Structure of the Atom

Quantum theory of Radiation – Pioneered by Plank + Einstein

↳ Modified by Louis Debroglie 1924 to include particles electrons (wave-Particle Duality)

Combination of Classical Mechanics + quantum theory

$\lambda = h/mv$

$\Downarrow$

$= h/p$

h = planks constant $= 6.26 \times 10^{-34} \frac{m^2 kg}{s}$

m = mass of particle

v = velocity of particle

$\rightarrow p$ = momentum

Shrödinger Equation – Allows us to describe wave properties of electrons in terms of:

$H\Psi = E\Psi$

1. Mass
2. Position
3. Total Energy
4. Potential Energy

H = Hamiltonian Operator

E = Energy

Ψ = Wavefunction

↳ Mathematical description of an orbital

Hamiltonian Operator (H)

$$H = \underbrace{\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial^2 x^2} + \frac{\partial^2}{\partial^2 y^2} + \frac{\partial^2}{\partial^2 z^2}\right)}_{\text{Kinetic energy of } e^-} + \underbrace{V(x,y,z)}_{\text{Potential Energy of } e^-}$$

Pos charge felt by e^-

$$V = \frac{-Ze^2}{\underbrace{4\pi\varepsilon_o}_{\text{permittivity of vaccuum}} r}$$

r = distance of e^- from nucleus.

V is large as $r \rightarrow 0$

V is small as $r \rightarrow \infty$

wavefunction (ψ) = Mathematical description of an orbital (behavior of an e^-)

Different orbitals correspond to different ψ

↳ Consists of 2 components → Radial → Angular

Each ψ is described by a unique set of QN

TABLE 2.2 Quantum Numbers and Their Properties

Symbol	Name	Values	Role
n	Principal	1, 2, 3, . . .	Determines the major part of the energy
l	Angular momentum*	0, 1, 2, . . ., $n-1$	Describes angular dependence and contributes to the energy
m_l	Magnetic	0, ± 1, ± 2, . . ., $\pm l$	Describes orientation in space (angular momentum in the z direction)
m_s	Spin	$\pm \frac{1}{2}$	Describes orientation of the electron spin (magnetic moment) in space

↳ Developed by Dirac

Orbitals with different l values are known by the following labels, derived from early terms for different families of spectroscopic lines:

l	0	1	2	3	4	5, …
Label	s	p	d	f	g	continuing alphabetically

$\Psi \rightarrow 2$ Components

$$\Psi_{n,l,m_l}(r,\theta,\phi) = \underbrace{R_{n,l}(r)}_{\text{Radial Component}} \; \underbrace{Y_{l,m_l}(\theta,\phi)}_{\text{Angular component}}$$

Radial Component → Distance from nucleus

Angular component

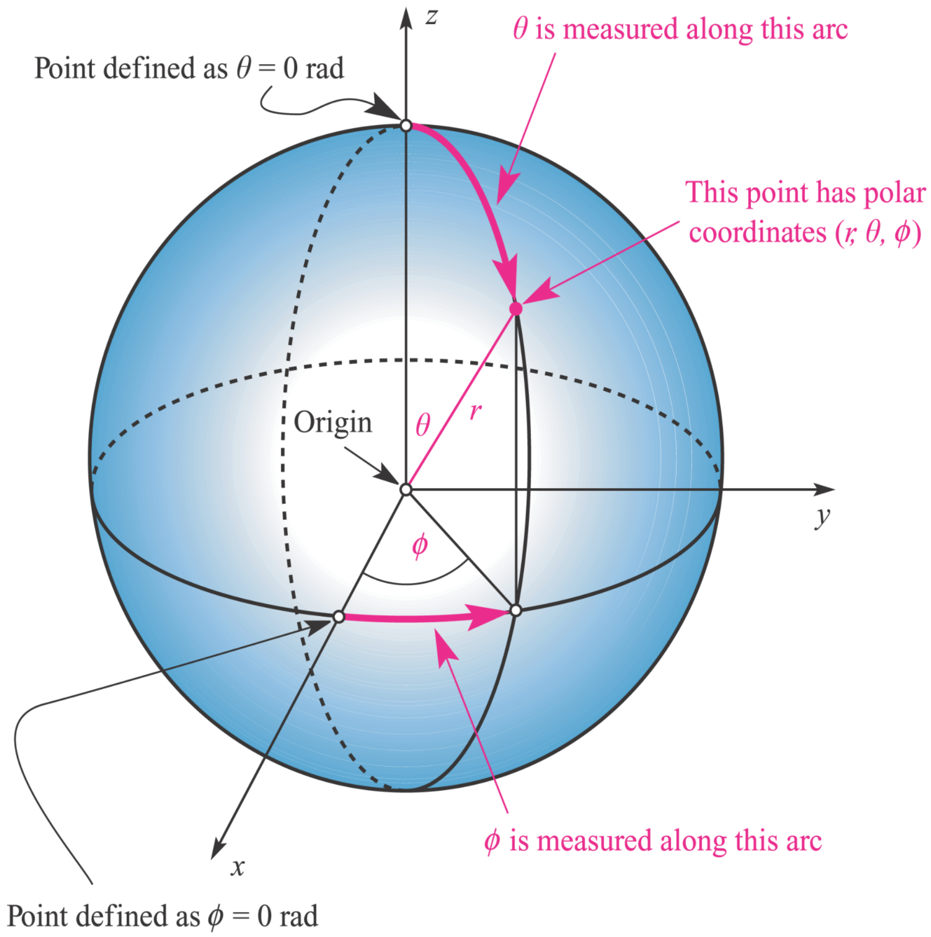
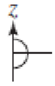
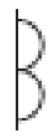
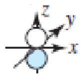
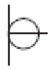
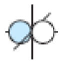
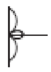
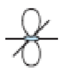
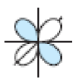
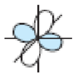
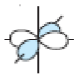
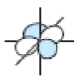


TABLE 2.3 Hydrogen Atom Wave Functions: Angular Functions

Angular Factors					Real Wave Functions			
Related to Angular Momentum				Functions of θ	In Polar Coordinates	In Cartesian Coordinates	Shapes	Label
l	m_l	Φ	Θ		$\Theta\Phi(\theta, \phi)$	$\Theta\Phi(x, y, z)$		
$0(s)$	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$		$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{2\sqrt{\pi}}$		s
$1(p)$	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2}\cos\theta$		$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{z}{r}$		p_z
	+1	$\frac{1}{\sqrt{2\pi}}e^{i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$		$\frac{1}{2}\sqrt{\frac{3}{\pi}}\sin\theta\cos\phi$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{x}{r}$		p_x
	−1	$\frac{1}{\sqrt{2\pi}}e^{-i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$		$\frac{1}{2}\sqrt{\frac{3}{\pi}}\sin\theta\sin\phi$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{y}{r}$		p_y
$2(d)$	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{2}\sqrt{\frac{5}{2}}(3\cos^2\theta - 1)$		$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$	$\frac{1}{4}\sqrt{\frac{5}{\pi}}\frac{(2z^2 - x^2 - y^2)}{r^2}$		d_{z^2}
	+1	$\frac{1}{\sqrt{2\pi}}e^{i\phi}$	$\frac{\sqrt{15}}{2}\cos\theta\sin\theta$		$\frac{1}{2}\sqrt{\frac{15}{\pi}}\cos\theta\sin\theta\cos\phi$	$\frac{1}{2}\sqrt{\frac{15}{\pi}}\frac{xz}{r^2}$		d_{xz}
	−1	$\frac{1}{\sqrt{2\pi}}e^{-i\phi}$	$\frac{\sqrt{15}}{2}\cos\theta\sin\theta$		$\frac{1}{2}\sqrt{\frac{15}{\pi}}\cos\theta\sin\theta\sin\phi$	$\frac{1}{2}\sqrt{\frac{15}{\pi}}\frac{yz}{r^2}$		d_{yz}
	+2	$\frac{1}{\sqrt{2\pi}}e^{2i\phi}$	$\frac{\sqrt{15}}{4}\sin^2\theta$		$\frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\cos 2\phi$	$\frac{1}{4}\sqrt{\frac{15}{\pi}}\frac{(x^2 - y^2)}{r^2}$		$d_{x^2-y^2}$
	−2	$\frac{1}{\sqrt{2\pi}}e^{-2i\phi}$	$\frac{\sqrt{15}}{4}\sin^2\theta$		$\frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\sin 2\phi$	$\frac{1}{4}\sqrt{\frac{15}{\pi}}\frac{xy}{r^2}$		d_{xy}

Source: Hydrogen Atom Wave Functions: Angular Functions, *Physical Chemistry*, 5th ed.,Gordon Barrow (c) 1988. McGraw-Hill Companies, Inc.

TABLE 2.4 Hydrogen Atom Wave Functions: Radial Functions

Radial Functions $R(r)$, with $\sigma = Zr/a_0$			
Orbital	***n***	***l***	***R(r)***
$1s$	1	0	$R_{1s} = 2\left[\frac{Z}{a_0}\right]^{3/2} e^{-\sigma}$
$2s$	2	0	$R_{2s} = 2\left[\frac{Z}{2a_0}\right]^{3/2} (2 - \sigma)e^{-\sigma/2}$
$2p$		1	$R_{2p} = \frac{1}{\sqrt{3}}\left[\frac{Z}{2a_0}\right]^{3/2} \sigma e^{-\sigma/2}$
$3s$	3	0	$R_{3s} = \frac{2}{27}\left[\frac{Z}{3a_0}\right]^{3/2} (27 - 18\sigma + 2\sigma^2)e^{-\sigma/3}$
$3p$		1	$R_{3p} = \frac{1}{81\sqrt{3}}\left[\frac{2Z}{a_0}\right]^{3/2} (6 - \sigma)\sigma e^{-\sigma/3}$
$3d$		2	$R_{3d} = \frac{1}{81\sqrt{15}}\left[\frac{2Z}{a_0}\right]^{3/2} \sigma^2 e^{-\sigma/3}$

$H\Psi = E\Psi$

No limit on # Ψ

only solveable for single e^- systems

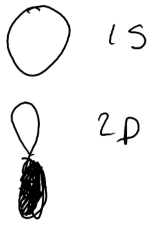
Multi-electron system

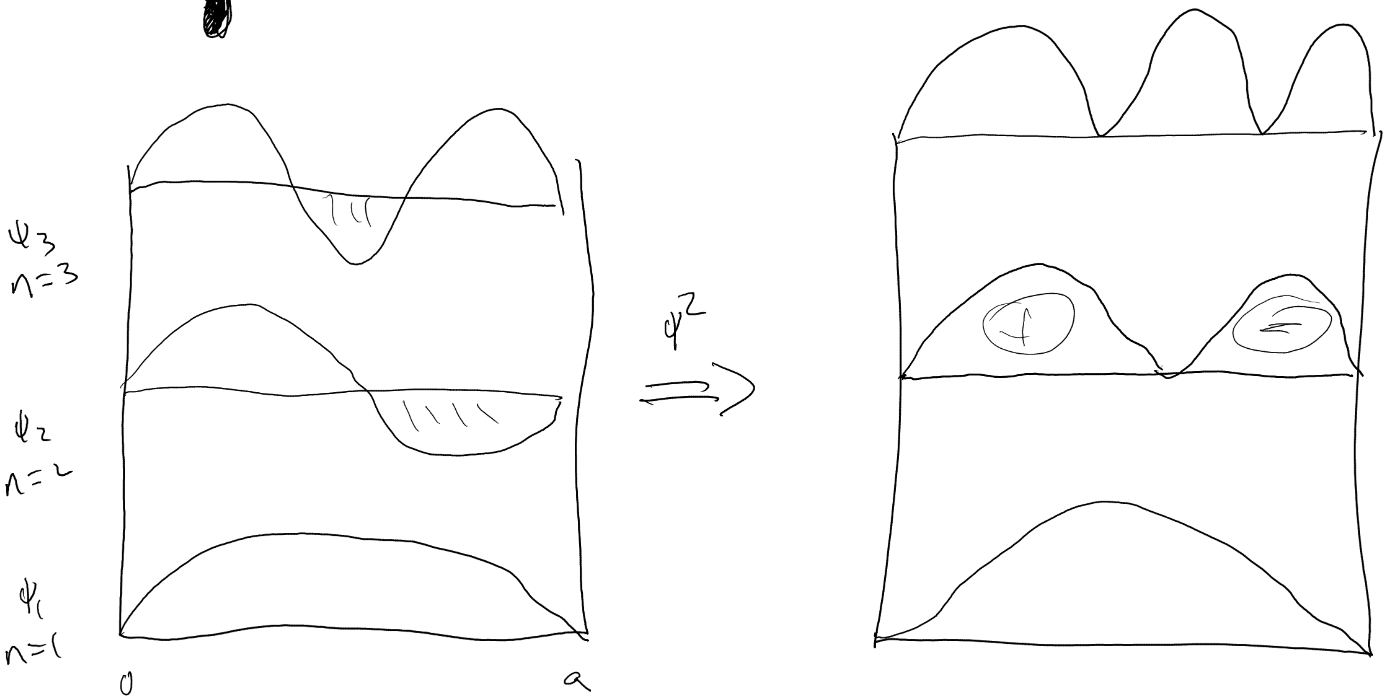
↳ ① $e^- \leftrightarrow e^-$ repulsion

② shielding

Heisenberg Uncertainty Principle

can't know exactly the position + energy of an e^- at the same time.

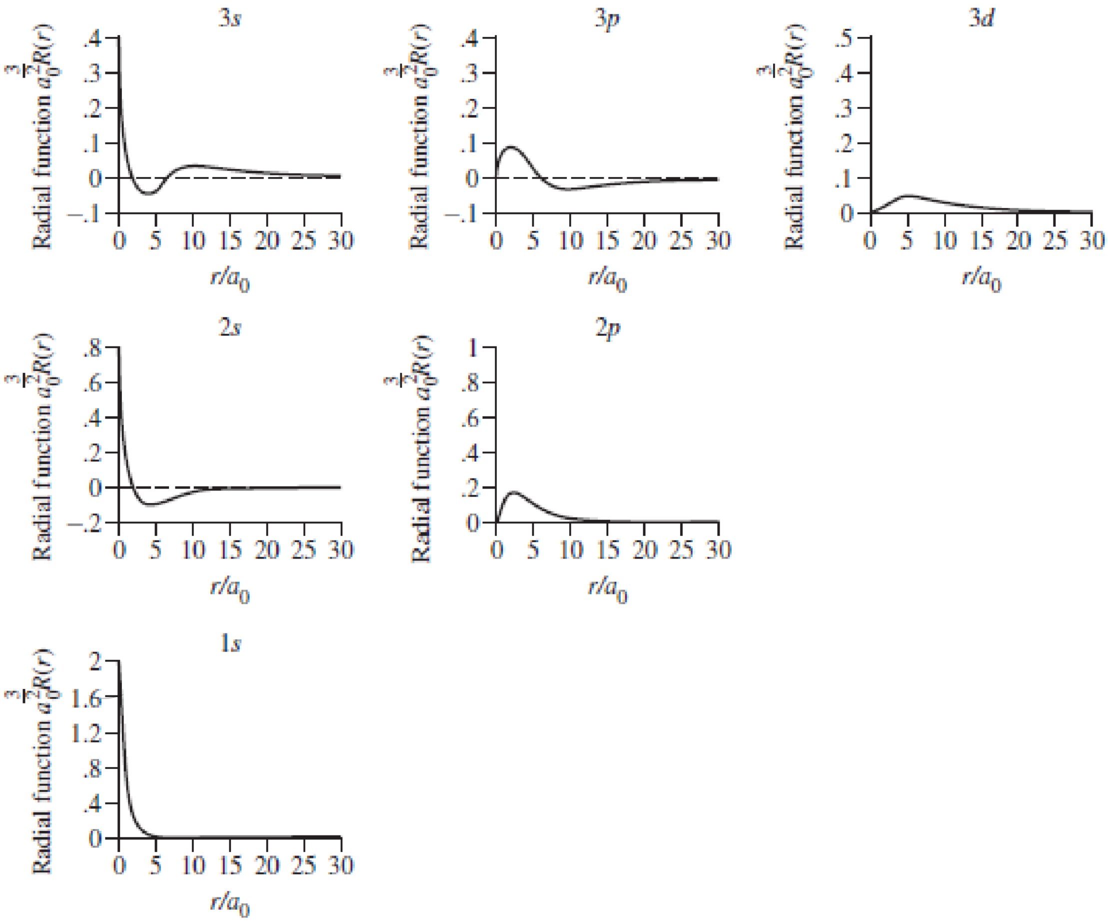




$\psi^2 \propto$ probability of finding an e^-

Squaring ψ → delivers a probability map w/ all values of 0 or greater

Radial Wave Functions



G. Hertzberg – Atomic Structure + Function – 1944

Radial Probability Functions

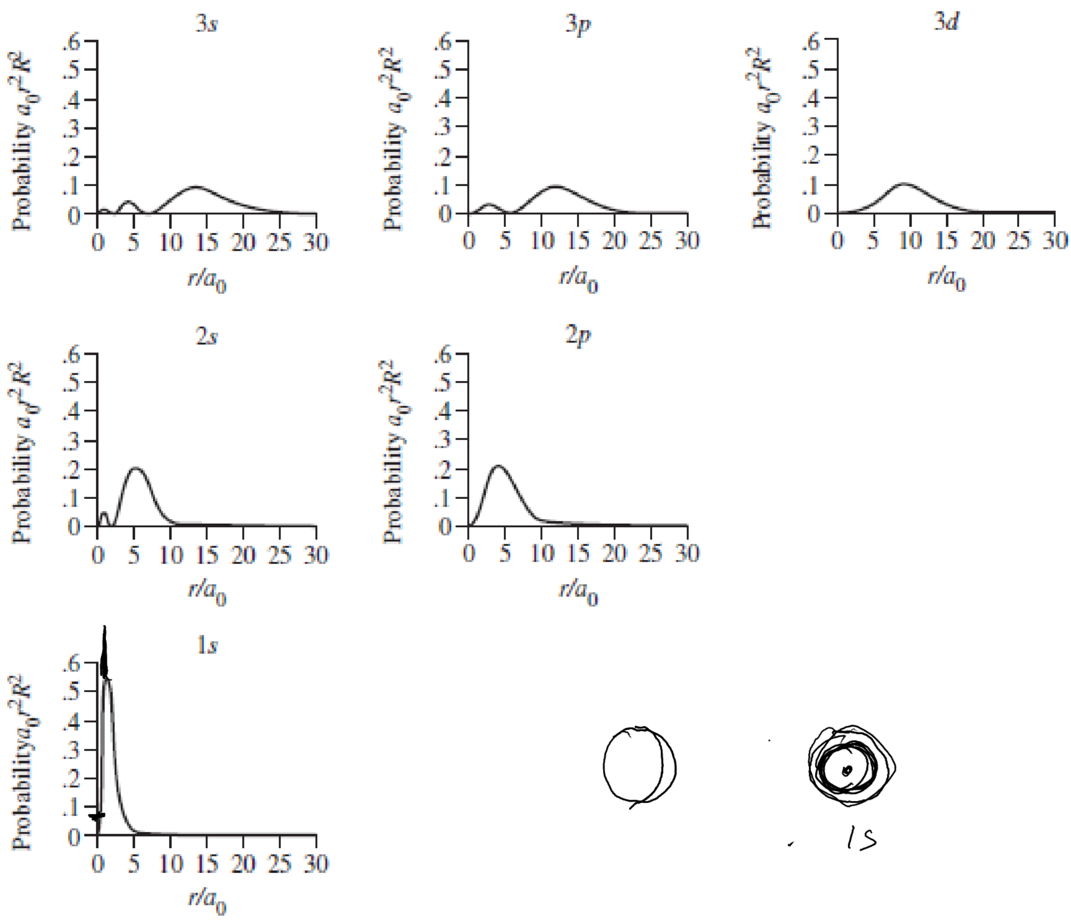


FIGURE 2.7 Radial Wave Functions and Radial Probability Functions.

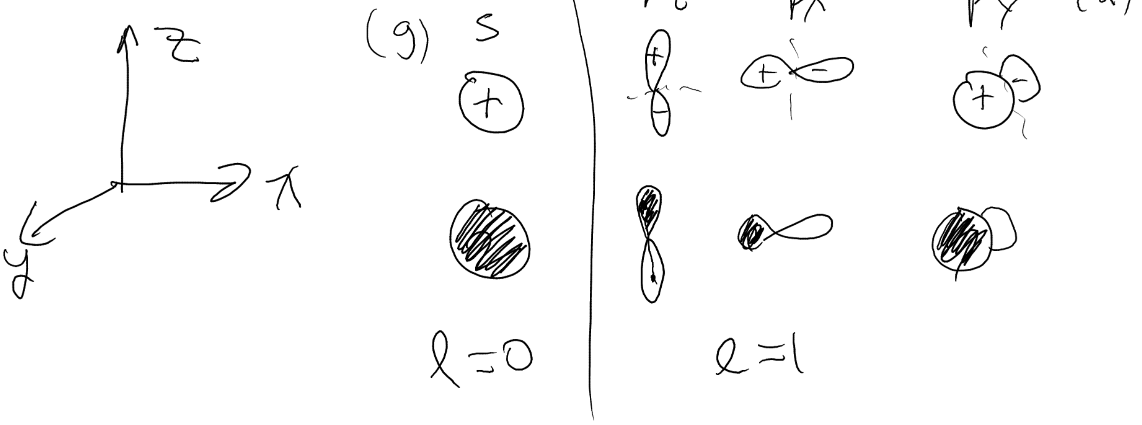
TABLE 2.5 Nodal Surfaces

Angular Nodes [$Y(\theta, \phi) = 0$]	
Examples (number of angular nodes)	
s orbitals	0
p orbitals	1 plane for each orbital
d orbitals	2 planes for each orbital except d_{z^2}
	1 conical surface for d_{z^2}

$l = 0$

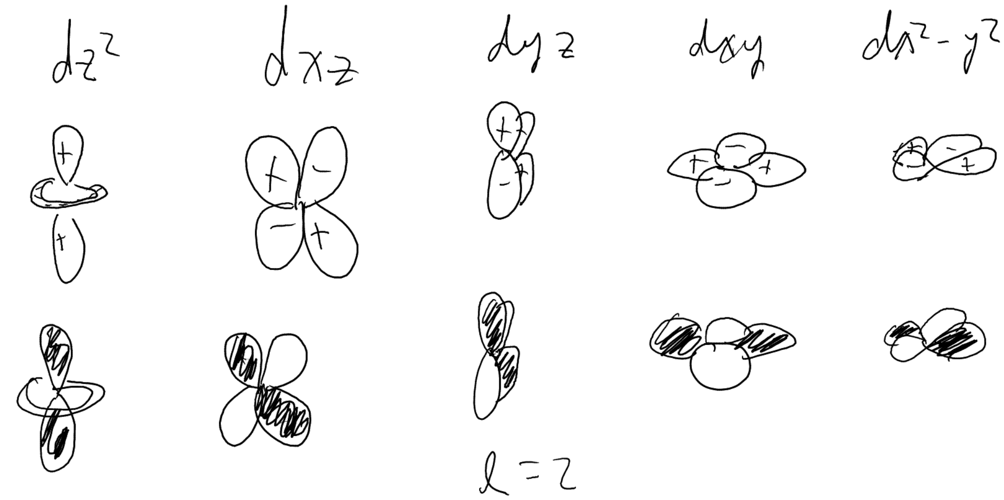
Radial Nodes [$R(r) = 0$]					
Examples (number of radial nodes)					
1*s*	0	2*p*	0	3*d*	0
2*s*	1	3*p*	1	4*d*	1
3*s*	2	4*p*	2	5*d*	2

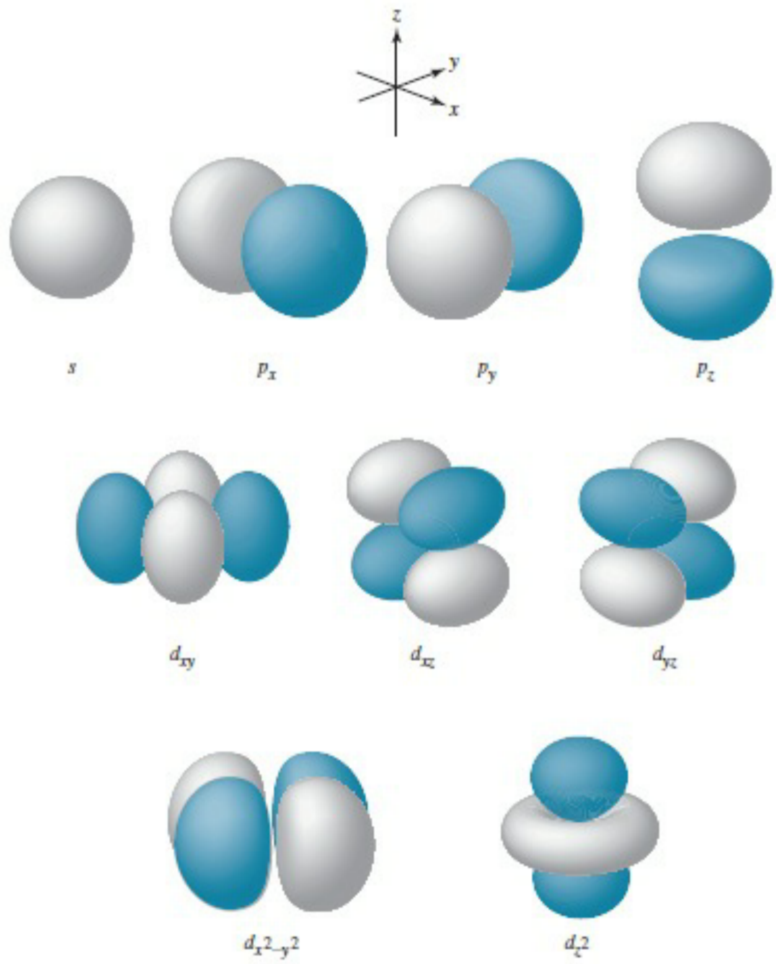
Maps of Orbitals



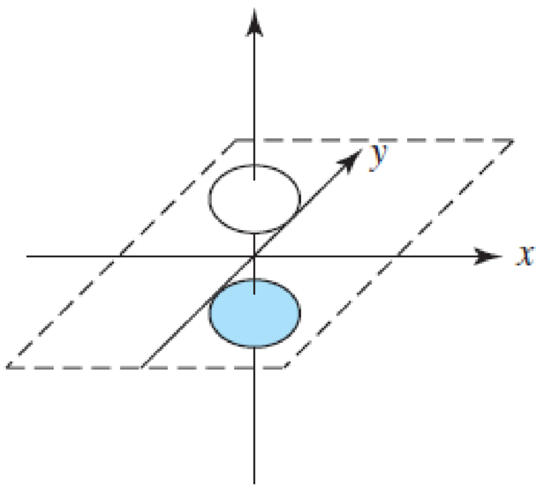
gerade + ungerade

(g)

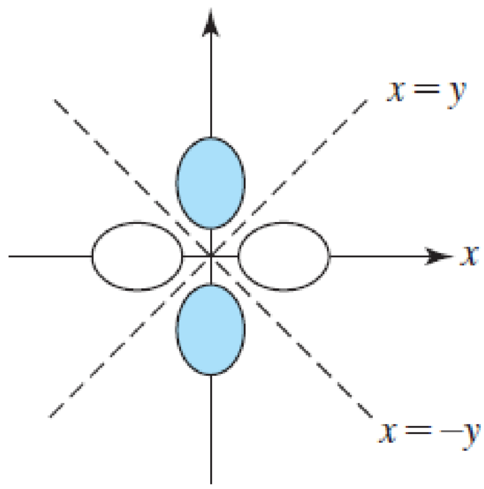




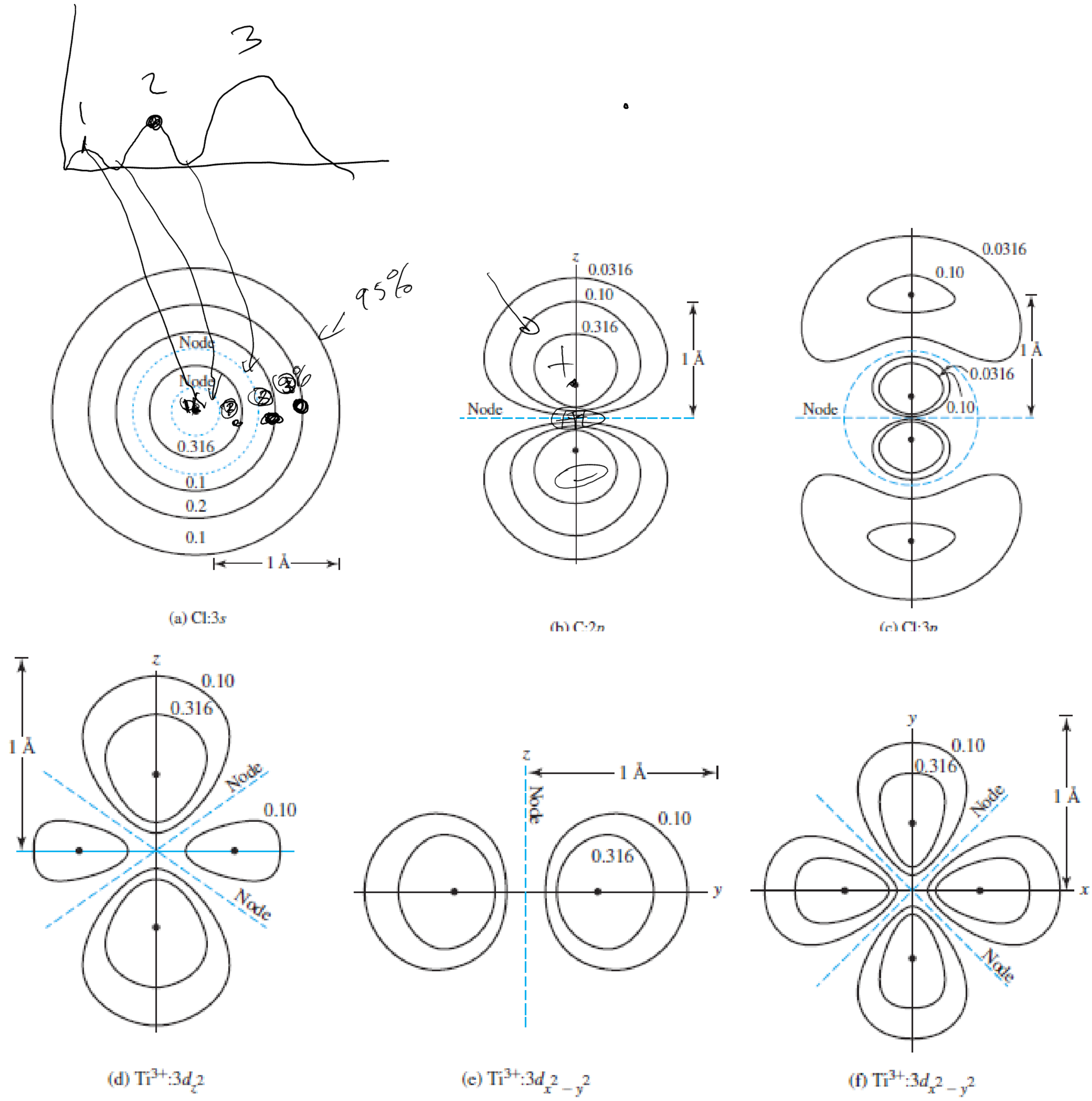
Angular Nodes for p + d orbs.



p_z



$d_{x^2-y^2}$



3
2
1
95%
Node
Node
0.316
0.1
0.2
0.1
1 Å
(a) Cl:3s
z
0.0316
0.10
0.316
1 Å
Node
(b) C:2p
0.0316
0.10
1 Å
0.0316
0.10
Node
(c) Cl:3p
z
0.10
0.316
1 Å
Node
0.10
Node
(d) Ti^{3+}:$3d_{z^2}$
z
1 Å
Node
0.10
0.316
y
(e) Ti^{3+}:$3d_{x^2-y^2}$
y
0.10
0.316
Node
1 Å
x
Node
(f) Ti^{3+}:$3d_{x^2-y^2}$