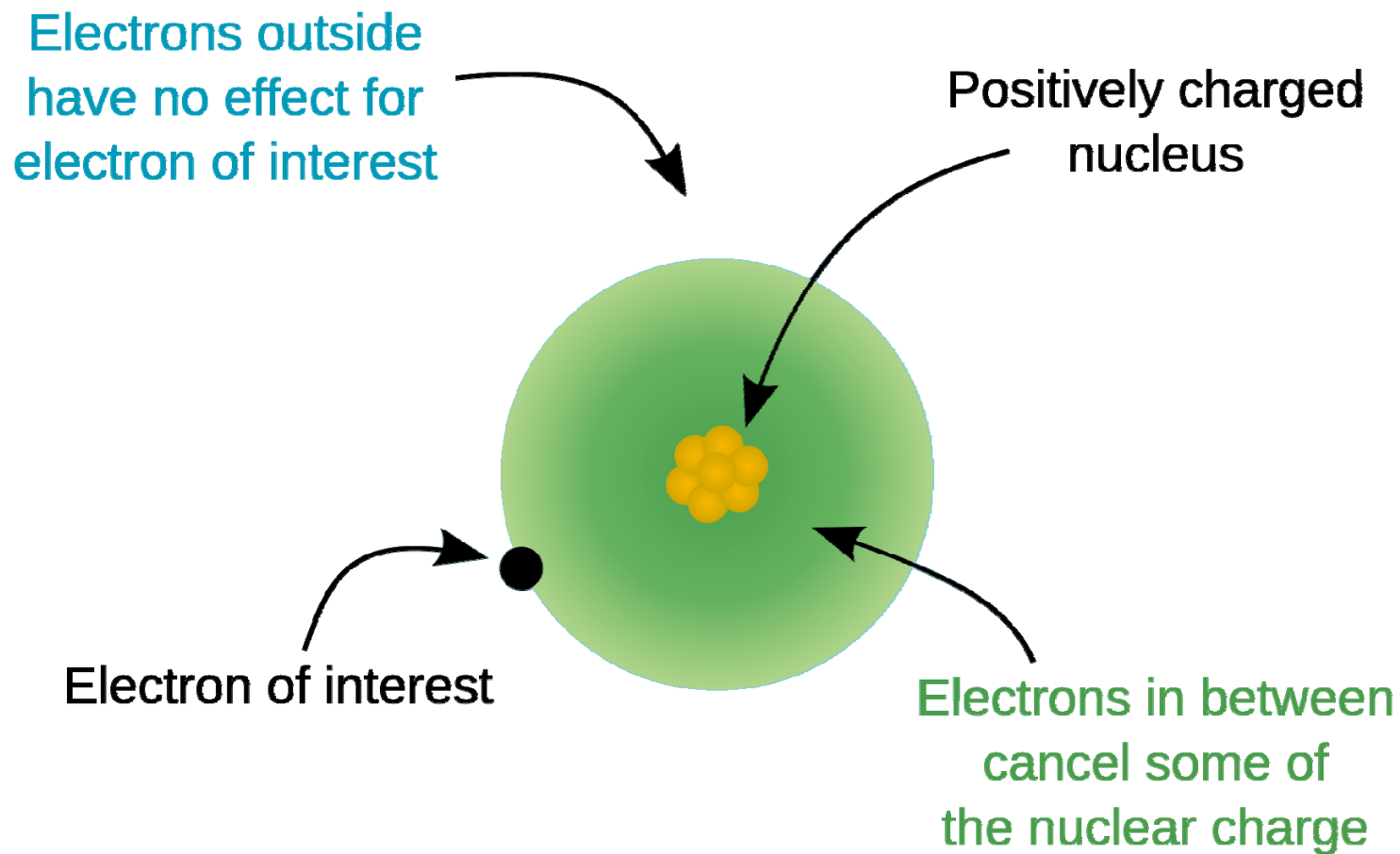


## *Lecture 4 362 January 23, 2019*

- *Contour Plots*
- *Electron assignments and Configurations*
- *Screening by inner and common electrons*
- *Effective Nuclear Charge*
- *Slater's Rules*

How to handle atoms larger than H? Effective Nuclear Charge or  $Z_{\text{eff}}$  (and,  $\ell$ , or no. of nodes)



Energies of the electrons

Nodes, (not toads)

Region of space of zero probability



Summary:

**Total # Nodes =  $n - 1$**

# Angular Nodes =  $\ell$

# Radial Nodes =  $n - \ell - 1$

Where  $n$  = principal quantum number;  
 $\ell$  = angular momentum quantum number



Vertical display of energy levels.

Horizontal is typical

$1s^2 2s^2 2p^6, 3s^2 3p^6 4s^2 3d^{10} 4p^6 \dots$

Heavier elements, more chances  
For close energy levels

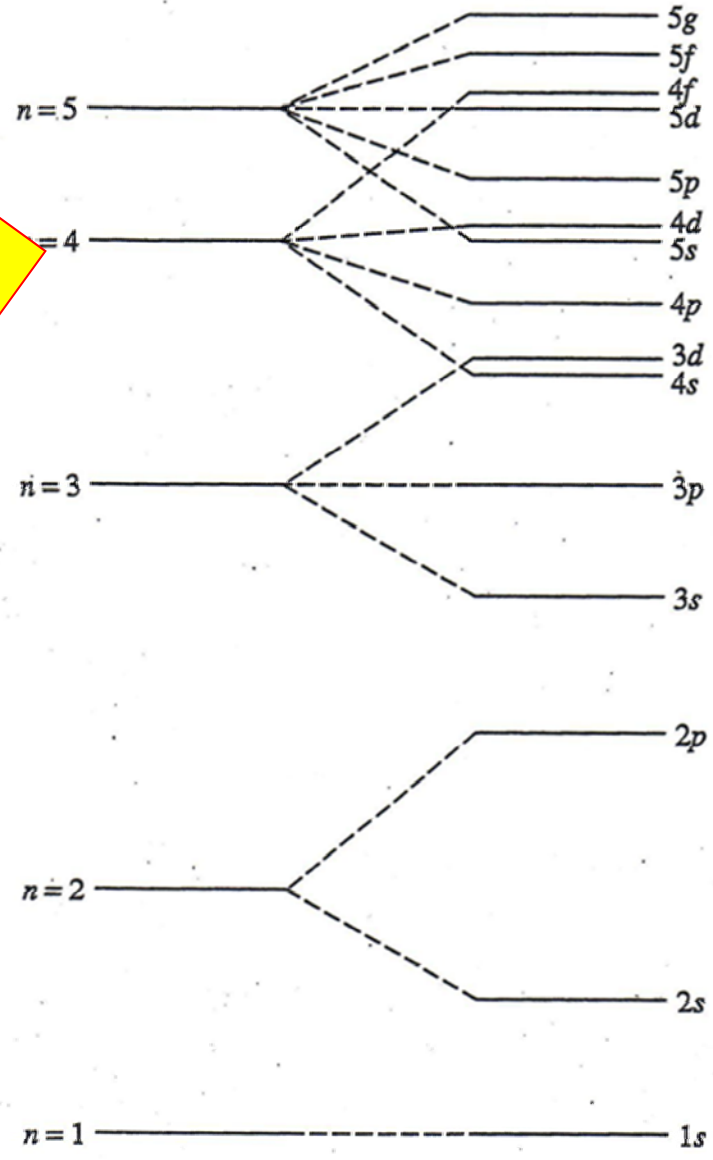


FIGURE 2-10 Energy Level Splitting and Overlap. The differences between the upper levels are exaggerated for easier visualization.

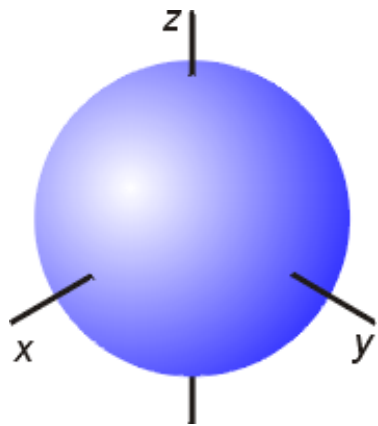
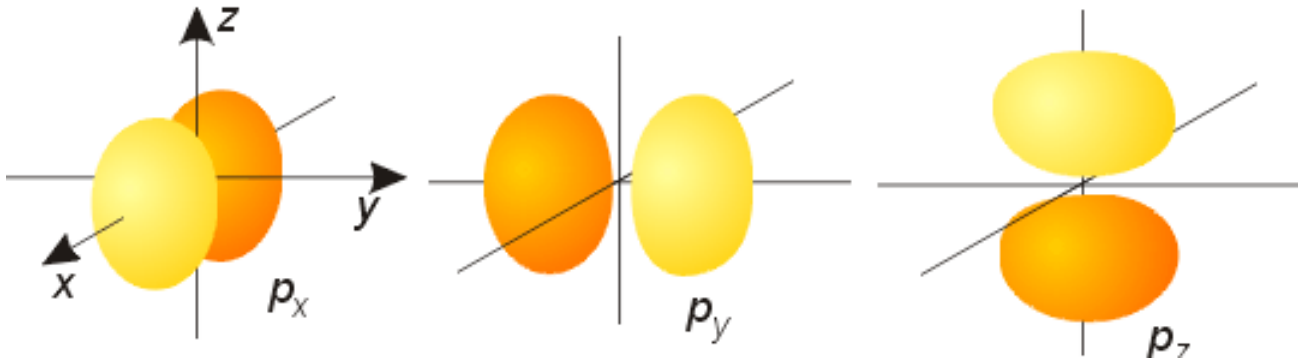
## *nd vs. (n + 1)s in the Transition Metals*

	<b>K</b>	<b>Ca</b>	<b>Sc</b>	<b>Ti</b>	<b>V</b>	<b>Cr</b>	<b>Mn</b>	<b>Fe</b>	<b>Co</b>	<b>Ni</b>	<b>Cu</b>	<b>Zn</b>
<b>4s</b>	<b>1</b>	<b>2</b>	<b>2</b>	<b>2</b>	<b>2</b>	<b>1</b>	<b>2</b>	<b>2</b>	<b>2</b>	<b>2</b>	<b>1</b>	<b>2</b>
<b>3d</b>			<b>1</b>	<b>2</b>	<b>3</b>	<b>5</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>10</b>	<b>10</b>
	<b>Rb</b>	<b>Sr</b>	<b>Y</b>	<b>Zr</b>	<b>Nb</b>	<b>Mo</b>	<b>Tc</b>	<b>Ru</b>	<b>Rh</b>	<b>Pd</b>	<b>Ag</b>	<b>Cd</b>
<b>5s</b>	<b>1</b>	<b>2</b>	<b>2</b>	<b>2</b>	<b>1</b>	<b>1</b>	<b>1</b>	<b>1</b>	<b>1</b>	<b>0</b>	<b>1</b>	<b>2</b>
<b>4d</b>			<b>1</b>	<b>2</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>10</b>	<b>10</b>	<b>10</b>
	<b>Cs</b>	<b>Ba</b>	<b>La</b>	<b>Hf</b>	<b>Ta</b>	<b>W</b>	<b>Re</b>	<b>Os</b>	<b>Ir</b>	<b>Pt</b>	<b>Au</b>	<b>Hg</b>
<b>6s</b>	<b>1</b>	<b>2</b>	<b>2</b>	<b>2</b>	<b>2</b>	<b>2</b>	<b>2</b>	<b>2</b>	<b>2</b>	<b>0</b>	<b>1</b>	<b>2</b>
<b>5d</b>			<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>10</b>	<b>10</b>	<b>10</b>

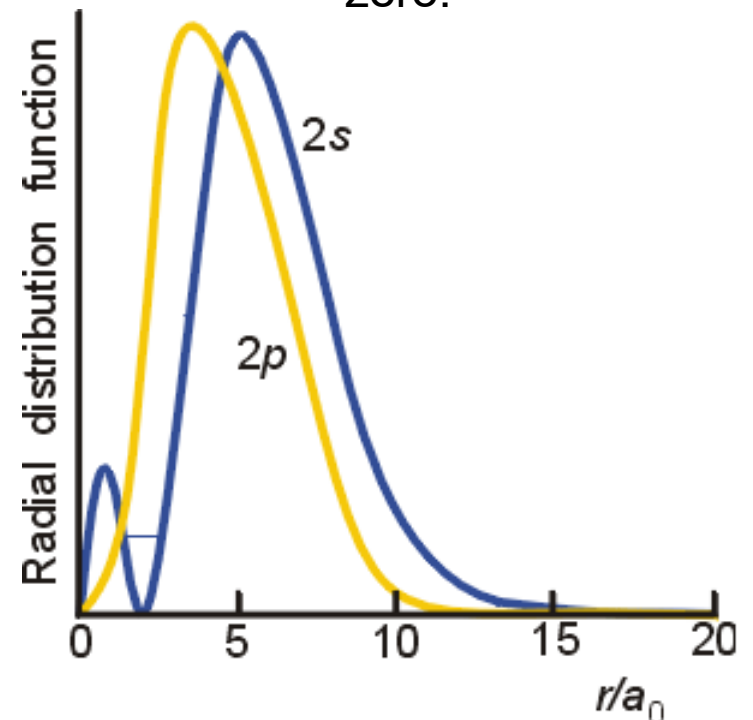
# Orbitals and Shapes/Electron Distribution *account for different energies of specific orbitals*

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

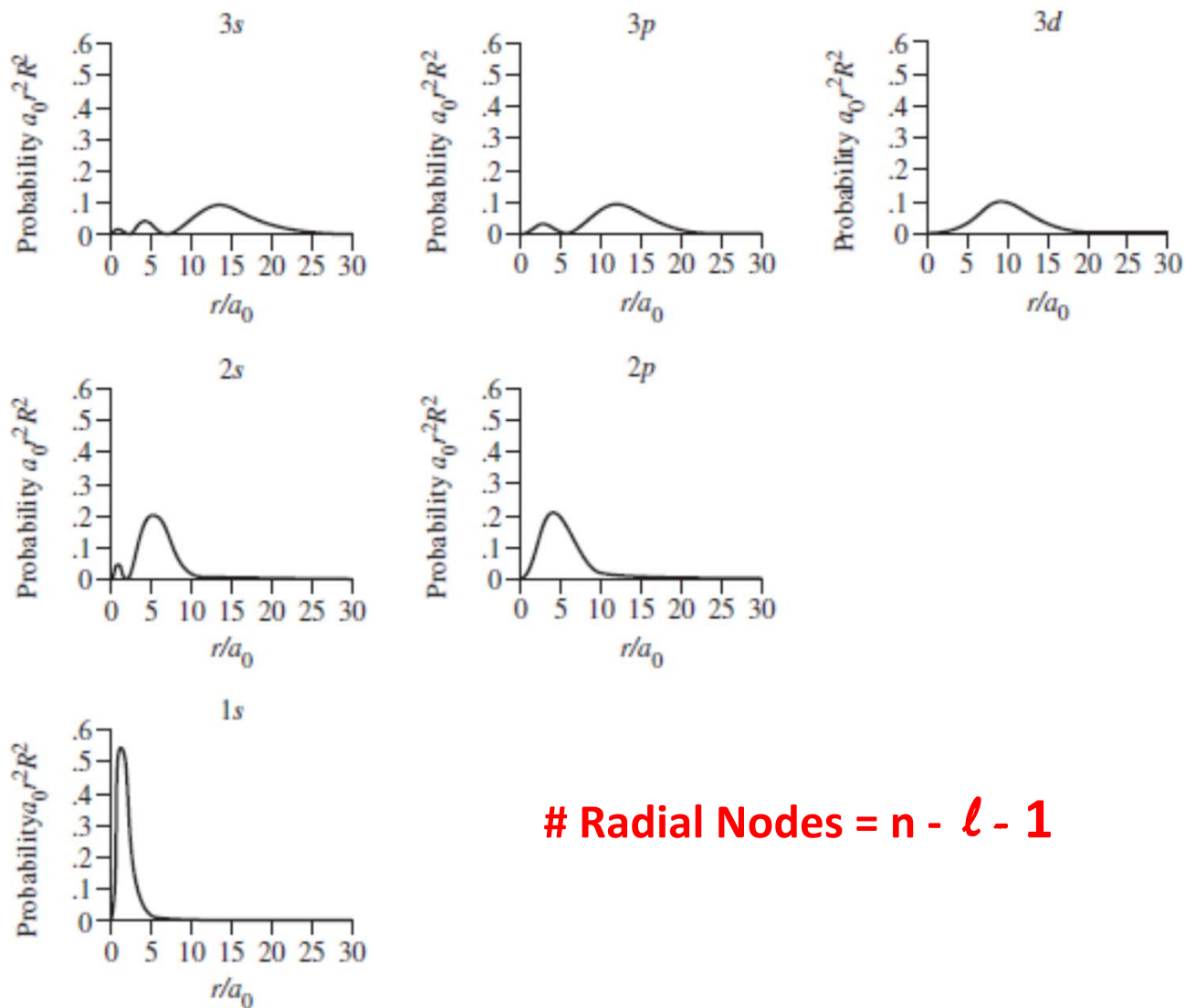


## The s-orbital



# Radial Probability Functions and Nodes

Radial Probability Functions

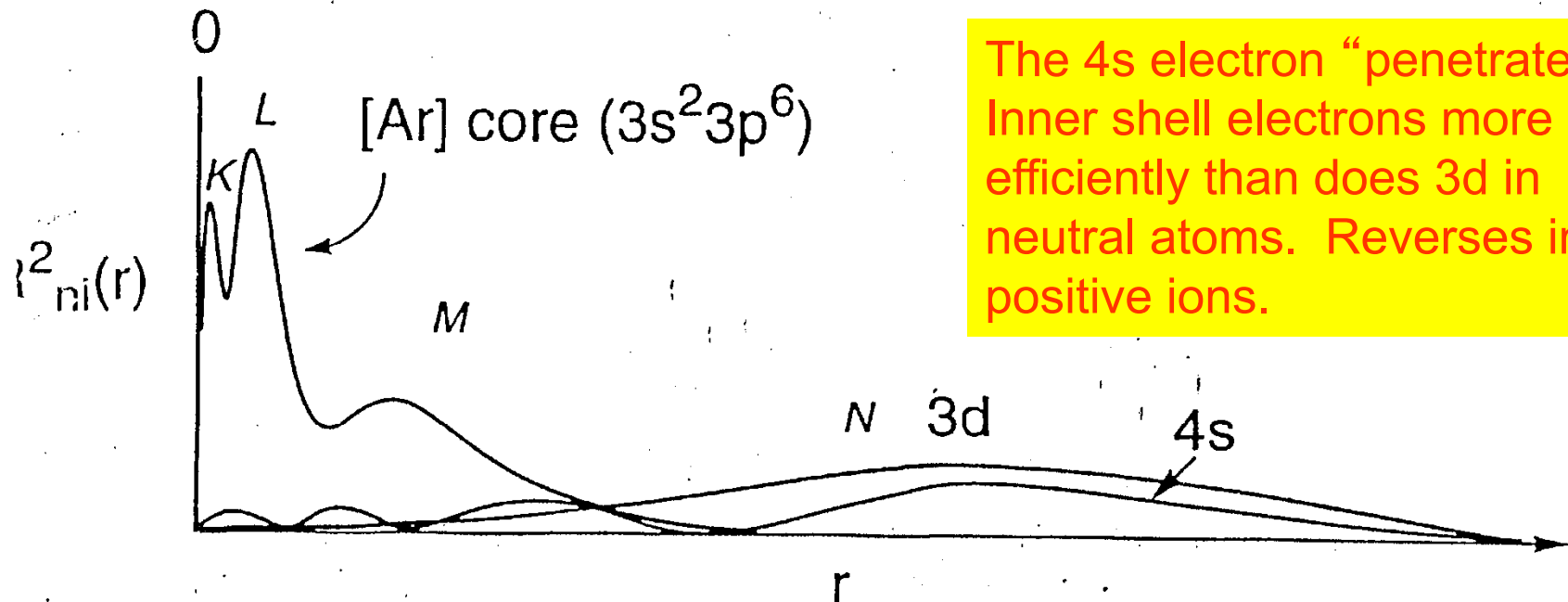


**# Radial Nodes =  $n - \ell - 1$**

**FIGURE 2.7** Radial Wave Functions and Radial Probability Functions.

## Screening:

Interpenetration of 4s and 3d orbitals at K:

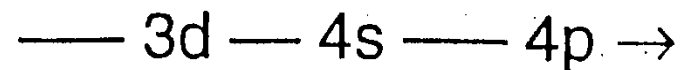


The 4s electron “penetrates” inner shell electrons more efficiently than does 3d in neutral atoms. Reverses in positive ions.

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

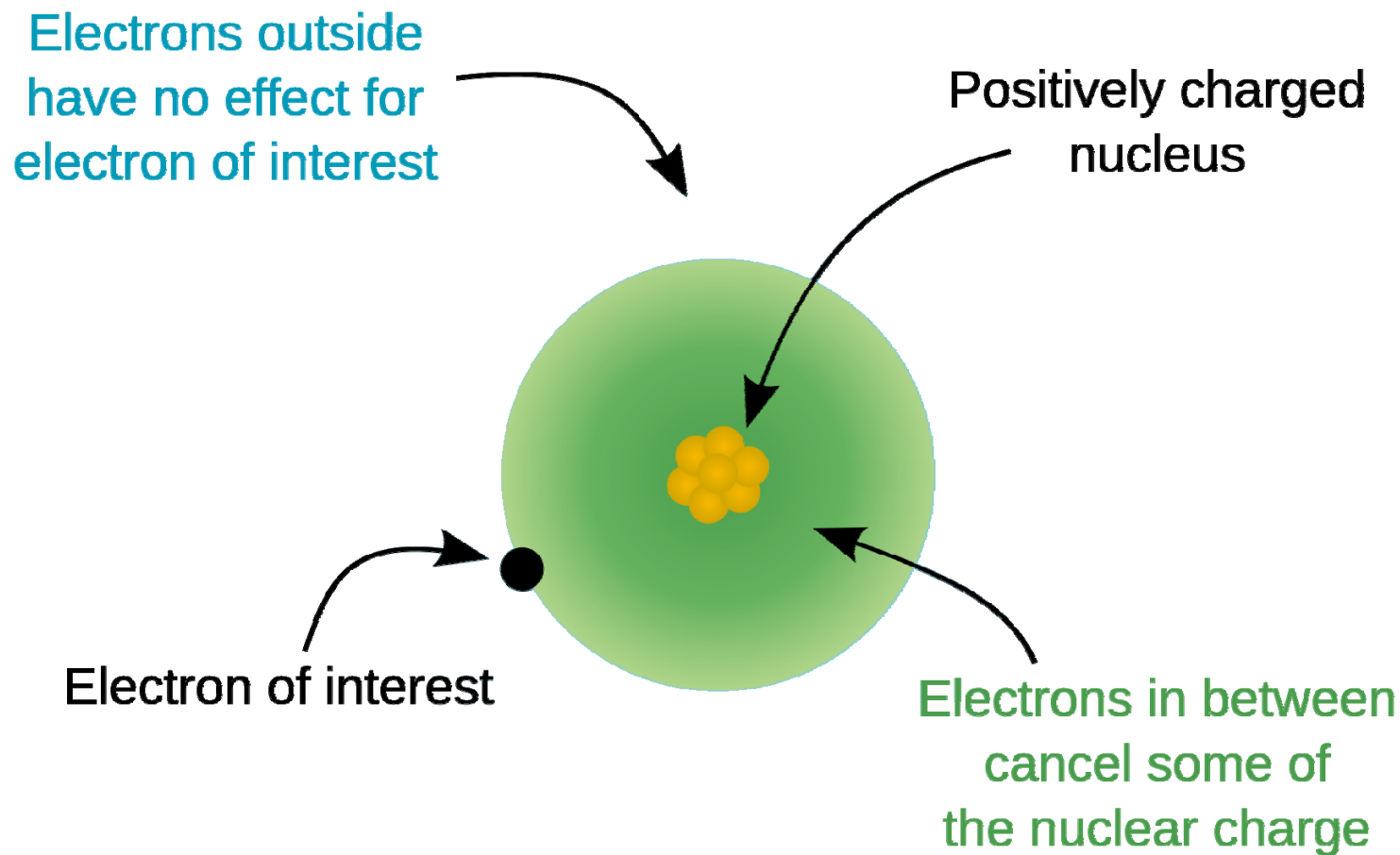


for positive ions, the order of 4s and 3d is reversed:





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



# Slater's Rules for Calculating $Z_{\text{eff}}$

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

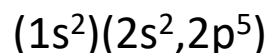
4) If the electron of interest is an *s* or *p* electron: All electrons with one less value of the principal quantum number shield to an extent of 0.85 units of nuclear charge. All electrons with two less values of the principal quantum number shield to an extent of 1.00 units.

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

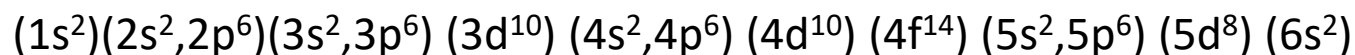
Calculate  $Z_{\text{eff}}$  for a valence electron in fluorine.



*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  $Z_{\text{eff}}$  for a 6s electron in Platinum.



*Rule 2 does not apply, and the shielding is:*

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

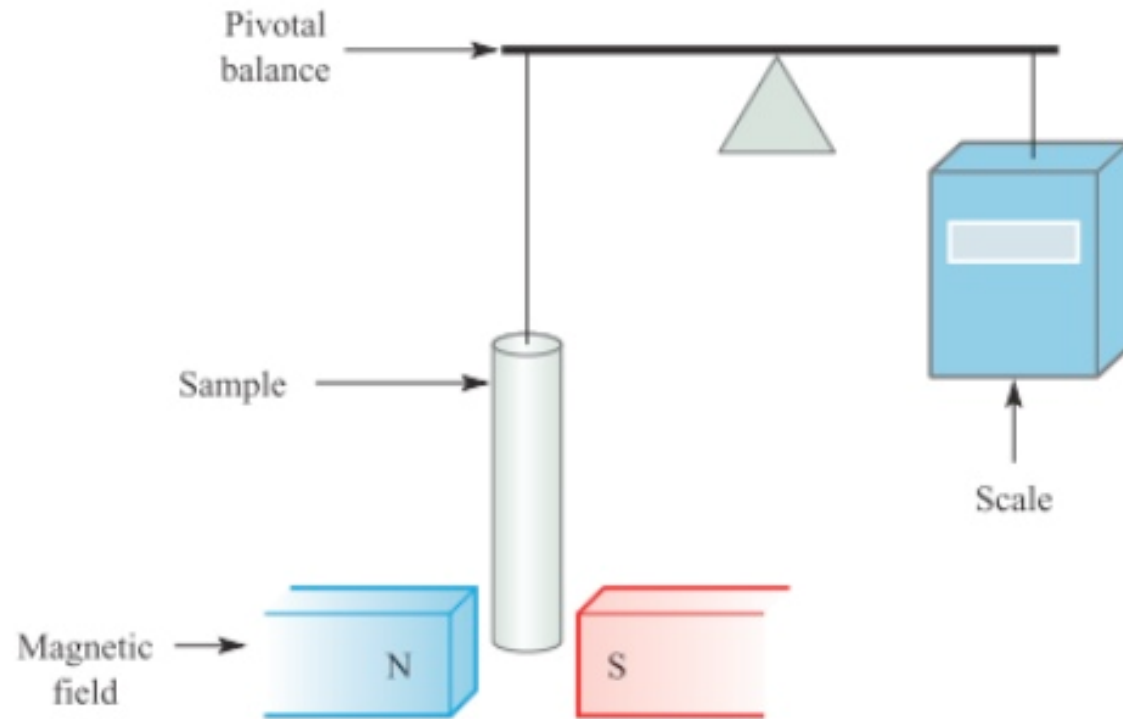
$$Z_{\text{eff}} = 78 - 73.95 = 4.15 \text{ for a valence electron.}$$

## Electrons in Atoms:

- $Z_{\text{eff}}$
- **Term Symbols**
- **Magnetism**
- **Periodic Properties**

OK We now have the electrostatic attraction of nucleus for electron/s.  
What properties or observables are readily explained?

# ***Gouy Balance for Magnetic Susceptibility***



**Fig. 20.21** Schematic representation of a Gouy balance.

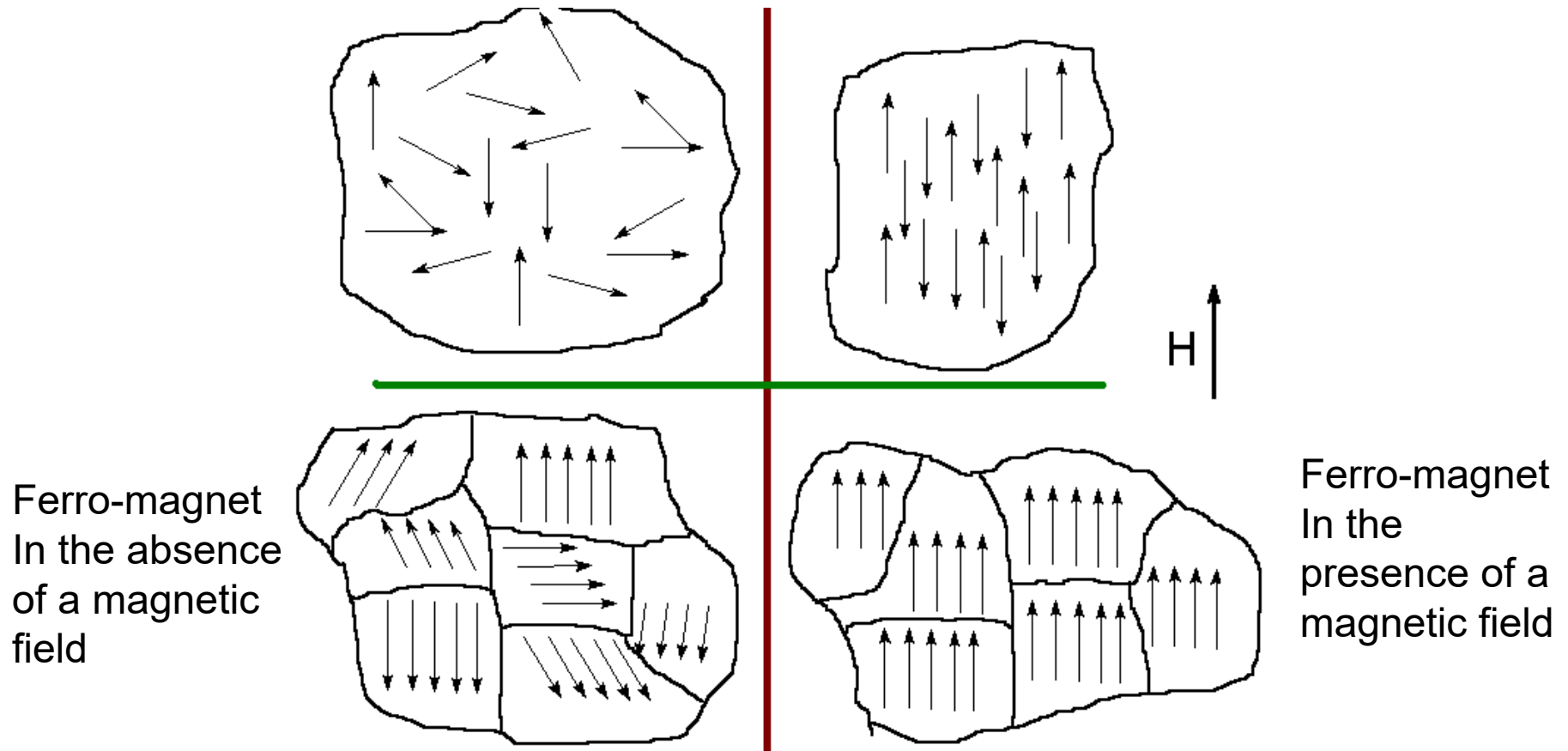
## Three types of Magnetic Behavior

**Paramagnetism:** atoms, molecules, and solids with unpaired electrons are attracted in a magnetic field

**Diamagnetic:** substances with no unpaired electrons which are weakly repelled in a magnetic field

**Ferro-magnetism:** the unpaired electrons are aligned with their neighbors even in the absence of a magnetic field

**Magnetic domains:** the groups of mutually aligned spins in a ferromagnetic substance



# Electrons Characterized by

- a) Principal energy level,  $n$
- b) Orbital or angular momentum,  $l = \#$  of angular nodes
- c)  $Z_{\text{eff}}$

---

In the presence of a magnetic field of  $\ell$  is oriented and composed of  $m_\ell$  components.

**d) Spin-spin and spin-orbital coupling**

## *How do we approach magnetism?*

Electron Assignments:  
Identifying each and every quantum  
number for each and every electron:

$$n \quad l \quad m_l \quad m_s$$

Summation of magnetic quantum numbers

=> overall magnetic moments

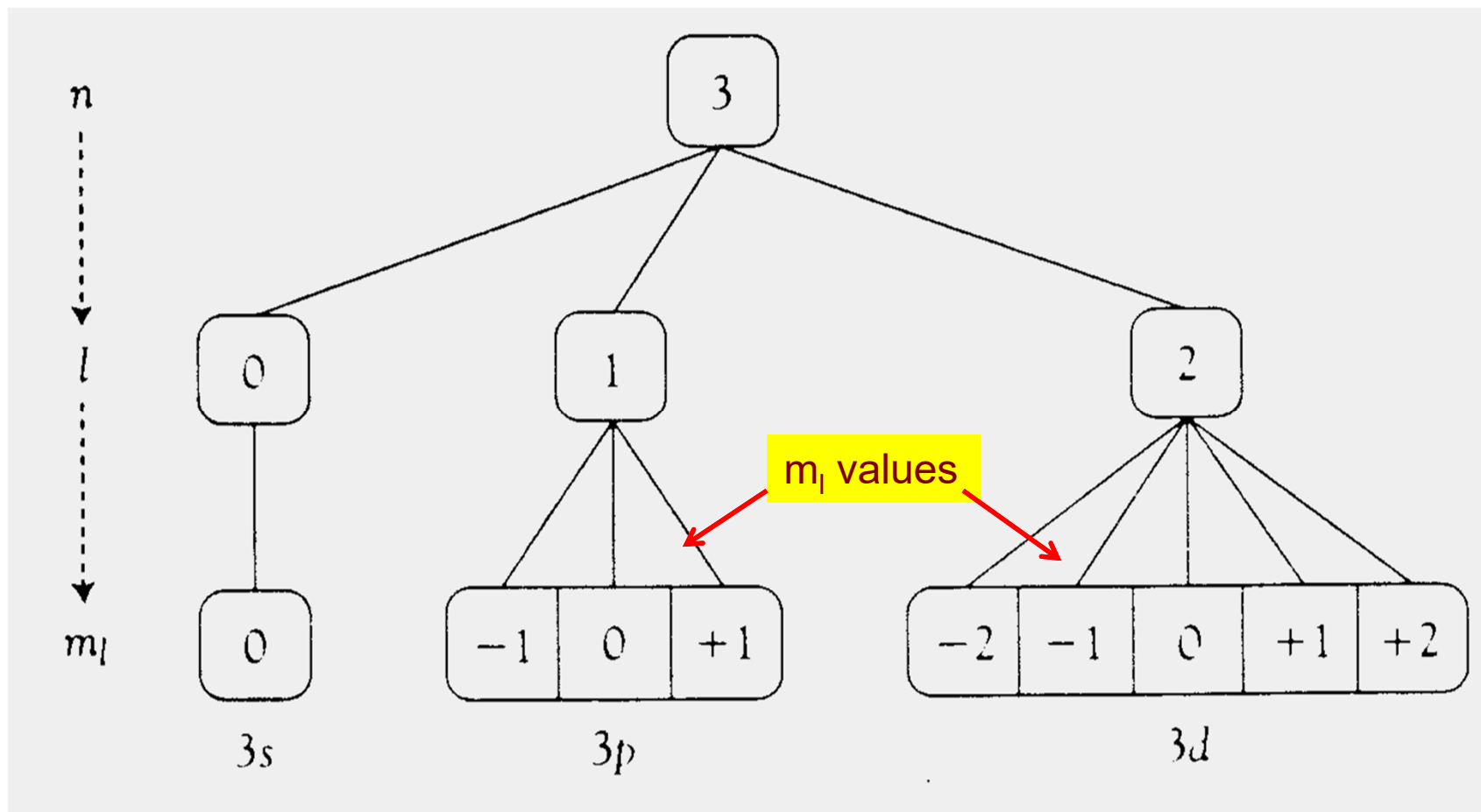
Summation of L quantum numbers

=> overall energy states and Terms



## Box Diagrams

Figure 1.5 The possible sets of quantum numbers for  $n = 3$ .

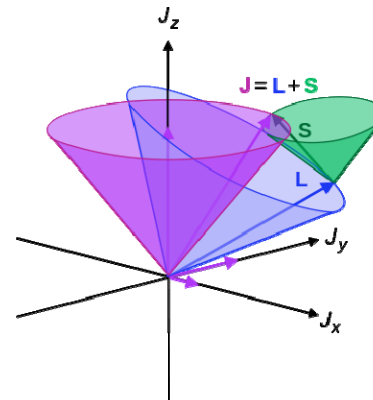


# Ground State vs. Excited State Configurations

***Term Symbols:  $2S + 1 L_J$***

Spin:  $S = \sum m_s$   
= total spin angular momentum  $2S + 1$   
(called spin "multiplicity")  
L = total orbital angular momentum

$$= \sum m_l \quad J = L + S$$



# Term Symbols for Ground State Electronic Configurations

- Pauli Exclusion Principle => Assignments to  $n$  and to  $l$  quantum numbers. But there are other possibilities within assignment
- Hund's Rule: Describes ground state only.
- Ground states will have

1<sup>st</sup> \* Maximum value of  $S$

2<sup>nd</sup> \* Maximum value of  $L$  within that  $S$

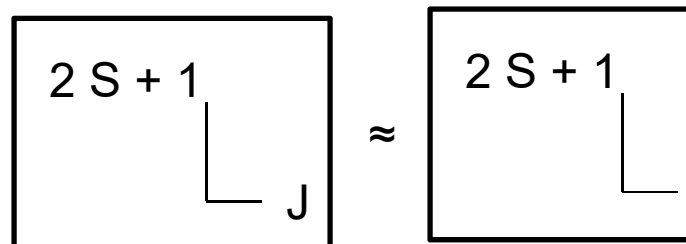
# Russell Saunders Coupling (L-S Coupling) for Ground States

Configuration => Term Symbol

$$\sum m_L = \text{max. } M_L \text{ or } L$$

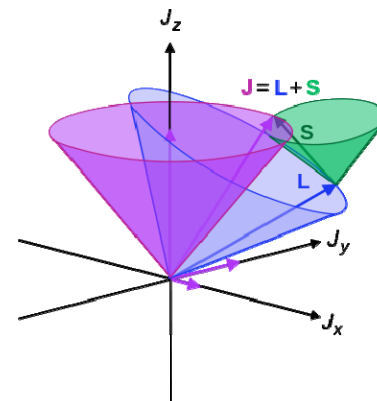
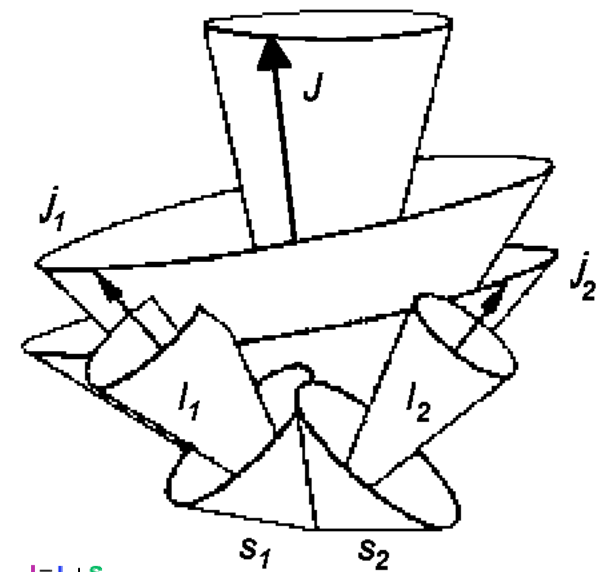
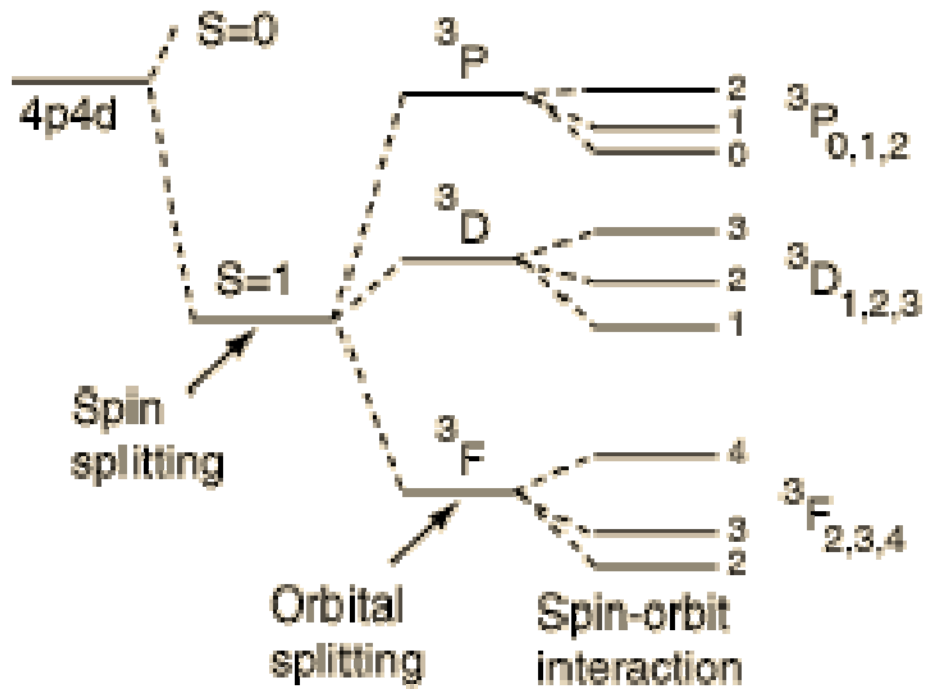
$$\sum m_S = M_S \text{ or } S$$

*Spin  
Multiplicity*



# unpaired $e^-$	$S$	$2S + 1$		$L$	State
1	1/2	2	⇒ double t	0	⇒ <b>S</b>
2	1	3	⇒ triplet	1	⇒ <b>P</b>
3	3/2	4	⇒ quartet	2	⇒ <b>D</b>
4	2	5	⇒ pentet	3	⇒ <b>F</b>
				4	⇒ <b>G</b>

# Russell Saunders Coupling: Spin/Orbit Coupling



## *Lecture 5 362 January 25, 2019*

- *Effect of Effective Nuclear Charge on Periodic Table Trends*
- *Electronegativity*