Lecture 6 Topics

- Hydrogen Atom Schrodinger Equation Solutions
  - Three quantum numbers
  - Wave functions
  - Degeneracies
  - Normalization
  - Radial solutions: Electron whereabouts
  - Orbital shapes: Electron probability densities

Schrodinger Equation: Hydrogen Atom

$$\frac{-\hbar^2}{2m}\nabla^2\psi(\vec{x}) + U(\vec{x})\psi(\vec{x}) = E\,\psi(\vec{x}) \qquad U(r) = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

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

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

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

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

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

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

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

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

Three quantum numbers

- Principal quantum number: *n*

$$E_n = -\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}\left(\frac{1}{n^2}\right) = -\left(\frac{e^2}{8\pi\varepsilon_0}\right)\left(\frac{me^2}{4\pi\varepsilon_0\hbar^2}\right)\left(\frac{1}{n^2}\right) =$$
$$-\left(\frac{e^2}{8\pi\varepsilon_0 a_0}\right)\left(\frac{1}{n^2}\right) = -13.6\ eV\left(\frac{1}{n^2}\right)$$

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

- Orbital quantum number: $l = 0, 1, 2, \ldots (n\text{-}1)$
- Magnetic quantum number: $m_l = 0, \pm 1, \pm 2, \ldots \pm l$

Degeneracies

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

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

n	l	m_l	E_n(eV)	$\lvert L \rvert$	L_z	ψ_{n,l,m_l} =	$R_{n,l}\mathbf{Y}_l^{m_l}$	degeneracies	Orbital name
1	0	0	-13.6	0	0	ψ_{100}	$R_{10}\mathbf{Y}_0^0$	Non-degenerate	1s
2	0	0	-3.40	0	0	ψ_{200}	$R_{20}\mathbf{Y}_0^0$	4 (=2^2)	2s
	1	-1		$\sqrt{2}\hbar$	$-\hbar$	ψ_{21-1}	$R_{21}\mathbf{Y}_1^{-1}$		2p
		0			0	ψ_{210}	$R_{21}\mathbf{Y}_1^0$		
		1			$+\hbar$	ψ_{211}	$R_{21}\mathbf{Y}_1^{+1}$		

n	l	m_l	E_n(eV)	$\lvert L \rvert$	L_z	ψ_{n,l,m_l} =	$R_{n,l}\mathbf{Y}_l^{m_l}$	degeneracies	Orbital name
1	0	0	-13.6	0	0	ψ_{100}	$R_{10}\mathbf{Y}_0^0$	Non-degenerate	1s
2	0	0	-3.40	0	0	ψ_{200}	$R_{20}\mathbf{Y}_0^0$	4 (=2²)	2s
	1	1		$\sqrt{2}\hbar$	$-\hbar$	ψ_{21-1}	$R_{21}\mathbf{Y}_1^{-1}$		2p
		0			0	ψ_{210}	$R_{21}\mathbf{Y}_1^0$		
		1			$+\hbar$	ψ_{211}	$R_{21}\mathbf{Y}_1^{+1}$		
3	0	0	-1.51	0	0	ψ_{300}	$R_{30}\mathbf{Y}_0^0$	9 (=3²)	3s
	1	-1		$\sqrt{2}\hbar$	$-\hbar$	ψ_{31-1}	$R_{31}\mathbf{Y}_1^{-1}$		3p
		0			0	ψ_{310}	$R_{31}\mathbf{Y}_1^0$		
		1			$+\hbar$	ψ_{311}	$R_{31}\mathbf{Y}_1^1$		
	2	-2		$\sqrt{6}\hbar$	$-2\hbar$	ψ_{32-2}	$R_{32}\mathbf{Y}_2^{-2}$		3d
		--1			$-\hbar$	ψ_{32-1}	$R_{32}\mathbf{Y}_2^{-1}$		
		0			0	ψ_{320}	$R_{32}\mathbf{Y}_2^0$		
		1			$+\hbar$	ψ_{321}	$R_{32}\mathbf{Y}_2^1$		
		2			$+2\hbar$	ψ_{322}	$R_{32}\mathbf{Y}_2^2$		

Normalization

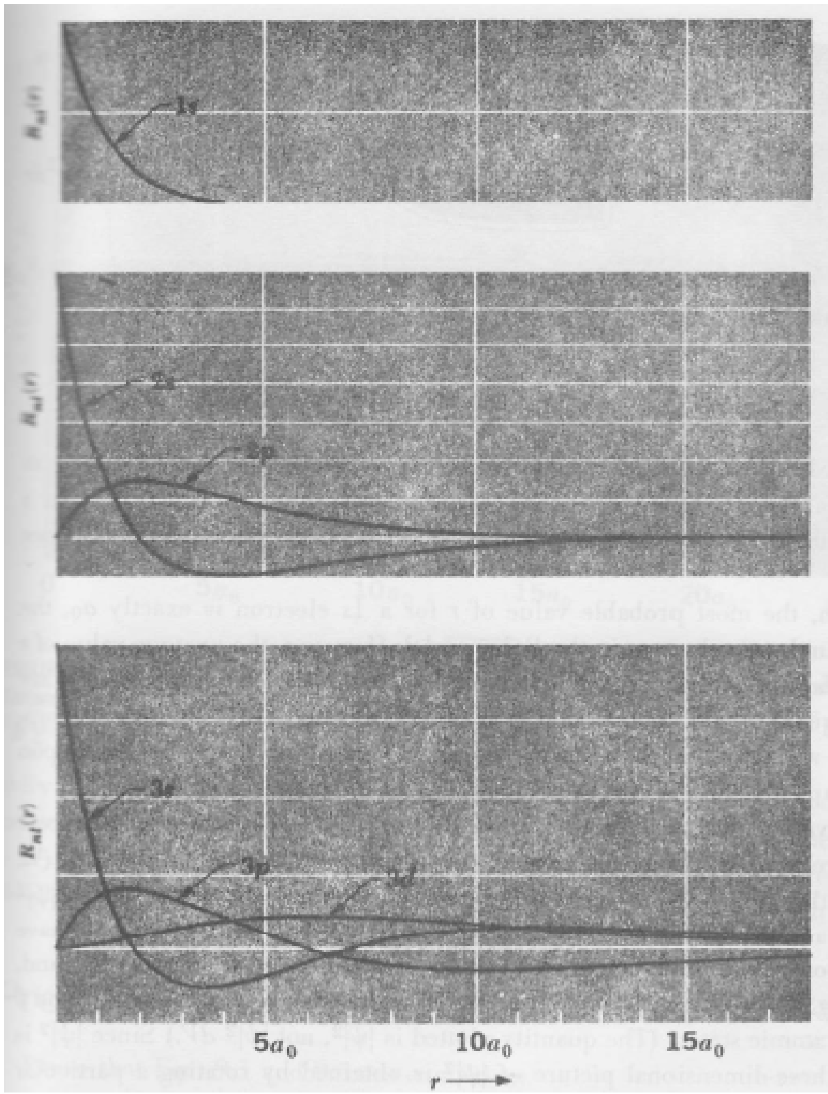
$$|\psi_{n,l,m_l}|^2 = R(r)^2\Theta(\theta)^2\Phi(\phi)^2$$

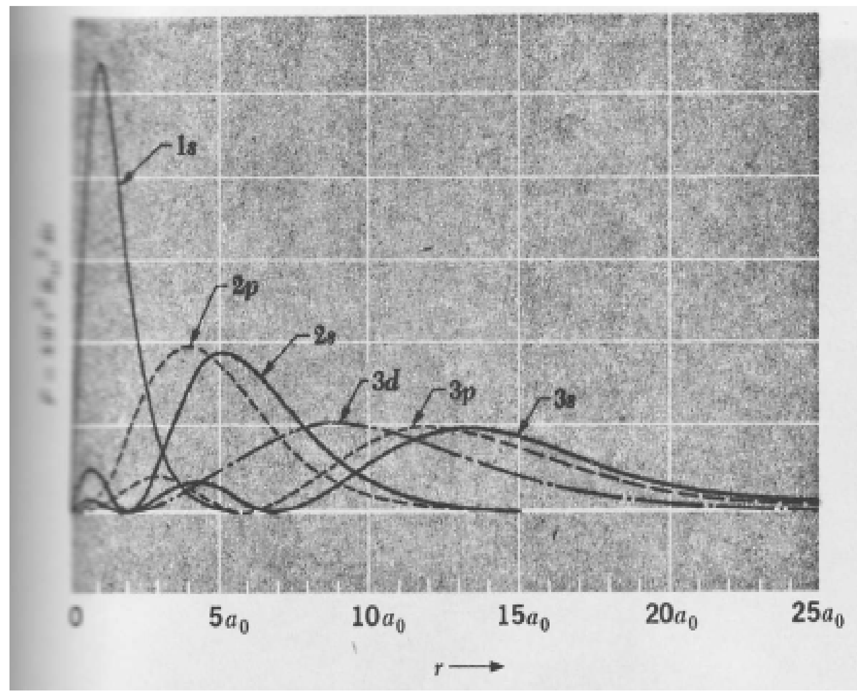
$$\int |\psi_{n,l,m_l}|^2\, dV = \int |\psi_{n,l,m_l}|^2\, r^2 sin\theta\ dr d\theta d\phi$$

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

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

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


1s
2s
2p
3s
3p
3d
5a0
10a0
15a0
r


1s
2p
2s
3d
3p
3s
0
5a0
10a0
15a0
20a0
25a0
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 $\frac{dP(r)}{dr} = \frac{d\, r^2 R_{n,l}(r)^2}{dr} = 0$

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

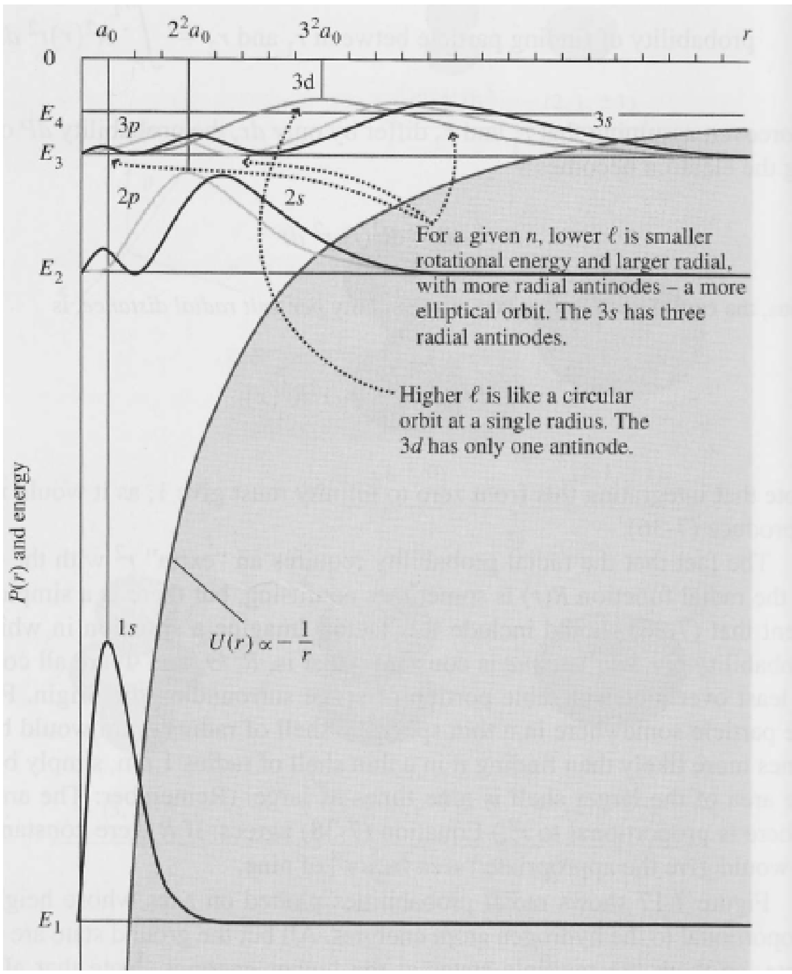
That is,

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

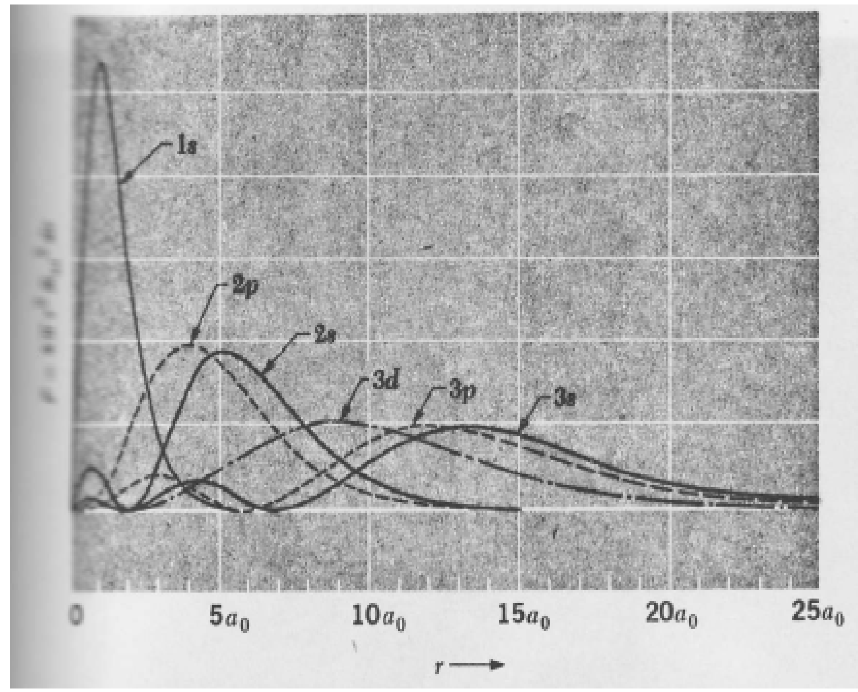
r_{21} (2p, *most probable*) $= 4a_0$

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

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



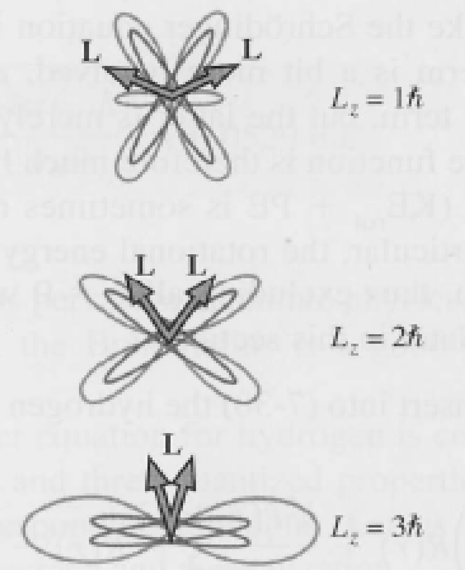
a_0
$2^2 a_0$
$3^2 a_0$
r
0
3d
E_4
3p
3s
E_3
2p
2s
For a given n, lower ℓ is smaller rotational energy and larger radial, with more radial antinodes – a more elliptical orbit. The 3s has three radial antinodes.
E_2
Higher ℓ is like a circular orbit at a single radius. The 3d has only one antinode.
$P(r)$ and energy
1s
$U(r) \propto -\frac{1}{r}$
E_1



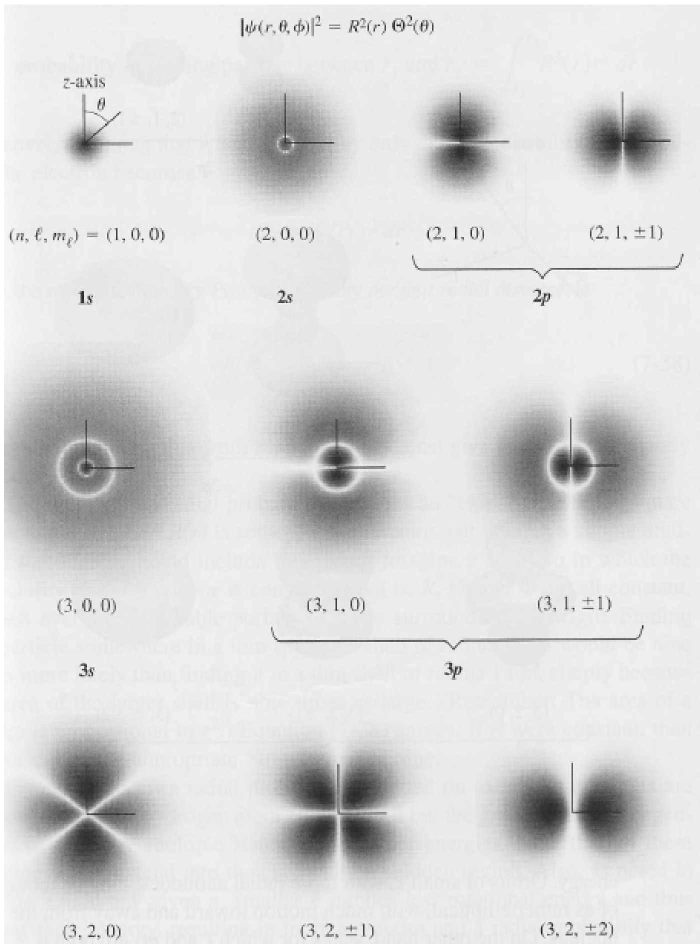
1s
2p
2s
3d
3p
3s
0
$5a_0$
$10a_0$
$15a_0$
$20a_0$
$25a_0$
r ⟶

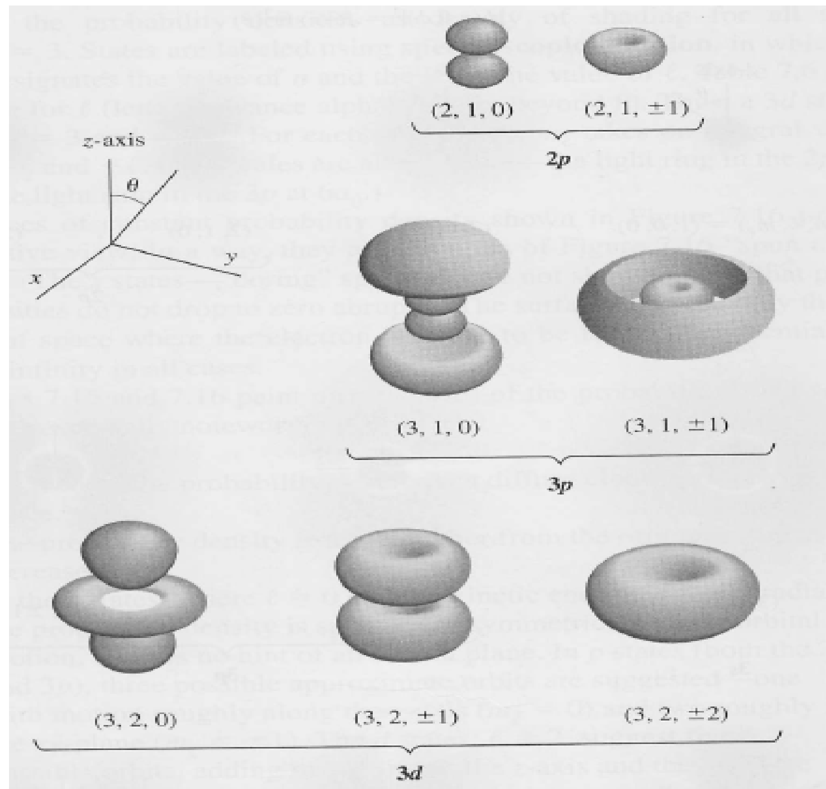
Angular Probability Density

Figure 7.14 A crude correspondence to orbital motion.

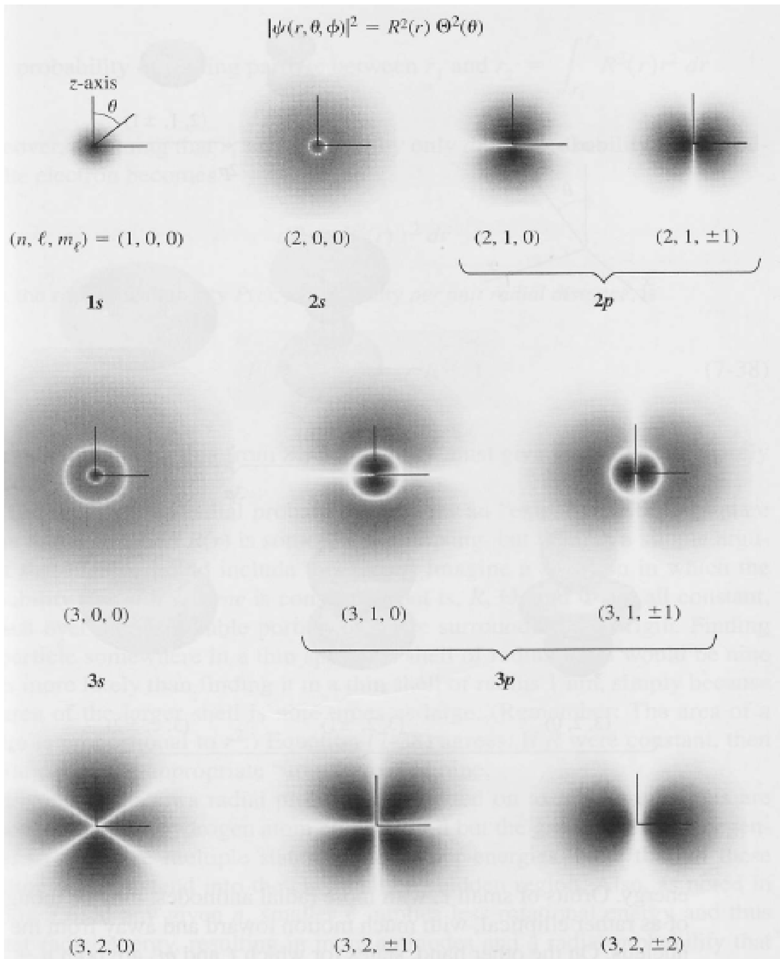


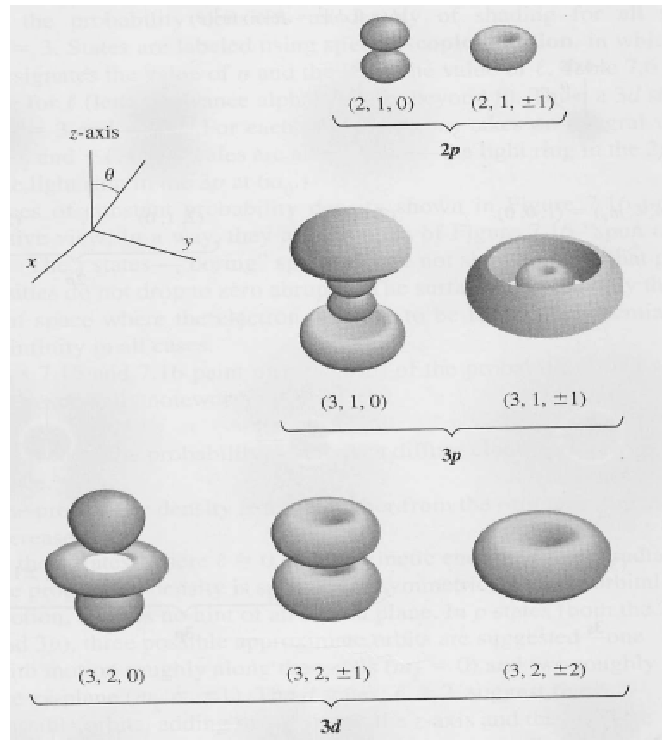
Angular Probability Density



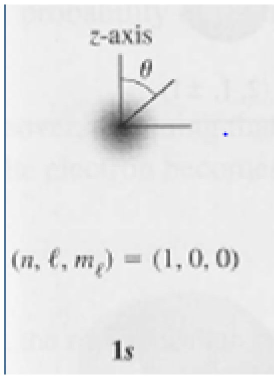


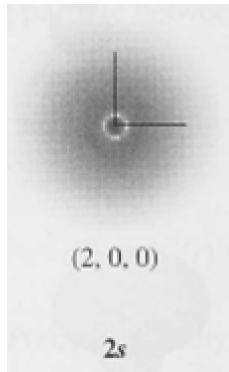
Angular Probability Density

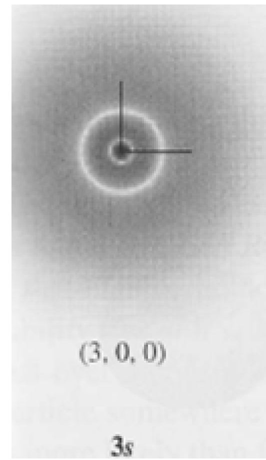




1s v. 2s vs. 3s



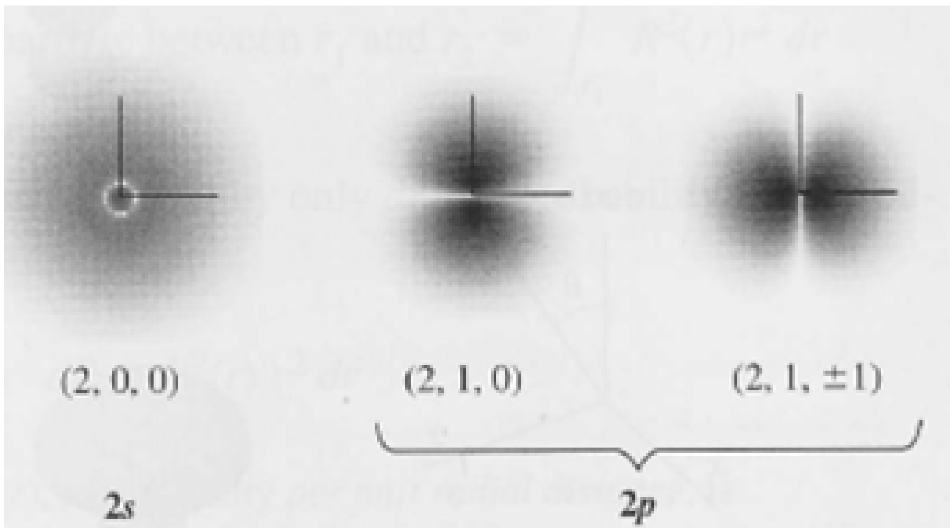




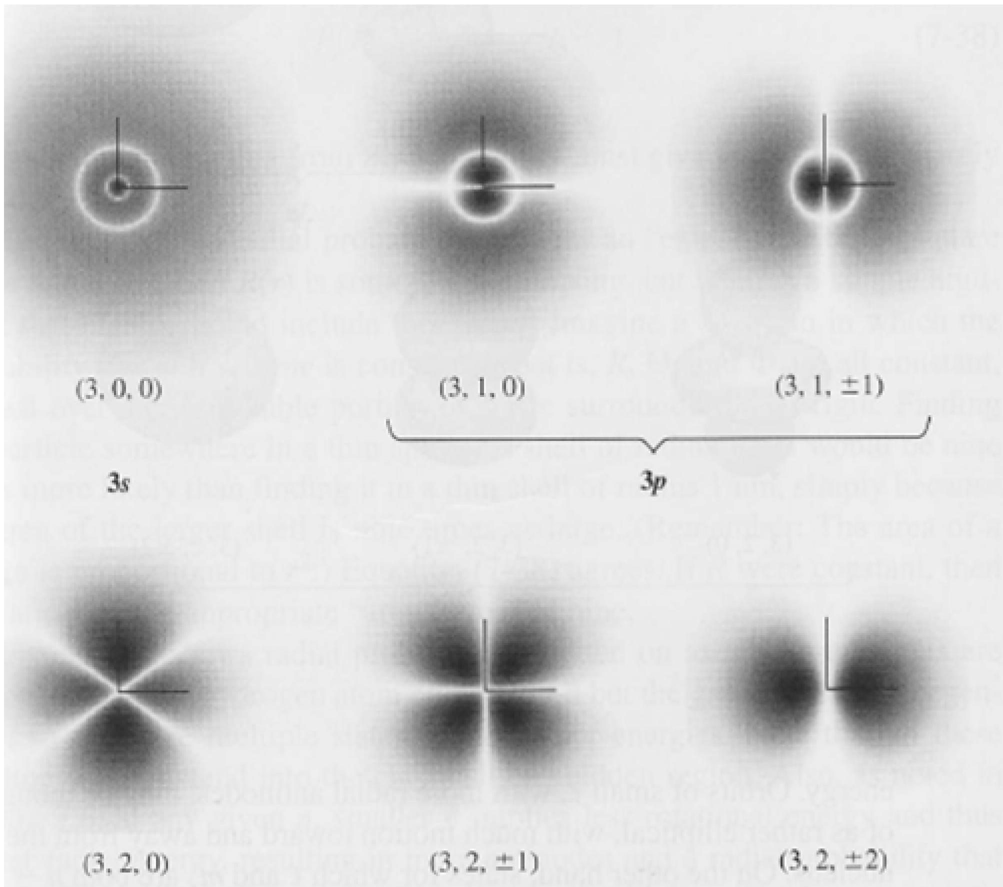
$$l = 0,\ m_l = 0, \quad \Theta_{00} = \frac{1}{\sqrt{2}}, \Phi_0 = \frac{1}{\sqrt{2\pi}}$$

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

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



(2, 0, 0)
(2, 1, 0)
(2, 1, ±1)
2s
2p


(3, 0, 0)
(3, 1, 0)
(3, 1, ±1)
3s
3p
(3, 2, 0)
(3, 2, ±1)
(3, 2, ±2)