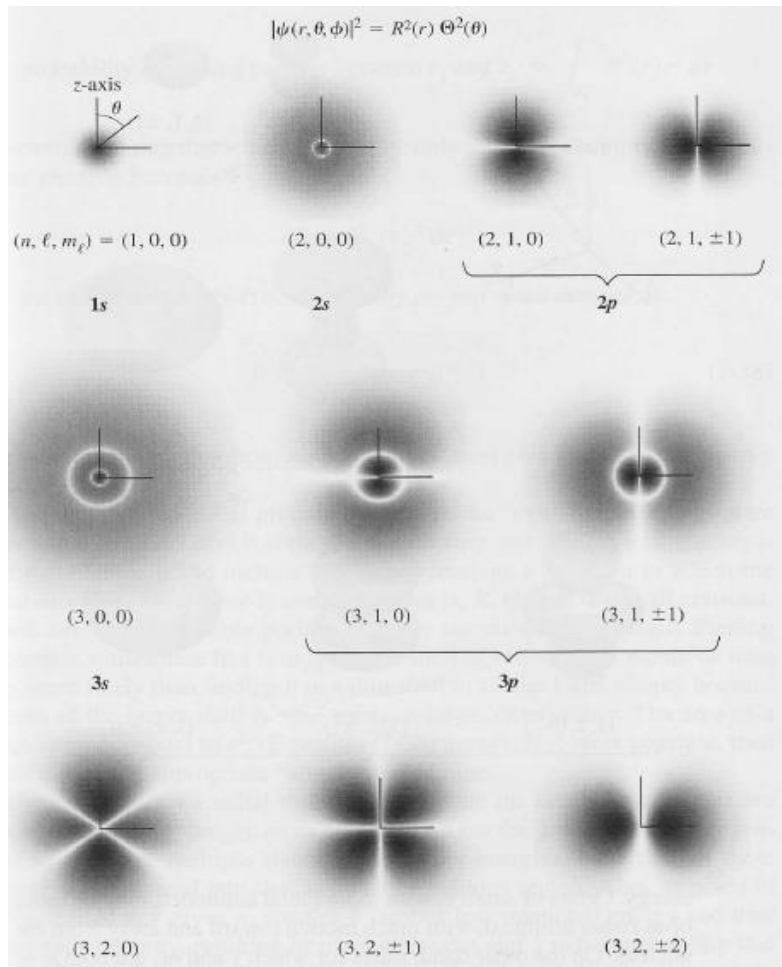


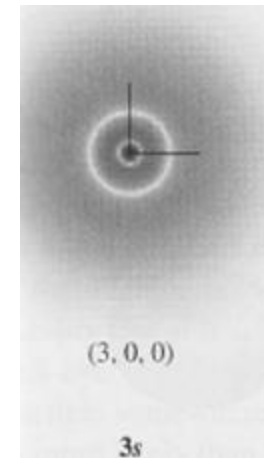
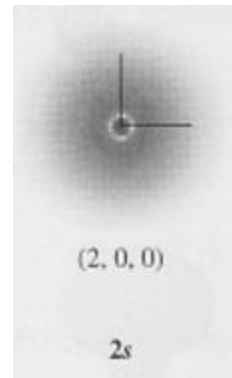
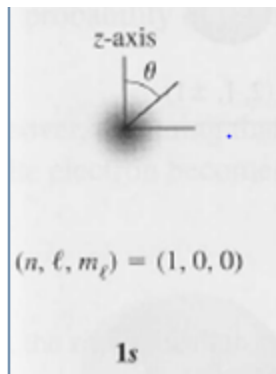
Figure 7.13 Angular probability densities for a central force.



Angular Probability Density



1s v. 2s vs. 3s



$$l = 0, m_l = 0, \quad \Theta_{00} = \frac{1}{\sqrt{2}}, \quad \Phi_0 = \frac{1}{\sqrt{2\pi}}$$

$$l = 1, m_l = 0, \quad \Theta_{10} = \frac{\sqrt{6}}{2} \cos\theta, \quad \Phi_0 = \frac{1}{\sqrt{2\pi}}$$

$$l = 2, m_l = 0, \quad \Theta_{20} = \frac{\sqrt{10}}{4} (3 \cos^2\theta - 1), \quad \Phi_0 = \frac{1}{\sqrt{2\pi}}$$

