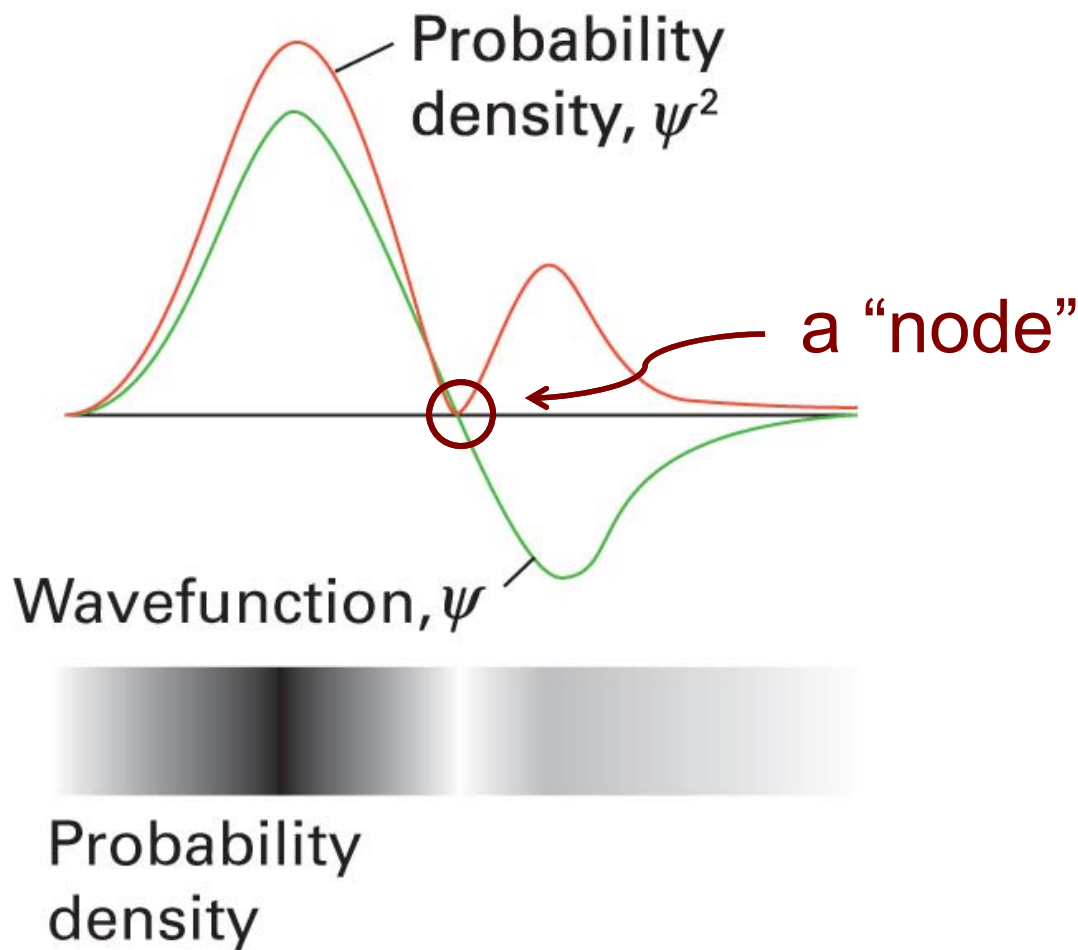


Lecture 3 362 January 18, 2019

Quantum Numbers
Electronic Configurations
Ionization Energies
Effective Nuclear Charge
Slater's Rules

Time-independent Schrödinger equation
(general—one dimension)

$$E\psi = H\psi$$



Summarizing: Solutions Required Quantum Numbers

Quantum Numbers

Atomic orbital	n	l	m_l	Radial part of the wavefunction, $R(r)^\dagger$	Angular part of wavefunction, $A(\theta, \phi)$
$1s$	1	0	0	$2e^{-r}$	$\frac{1}{2\sqrt{\pi}}$
$2s$	2	0	0	$\frac{1}{2\sqrt{2}}(2-r)e^{-r/2}$	$\frac{1}{2\sqrt{\pi}}$
$2p_x$	2	1	+1	$\frac{1}{2\sqrt{6}}re^{-r/2}$	$\frac{\sqrt{3}(\sin\theta\cos\phi)}{2\sqrt{\pi}}$
$2p_z$	2	1	0	$\frac{1}{2\sqrt{6}}re^{-r/2}$	$\frac{\sqrt{3}(\cos\theta)}{2\sqrt{\pi}}$
$2p_y$	2	1	-1	$\frac{1}{2\sqrt{6}}re^{-r/2}$	$\frac{\sqrt{3}(\sin\theta\sin\phi)}{2\sqrt{\pi}}$

[†] For the $1s$ atomic orbital, the formula for $R(r)$ is actually $2\left(\frac{Z}{a_0}\right)^{3/2}e^{-Zr/a_0}$ but for the hydrogen atom, $Z = 1$ and $a_0 = 1$ atomic unit. Other functions are similarly simplified.

Table 1.2 Solutions of the Schrödinger equation for the hydrogen atom which define the $1s$, $2s$ and $2p$ atomic orbitals. For these forms of the solutions, the distance r from the nucleus is measured in atomic units.

Quantum Numbers

n is the principal quantum number, indicates the size of the orbital, has all positive integer values of 1 to ∞ (infinity)

ℓ is the angular momentum quantum number, represents the shape of the orbital, has integer values of $(n - 1)$ to 0

m_ℓ is the magnetic quantum number, represents the spatial direction of the orbital, can have integer values of $-\ell$ to 0 to ℓ

m_s is the spin quantum number, has little physical meaning, can have values of either $+1/2$ or $-1/2$

Pauli Exclusion principle: no two electrons can have all four of the same quantum numbers in the same atom (Every electron has a unique set.)

Hund's Rule: when electrons are placed in a set of degenerate orbitals, the *ground state* has as many electrons as possible in different orbitals, and with *parallel spin*.

Aufbau (Building Up) Principle: the ground state electron configuration of an atom can be found by putting electrons in orbitals, starting with the lowest energy and moving progressively to higher energy.

ℓ (angular momentum)	orbital
0	s
1	p
2	d
3	f

Other terms: electron configuration, noble gas configuration, valence shell

While n is the principal energy level, the l value also has an effect

Heavier elements, more chances
For close energy levels

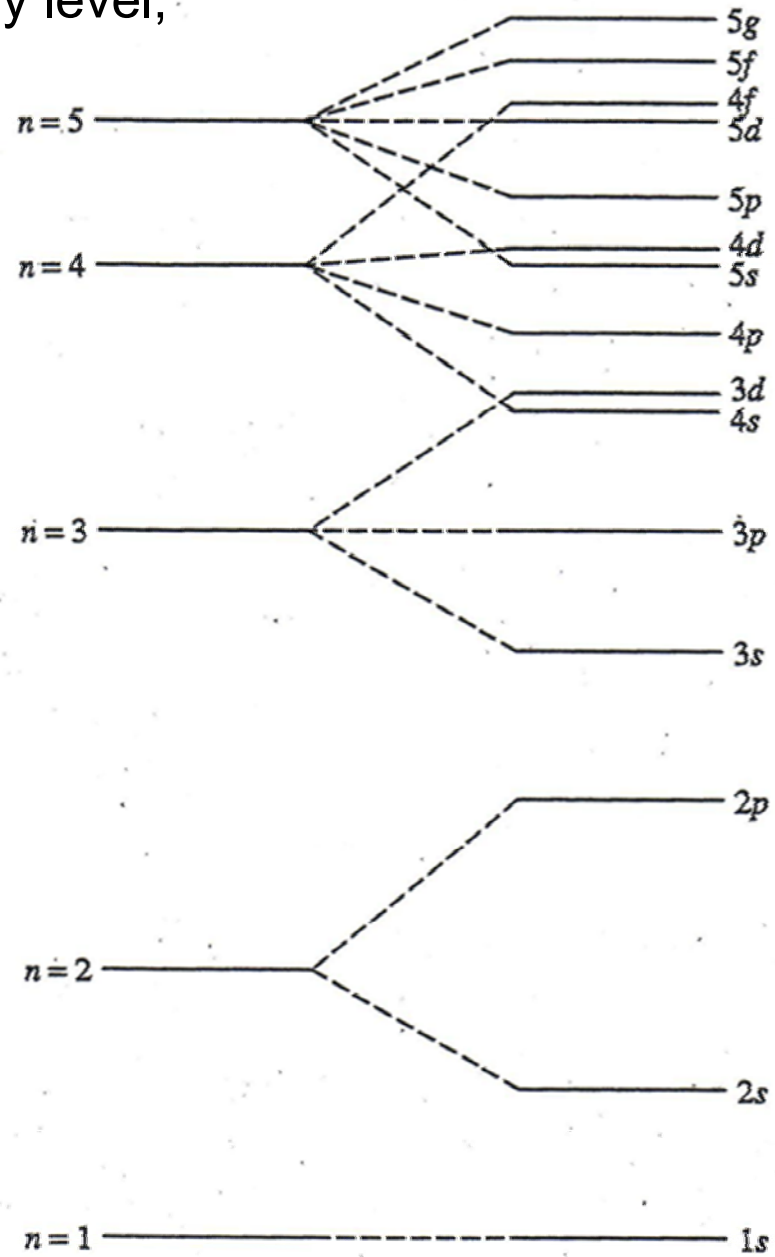
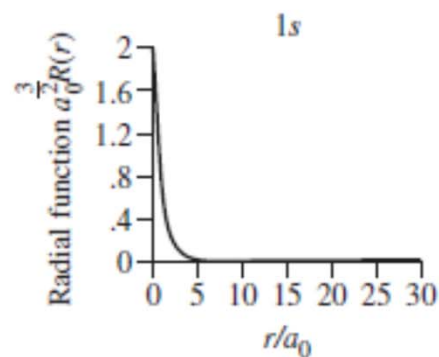
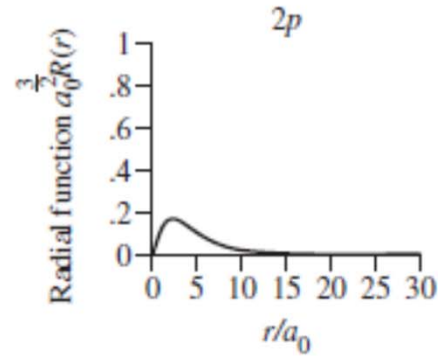
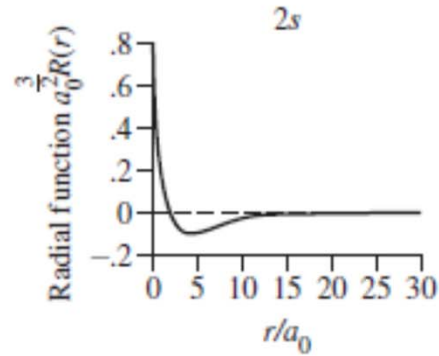
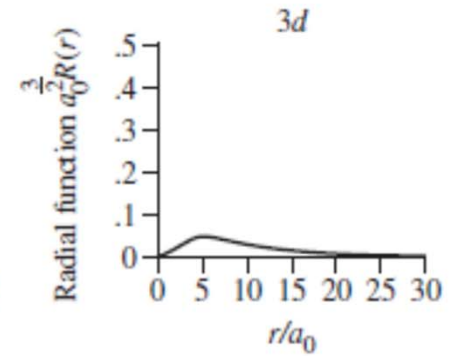
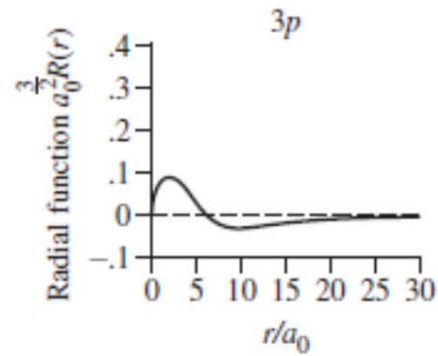
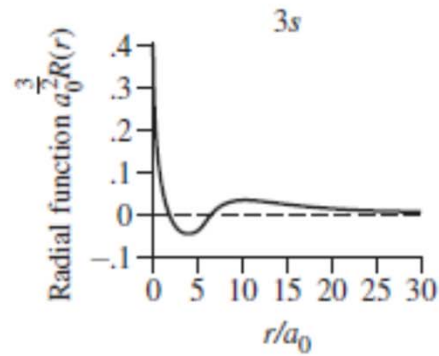


FIGURE 2-10 Energy Level Splitting and Overlap. The differences between the upper levels are exaggerated for easier visualization.

Radial Wave Functions and Nodes

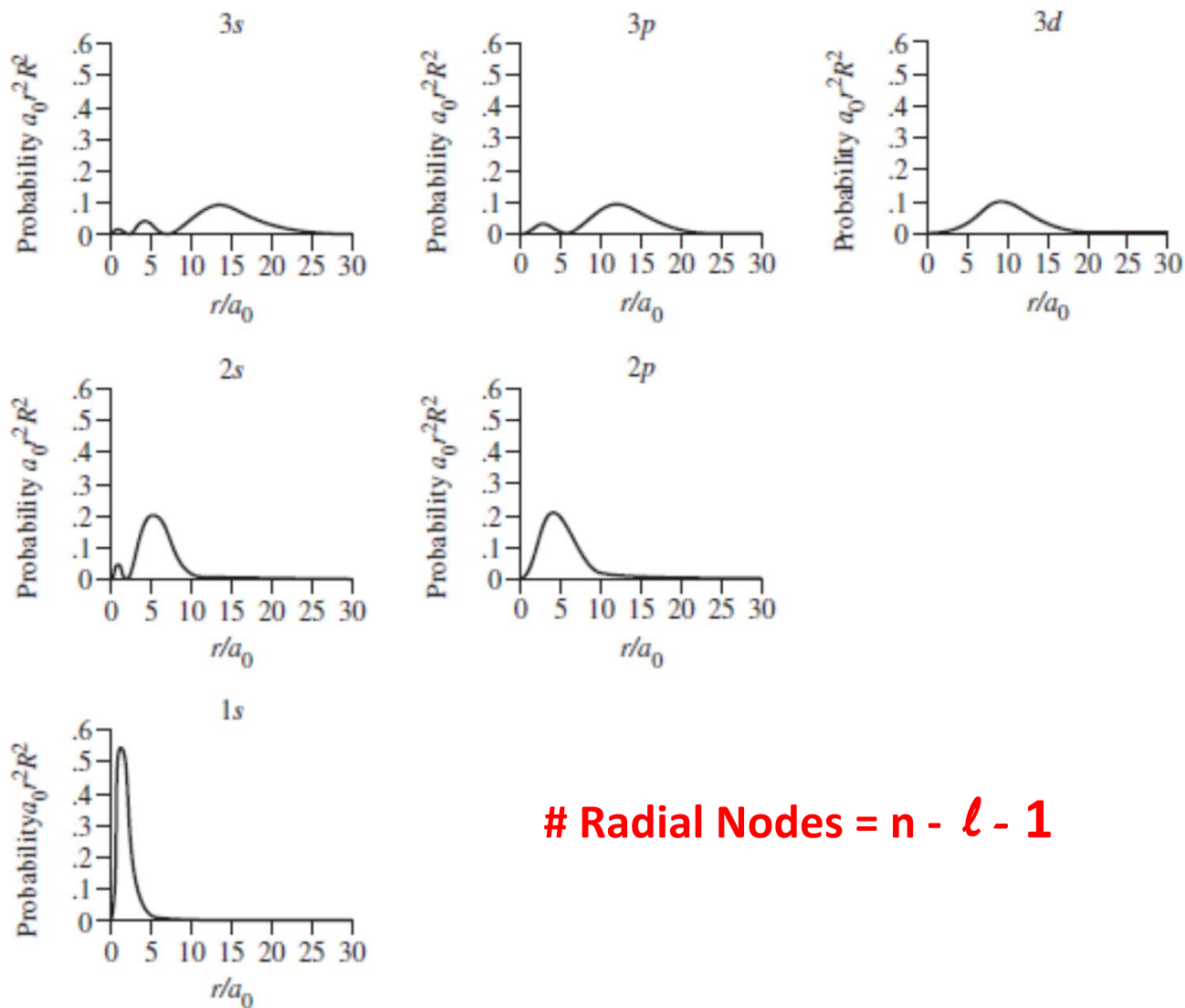
Radial Wave Functions



Radial Nodes = $n - \ell - 1$

Radial Probability Functions and Nodes

Radial Probability Functions



Radial Nodes = $n - \ell - 1$

FIGURE 2.7 Radial Wave Functions and Radial Probability Functions.

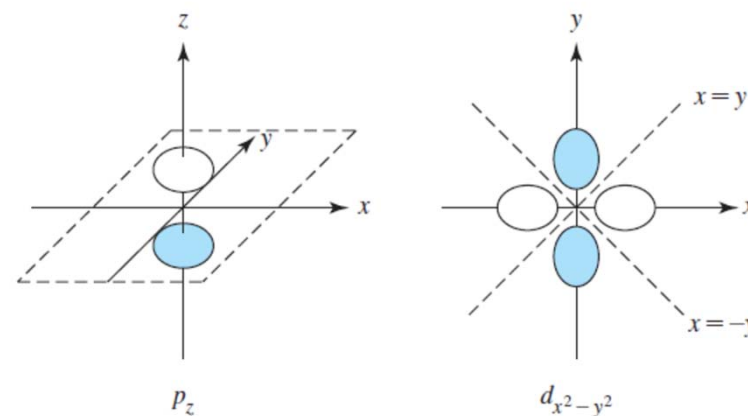
TABLE 2.5 Nodal Surfaces

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

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

Radial Nodes = $n - \ell - 1$

Angular Nodes = ℓ



Summary:

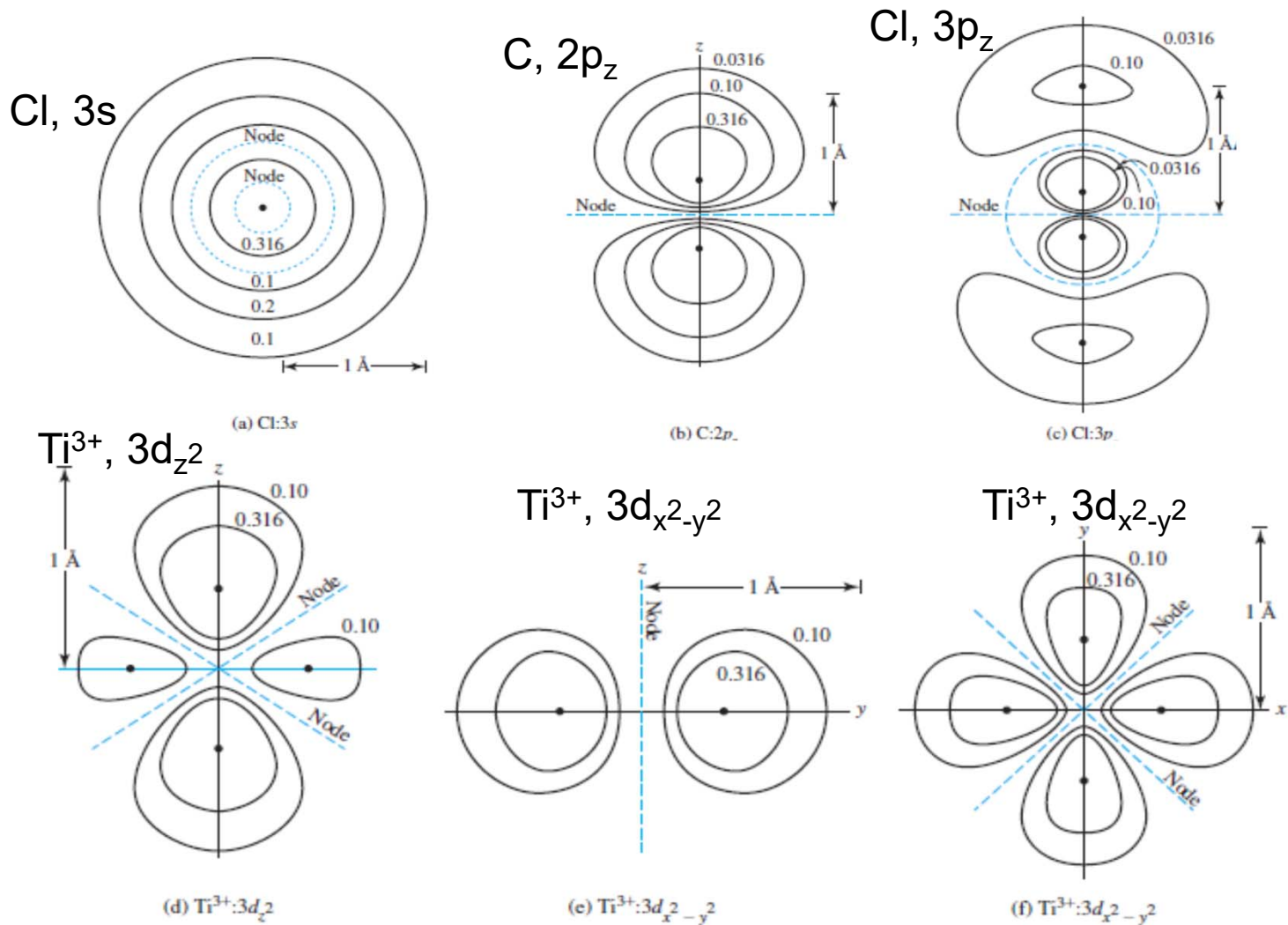
Radial Nodes = $n - \ell - 1$

Angular Nodes = ℓ

Total # Nodes = $n - 1$

Where are the nodes in orbitals???

(MFT, Figure 2.8 shows both radial and angular)

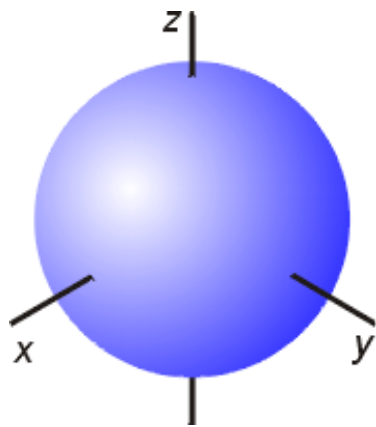
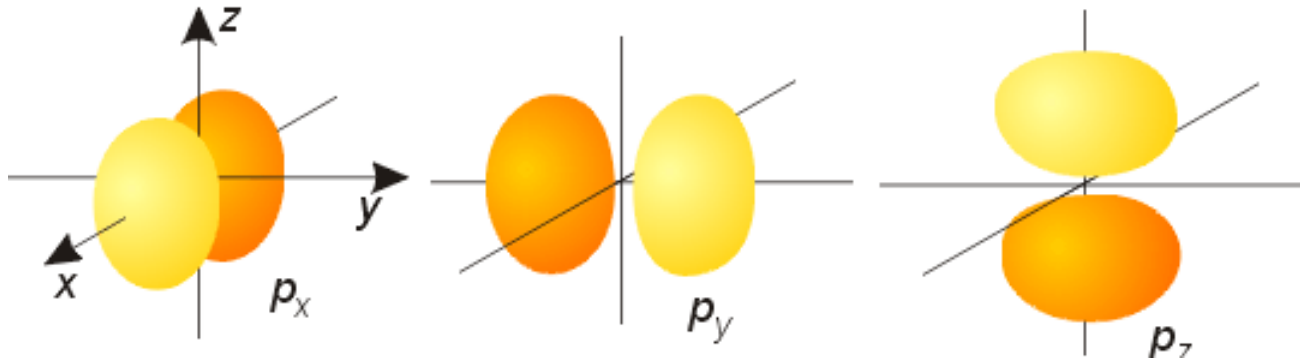


Note the orientation of the viewer: down z or x or y axes

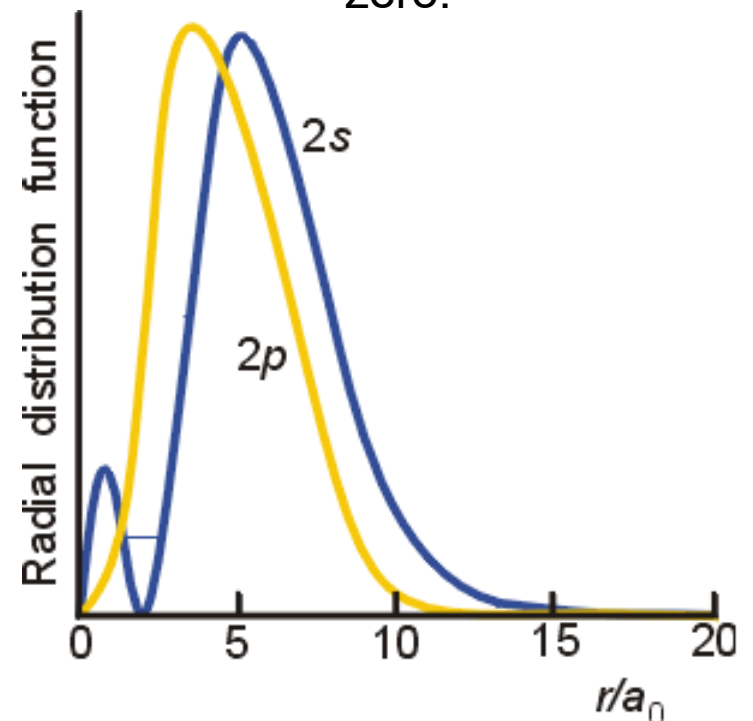
Orbitals and Shapes/Electron Distribution

Each p-orbital has two lobes with positive and negative values (**phases**) of the wavefunction either side of the nucleus separated by a **nodal plane** where the wavefunction is zero.

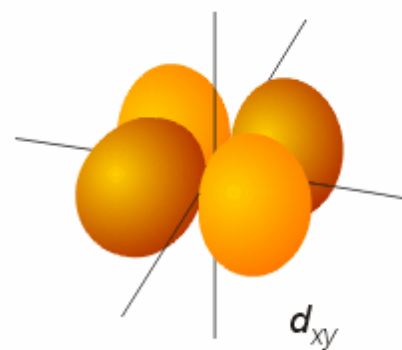
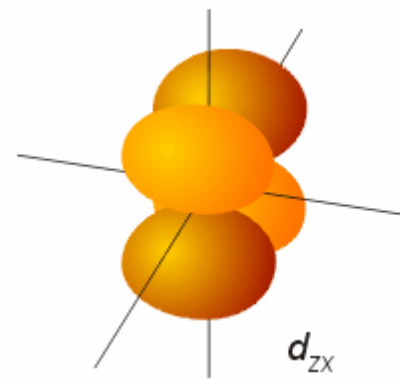
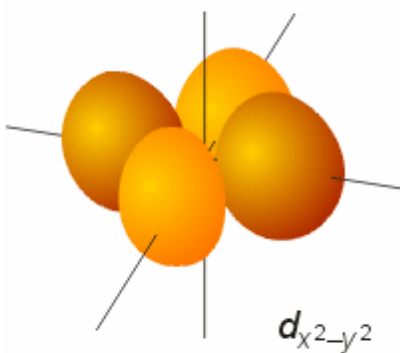
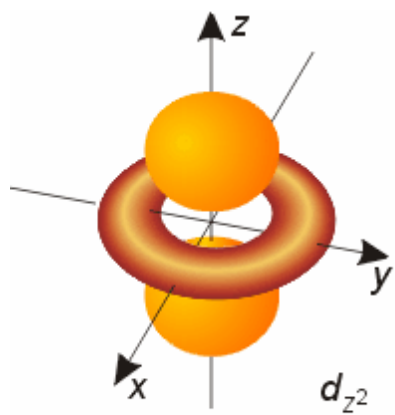
The p-orbitals



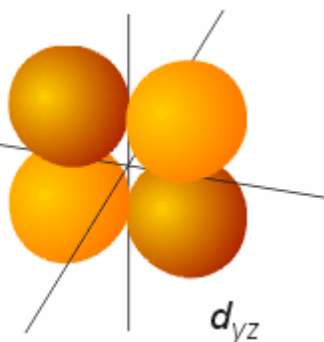
The s-orbital



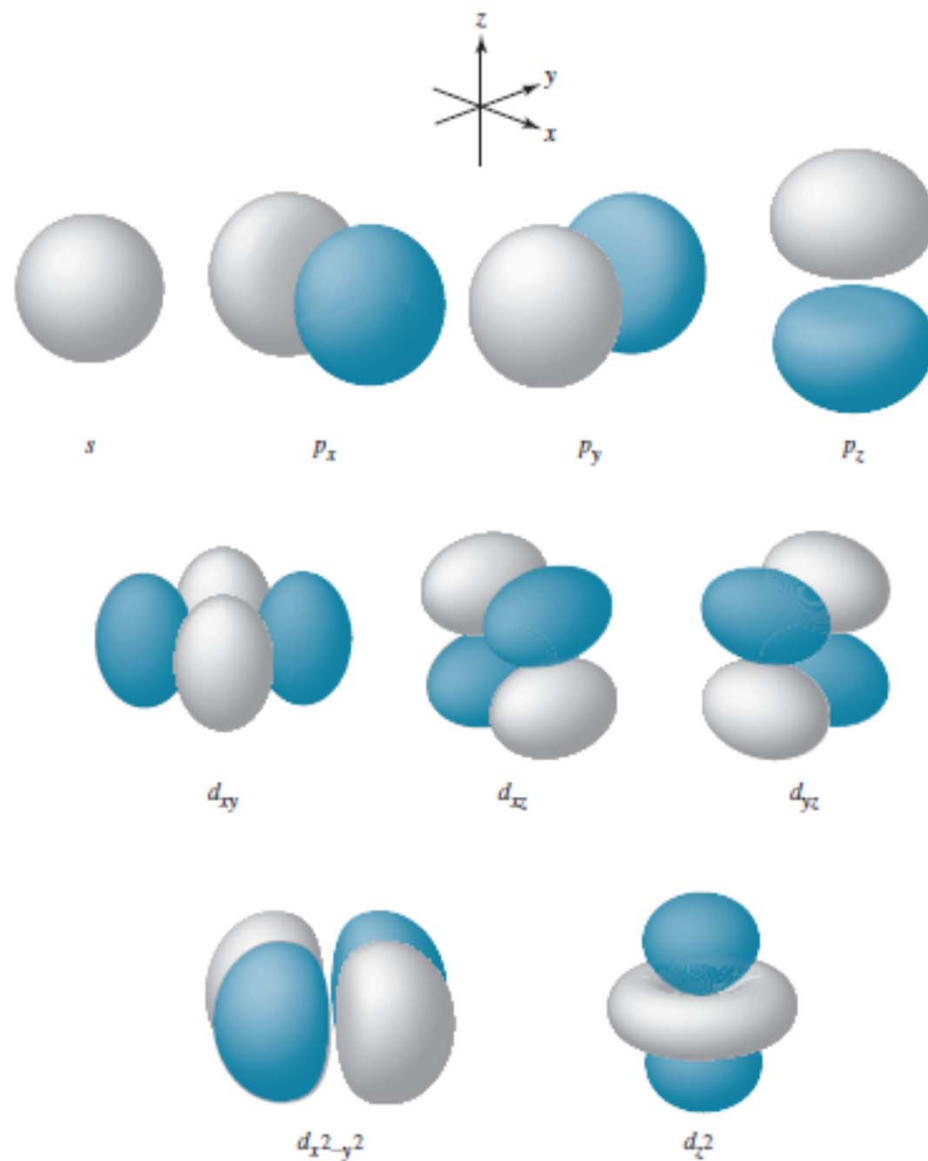
The d-orbitals



Two angular nodes



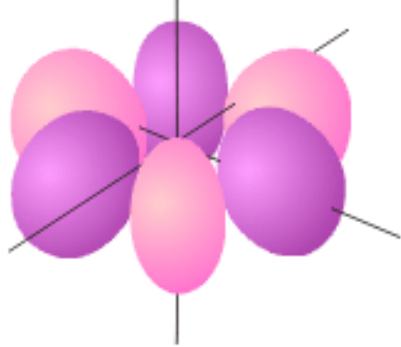
Memorize these shapes and how they are positioned on Cartesian Coordinates!



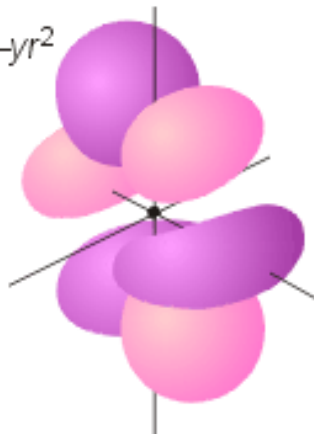
As pictured in MFT, Figure 2.6

The f-orbitals

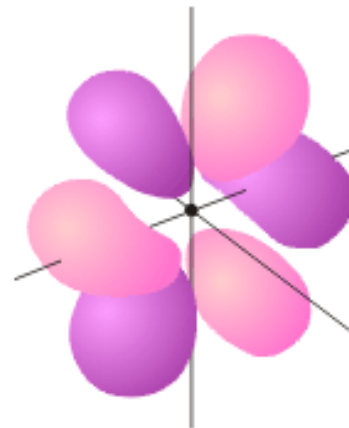
$$4f_{y^3-3yx^2}$$



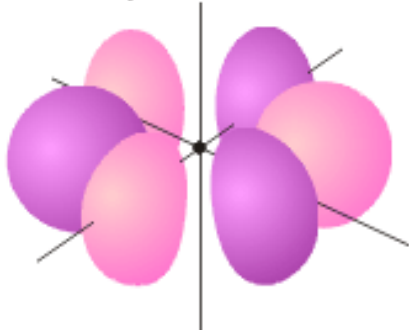
$$4f_{5yz^2-yr^2}$$



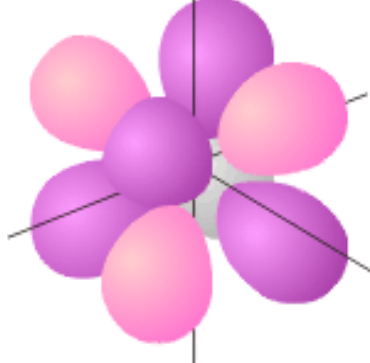
$$4f_{5xz^2-3xr^2}$$



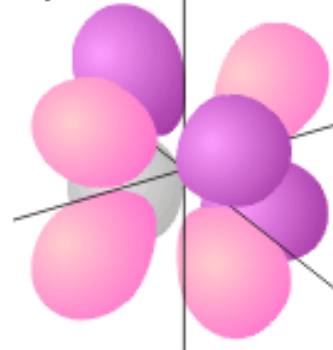
$$4f_{x^3-3xy^2}$$



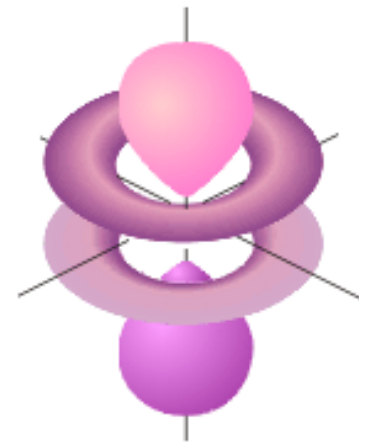
$$4f_{zx^2-zy^2}$$



$$4f_{xyz}$$



$$4f_{5z^3-3zr^2}$$



Quantum Numbers

n is the principal quantum number, indicates the size of the orbital, has all positive integer values of 1 to ∞ (infinity)

ℓ is the angular momentum quantum number, represents the shape of the orbital, has integer values of $n-1$ to 0

m_ℓ is the magnetic quantum number, represents the spatial direction of the orbital, can have integer values of $-\ell$ to 0 to ℓ

m_s is the spin quantum number, has little physical meaning, can have values of either $+1/2$ or $-1/2$

Pauli Exclusion principle: no two electrons can have all four of the same quantum numbers in the same atom

Hund's Rule: when electrons are placed in a set of degenerate orbitals, the *ground state* has as many electrons as possible in different orbitals, and with *parallel spin*.

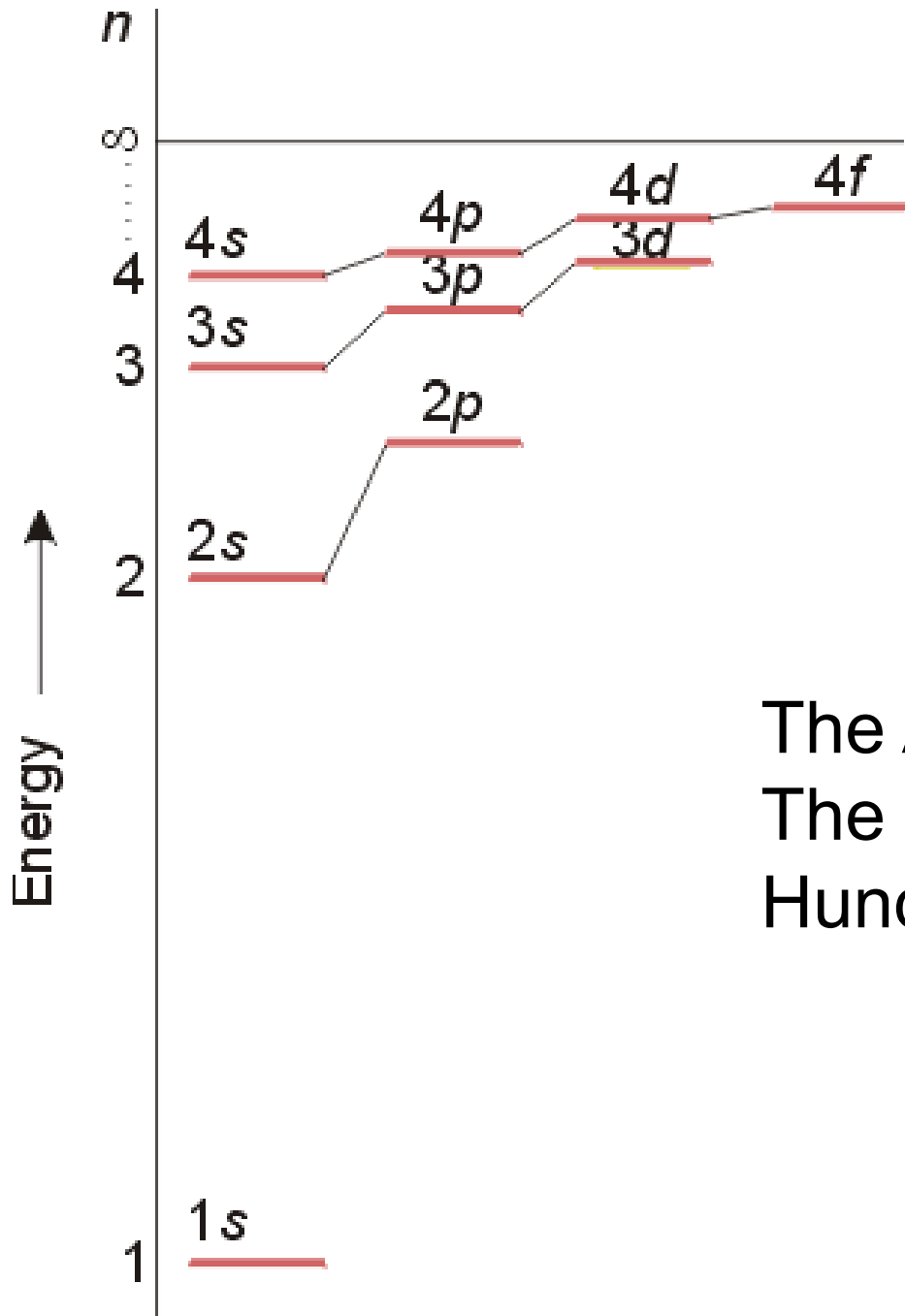
Aufbau (Building Up) Principle: the ground state electron configuration of an atom can be found by putting electrons in orbitals, starting with the lowest energy and moving progressively to higher energy.

ℓ (angular momentum)	orbital
0	s
1	p
2	d
3	f

Other terms: electron configuration, noble gas configuration, valence shell

Assigning Electrons

Energy Levels for Electron Configurations

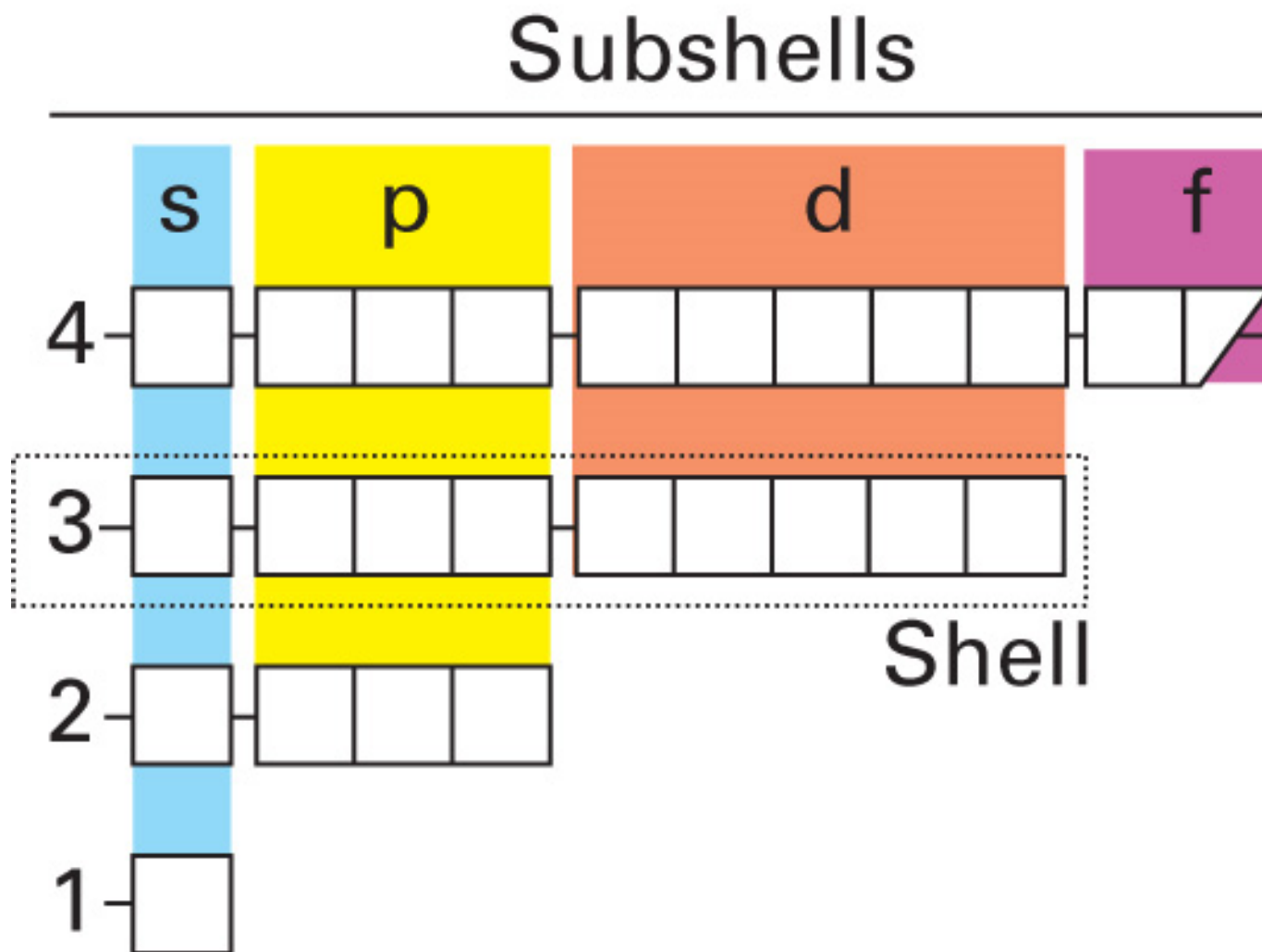


The Aufbau Principle

The Pauli Exclusion Principle

Hund's Rules

Box Diagrams



While n is the principal energy level, the l value also has an effect

Heavier elements, more chances
For close energy levels

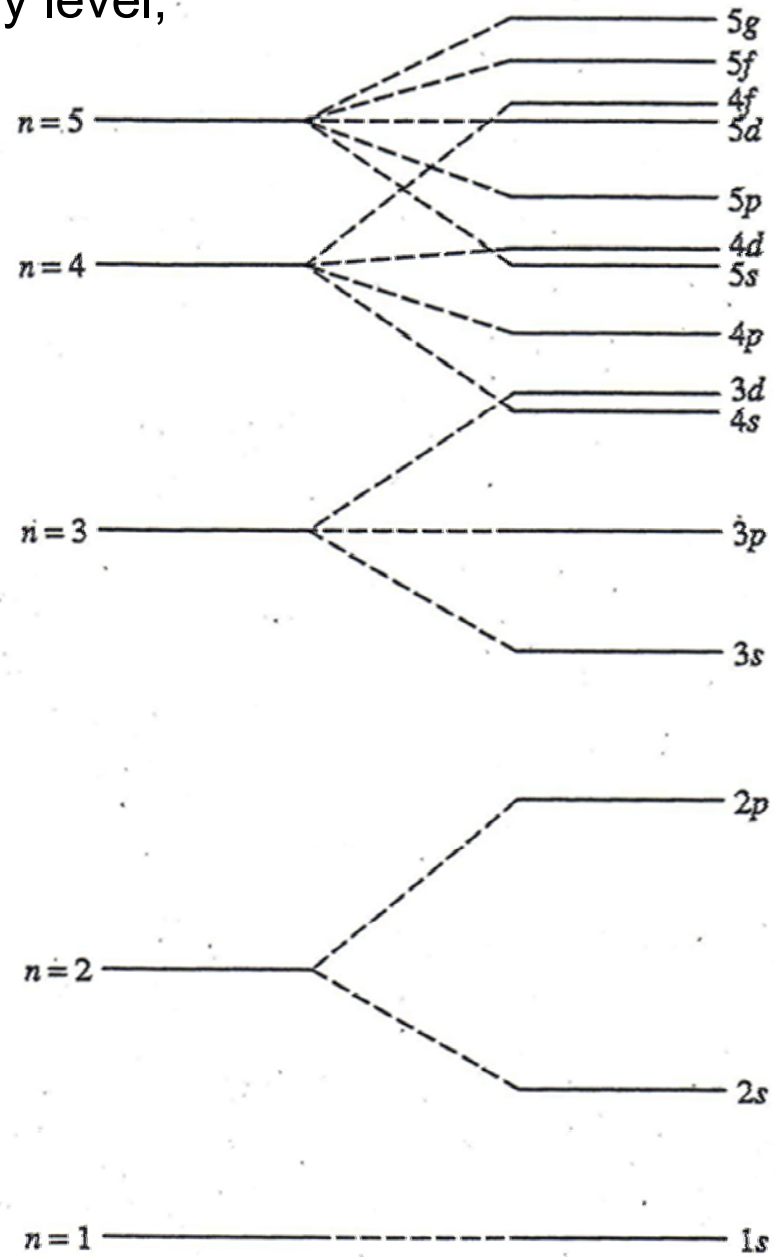
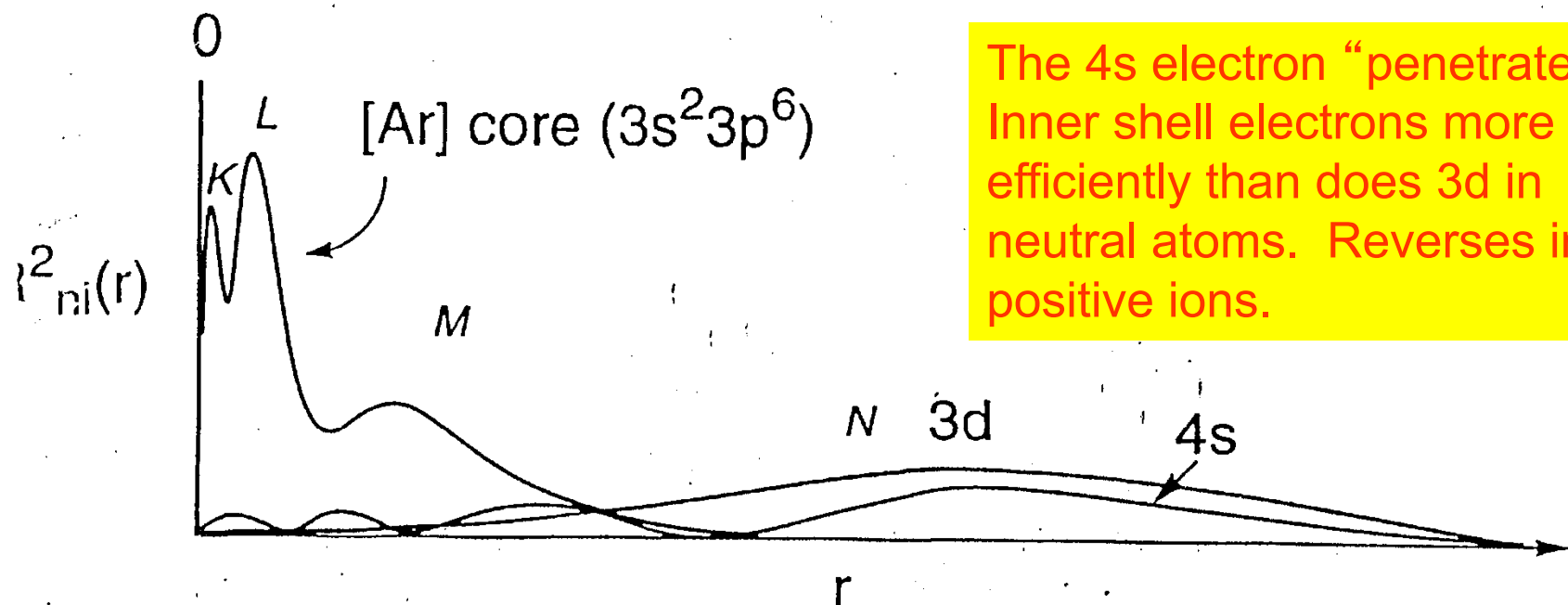


FIGURE 2-10 Energy Level Splitting and Overlap. The differences between the upper levels are exaggerated for easier visualization.

Screening:

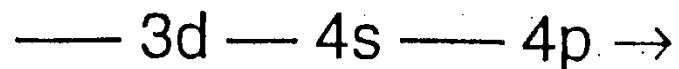
Interpenetration of 4s and 3d orbitals at K:



order of orbital filling, $Z = 19-36$, for neutral atoms:



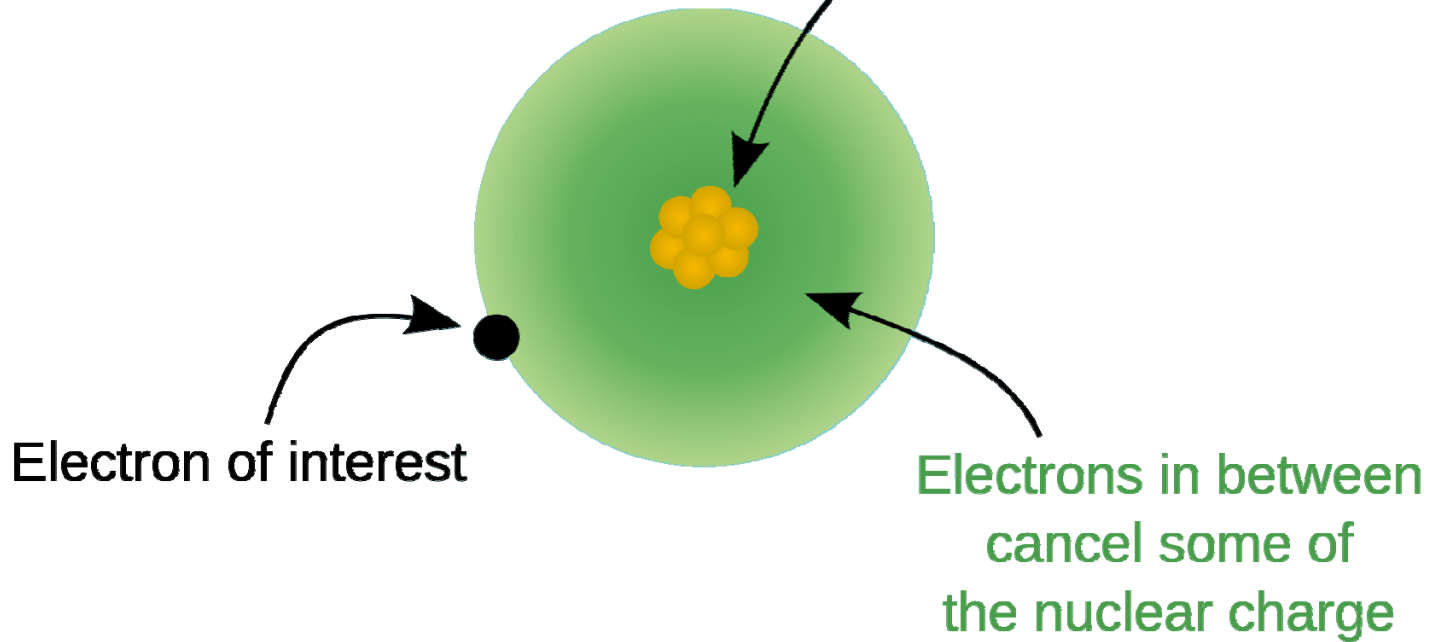
for positive ions, the order of 4s and 3d is reversed:



How to handle atoms larger than H? Effective Nuclear Charge or Z_{eff}

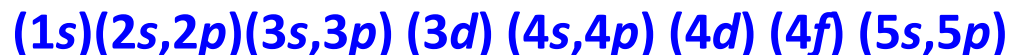
Electrons outside
have no effect for
electron of interest

Positively charged
nucleus



Slater's Rules for Calculating Z_{eff}

1) Write the electron configuration for the atom as follows:



2) Any electrons to the right of the electron of interest contributes no shielding. (Approximately correct statement.)

3) All other electrons in the same group as the electron of interest shield to an extent of 0.35 nuclear charge units

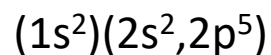
4) If the electron of interest is an *s* or *p* electron: All electrons with one less value of the principal quantum number shield to an extent of 0.85 units of nuclear charge. All electrons with two less values of the principal quantum number shield to an extent of 1.00 units.

5) If the electron of interest is an *d* or *f* electron: All electrons to the left shield to an extent of 1.00 units of nuclear charge.

6) Sum the shielding amounts from steps 2 - 5 and subtract from the nuclear charge value to obtain the effective nuclear charge.

Slater's Rules: Examples

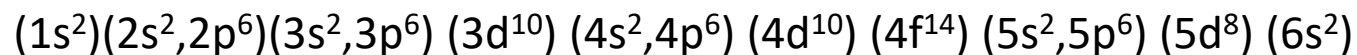
Calculate Z_{eff} for a valence electron in fluorine.



Rule 2 does not apply; therefore, for a valence electron the shielding or screening is $(0.35 \cdot 6) + (0.85 \cdot 2) = 3.8$

$$Z_{\text{eff}} = 9 - 3.8 = 5.2$$

Calculate Z_{eff} for a 6s electron in Platinum.



Rule 2 does not apply, and the shielding is:

$$(0.35 \cdot 1) + (0.85 \cdot 16) + (60 \cdot 1.00) = 73.95$$

$$Z_{\text{eff}} = 78 - 73.95 = 4.15 \text{ for a valence electron.}$$

Table 1.2 Effective nuclear charge, Z_{eff}

	H								He
Z	1								2
1s	1.00								1.69
	Li	Be	B	C	N	O	F		Ne
Z	3	4	5	6	7	8	9		10
1s	2.69	3.68	4.68	5.67	6.66	7.66	8.65		9.64
2s	1.28	1.91	2.58	3.22	3.85	4.49	5.13		5.76
2p			2.42	3.14	3.83	4.45	5.10		5.76
	Na	Mg	Al	Si	P	S	Cl		Ar
Z	11	12	13	14	15	16	17		18
1s	10.63	11.61	12.59	13.57	14.56	15.54	16.52		17.51
2s	6.57	7.39	8.21	9.02	9.82	10.63	11.43		12.23
2p	6.80	7.83	8.96	9.94	10.96	11.98	12.99		14.01
3s	2.51	3.31	4.12	4.90	5.64	6.37	7.07		7.76
3p			4.07	4.29	4.89	5.48	6.12		6.76