

## Chemistry 475

Atoms and Elements

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## Challenges of Chemistry

- Organize the Chemical and Physical Properties of Matter
- Develop Means to Control the Physical and Chemical Properties of Matter
- Understand how Matter and Energy interact with Each Other
- Derive a Self-Consistent Model for the Universe at its most Accessible Level

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## Organization of Chemical and Physical Properties of Matter

- Ancient Greeks believed that there were only Four Elements
- Modern Chemistry recognizes more than 100 Elements
  - Pure substances that can not be broken down by chemical means
  - Form infinite number of compounds
  - Only about 30 are needed for living organisms

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## Periodic Table of the Elements

Alkali Metals, Alkaline Earth Metals, Transition Metals, p-Block Metals, Lanthanides, Actinides, Chalcogens, Pnictogens, Halogens, Noble Gases

<http://www.webelements.com/webelements/scholar/index.html>

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## Properties of Groups

- Group 1
  - Most salts are soluble in water
  - Halides:  $MX$
  - Oxides:  $M_2O$
  - Hydrides:  $HM$
- Group 2
  - Many salts are water soluble, but not all
  - Halides:  $MX_2$
  - Oxides:  $MO$
  - Hydrides:  $H_2M$

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## Properties of Groups

- p-Block Metals
  - Solubility varies widely
  - Lighter members form ions of maximum valence. Examples:  $AlCl_3$ ,  $GaCl_3$
  - Heavier members most stable ion is that with charge two less than maximum (*inert pair effect*). Examples:  $SnCl_2$ ,  $SnCl_4$
- Noble Gases
  - Essentially inert, but compounds of Xe with F and O are known

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## Challenges of Chemistry

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## Derivation of a Model for the Chemical Universe

- Atomic Theory
  - Stoichiometry
- Kinetic-Molecular Theory
  - Kinetics
  - Thermodynamics
- Quantum Theory
  - Bonding
  - Spectroscopy and magnetism
  - Statistical thermodynamics

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## Quantum Theory

- Central to Quantum Mechanics is the *Wavefunction* ( $\psi$ )
  - Contains information on position and energy
  - Mathematically  $\psi$  must be a continuous, single-valued function which equals 0 at infinity and has a continuous first derivative
- Measurable Quantities (*Scalars*) are retrieved from  $\psi$  using an *Operator*

$$\hat{O}\psi = s\psi$$

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## Hamiltonian Operator

- Extracts Energy (Schrödinger Equation)
  - For the hydrogen atom ( $n = 1$ )

$$\hat{H}_0 = \sum_{i=1}^n \left[ \frac{-\hbar^2 \nabla_i^2}{2\mu} - \frac{Ze^2}{r_i} \right]$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad \mu = \frac{m_e m_N}{m_e + m_N} \approx m_e \quad e' = \frac{e}{\sqrt{4\pi\epsilon_0}}$$

- The  $\psi$  that are Solutions (*Orbitals*) are in the form:

$$\psi(r, \theta, \phi) = R_{n,\ell}(r) Y_{\ell, m_\ell}(\theta, \phi)$$

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## Quantum Numbers

- Angular Momentum of Electron in the Hydrogen Atom is Quantized ( $\ell$  and  $m_\ell$ )
- *Principle Quantum Number* ( $n$ )
  - Distance from electron to nucleus
  - Values:  $n = 1$  (K shell),  $2$  (L shell),  $3$  (M shell),  $4$  (N shell),  $5$  (O shell), etc.
  - Determines orbital energy in absence of magnetic field or other electrons

$$E_n = -\frac{hc \mathfrak{R}}{n^2} \quad hc \mathfrak{R} = \frac{Z^2 \mu e^4}{32 \pi^2 \epsilon_0^2 \hbar^2}$$

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## Quantum Numbers

- *Angular Quantum Number* ( $\ell$ )
  - Describes the *orbital angular momentum*
  - Values  $\ell = 0, 1, 2 \dots n - 1$
  - Trivial Names:  $\ell = 0$  (s),  $\ell = 1$  (p),  $\ell = 2$  (d),  $\ell = 3$  (f), etc. (no j!)
  - Magnitude of orbital angular momentum
 
$$\hbar \sqrt{\ell(\ell + 1)}$$
  - Increasing angular momentum leads to distortion of electron density (orbital “shape”)

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## Quantum Numbers

- **Magnetic Quantum Number ( $m_\ell$ )**
  - z-Component of orbital angular momentum
  - Values:  $m_\ell = 0, \pm 1, \pm 2 \dots \pm \ell$
  - z-Component =  $m_\ell \hbar$
  - Orbitals with same  $\ell$  can have different z-components and different orientations (one orientation for s orbitals, three for p orbitals, five for d orbitals and seven for f orbitals, etc.)

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## Relativistic Treatment

- Adds the Electron's Intrinsic Angular Momentum (**Spin, S**)
  - Value:  $S = 1/2$
  - z-Component:  $m_s = \pm 1/2$
- Electron in an Atom experiences Orbital Angular Momentum and Spin Angular Momentum!
  - Spin-orbit coupling
  - Important in multi-electron systems

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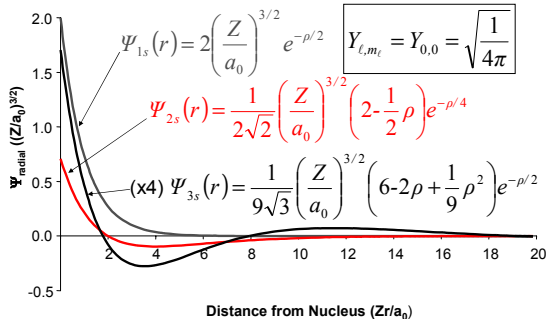
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## A Closer Look at s Orbitals




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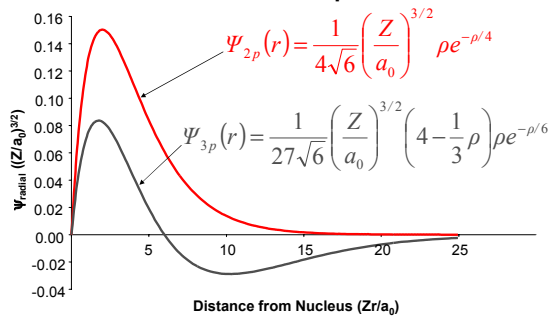
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## A Closer Look at p Orbitals




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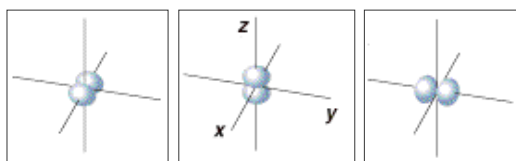
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## A Closer Look at p Orbitals



$p_x$  orbital

$p_z$  orbital

$p_y$  orbital

$$-\frac{1}{\sqrt{2}}(Y_{1,+1} - Y_{1,-1})$$

$$Y_{1,0}$$

$$\frac{i}{\sqrt{2}}(Y_{1,+1} + Y_{1,-1})$$

$$\psi_{p_x} = x f(r)$$

$$\psi_{p_z} = z f(r)$$

$$\psi_{p_y} = y f(r)$$

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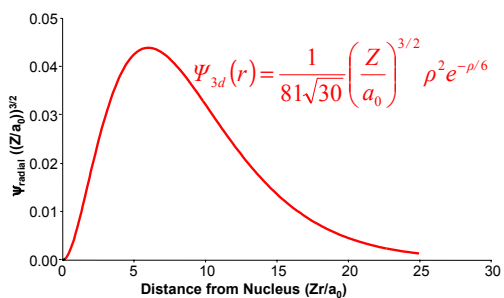
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## A Closer Look at d Orbitals




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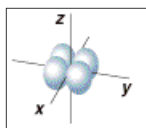
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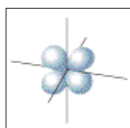
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## A Closer Look at d Orbitals



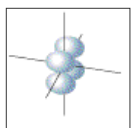
$d_{xy}$  orbital

$$\psi_{d_{xy}} = xy f(r)$$



$d_{yz}$  orbital

$$\psi_{d_{yz}} = yz f(r)$$



$d_{xz}$  orbital

$$\psi_{d_{xz}} = xz f(r)$$

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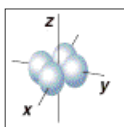
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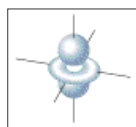
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## A Closer Look at d Orbitals



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

$$\psi_{d_{x^2-y^2}} = \frac{1}{2}(x^2 - y^2) f(r)$$



$d_{z^2}$  orbital

$$\psi_{d_{z^2}} = \frac{1}{2\sqrt{3}}(3z^2 - r^2) f(r) Y_{2,0}$$

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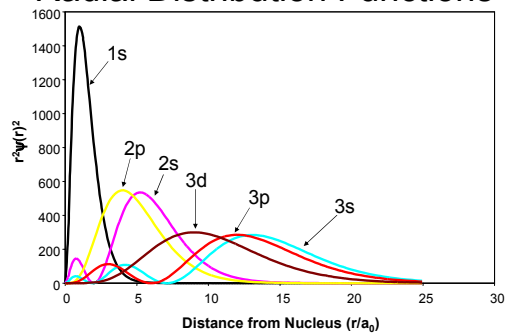
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## Radial Distribution Functions




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## The Multi-Electron Atom

- Need to add Terms to Hamiltonian for
  - Electron-electron repulsion
  - Decrease of Z for outer electrons caused by inner electrons (*shielding*)
  - Spin-orbit coupling and other effects

$$\hat{H} = \hat{H}_0 + \hat{H}_{e^-e^- \text{ repulsion}} + \hat{H}_{\text{spin-orbit}} + \dots$$

$$\hat{H}_0 = \sum_{i=1}^n \left[ \frac{-\hbar^2 \nabla_i^2}{2\mu} - \frac{Z_i^* e^2}{r_i} \right] \quad \hat{H}_{e^-e^- \text{ repulsion}} = \sum_{i=1}^n \sum_{j>i}^n \frac{e^2}{r_{ij}}$$

$$Z_i^* = Z - \sigma_i \quad \hat{H}_{\text{spin-orbit}} = \sum_{i=1}^n \xi_i \hat{L}_i \cdot \hat{S}_i$$

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## Multi-Electron Atoms

- Hamiltonian not Exactly Solvable for more than one Electron because of
  - Indistinguishability of electrons
  - Pauli Exclusion Principle
  - Spin-spin (exchange) interactions
- Make the *Orbital Approximation* and Consider Angular Momentum
  - In absence of electron-electron interactions orbitals would be exact solutions

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## Methods for Coupling Angular Momentum

- Russell-Saunders (L-S) coupling
  - Orbital and spin treated separately
  - Then coupled to get total angular momentum
  - Adequate for  $Z < 30$
- j-j Coupling
  - Couple spin and orbital angular momenta for each electron then couple these total angular momenta
- Reality is Somewhere between Extremes

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## Russell-Saunders Coupling

- Total Orbital Angular Momentum, L
  - Given by  $L = \sum L_i$
  - With  $M_L = \pm L, \pm(L - 1), \pm(L - 2), \dots, 0$
- Total Spin Angular Momentum, S
  - Given by  $S = \sum s_i$  (always positive)
  - With  $M_S = \pm S, \pm(S - 1), \pm(S - 2), \dots, 0$
- Total Angular Momentum, J
  - Values  $J = L + S, L + S - 1, \dots, |L - S|$
  - With  $M_J = \pm J, \pm(J - 1), \pm(J - 2), \dots, 0$

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## Russell-Saunders Coupling

- States described by *Atomic Term Symbols*

$$n^m \Gamma_j$$

- Where
  - n is an integer (for multiple occurrences of same state)
  - m is *Multiplicity* ( $m = 2S + 1$ )

m =	1	2	3	4	5
	singlet	doublet	triplet	quartet	quintet

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## Russell-Saunders Coupling

- $\Gamma$  is a Letter designating Total Orbital Angular Momentum
  - S ( $L=0$ ), P ( $L=1$ ), D ( $L=2$ ), F ( $L=3$ ), G ( $L=4$ ), etc. (not J)
  - Corresponds to old spectroscopic terms
- j is One of the possible values of J
  - Often omitted for light elements

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## Russell-Saunders Coupling

- Reading Term Symbols
  - $4^2P_{1/2}$  is read as “four doublet p one-half”
  - $2^2S_{1/2}$  is read as “doublet s one-half”
  - $4D$  is “quartet d”
- Derivable from *Microstates*
  - Actual arrangement of electrons in orbitals
  - Determining microstates complicated by presence of multiple electrons which lifts degeneracy of states with same  $n$

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## Microstates

- All Possible Arrangement of Electrons within the Orbitals
- A Simple Sorting Problem
$$\text{Number of Microstates} = \frac{n!}{e!h!}$$

$n = \# \text{ orbital sites} = 2 \times \# \text{ orbitals}$   
 $e = \# \text{ electrons to place}$   
 $h = \# \text{ holes} = n - e$

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## Russell-Saunders Coupling

- Example: He
  - Place both electrons in 1s (why not  $1s^12s^1$ ?)
  - Ground state electronic configuration is  $1s^2$

$$\text{Number of Microstates} = \frac{2!}{2!0!} = \frac{2 \cdot 1}{2 \cdot 1 \cdot 1} = 1$$

$$m_\ell = \begin{array}{c} \uparrow \downarrow \\ 0 \quad 0 \end{array} \quad \boxed{\text{Obey Pauli principle and pair electrons.}}$$

$$M_S = +1/2 + -1/2 = 0 \quad M_L = 0 + 0 = 0$$

- Only L with only  $M_L = 0$  is  $L = 0$
- Ground State of He is predicted to be  $1S_0$

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## Russell-Saunders Coupling

- Consider Li with 2s and 2p Degenerate

– Ignore 1s electrons because filled shells and subshells always give  $^1S_0$  and make no contribution to *ground state*

$$\text{Number of Microstates} = \frac{8!}{1!7!} = 8$$

$$\begin{array}{c} \uparrow \\ m_\ell = 0 \end{array}
 \begin{array}{c} \uparrow \\ m_\ell = +1 \end{array}
 \begin{array}{c} \uparrow \\ 0 \end{array}
 \begin{array}{c} \uparrow \\ -1 \end{array}
 \quad M_L = 0 \quad M_S = +1/2$$

$$\begin{array}{c} \downarrow \\ m_\ell = 0 \end{array}
 \begin{array}{c} \uparrow \\ m_\ell = +1 \end{array}
 \begin{array}{c} \uparrow \\ 0 \end{array}
 \begin{array}{c} \uparrow \\ -1 \end{array}
 \quad M_L = 0 \quad M_S = -1/2$$

$$\begin{array}{c} \uparrow \\ m_\ell = 0 \end{array}
 \begin{array}{c} \uparrow \\ m_\ell = +1 \end{array}
 \begin{array}{c} \uparrow \\ 0 \end{array}
 \begin{array}{c} \uparrow \\ -1 \end{array}
 \quad M_L = +1 \quad M_S = +1/2$$

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## Russell-Saunders Coupling

$$\begin{array}{c} \uparrow \\ m_\ell = 0 \end{array}
 \begin{array}{c} \uparrow \\ m_\ell = +1 \end{array}
 \begin{array}{c} \uparrow \\ 0 \end{array}
 \begin{array}{c} \uparrow \\ -1 \end{array}
 \quad M_L = 0 \quad M_S = +1/2$$

$$\begin{array}{c} \uparrow \\ m_\ell = 0 \end{array}
 \begin{array}{c} \uparrow \\ m_\ell = +1 \end{array}
 \begin{array}{c} \uparrow \\ 0 \end{array}
 \begin{array}{c} \uparrow \\ -1 \end{array}
 \quad M_L = -1 \quad M_S = +1/2$$

$$\begin{array}{c} \downarrow \\ m_\ell = 0 \end{array}
 \begin{array}{c} \uparrow \\ m_\ell = +1 \end{array}
 \begin{array}{c} \uparrow \\ 0 \end{array}
 \begin{array}{c} \uparrow \\ -1 \end{array}
 \quad M_L = +1 \quad M_S = -1/2$$

$$\begin{array}{c} \downarrow \\ m_\ell = 0 \end{array}
 \begin{array}{c} \uparrow \\ m_\ell = +1 \end{array}
 \begin{array}{c} \uparrow \\ 0 \end{array}
 \begin{array}{c} \uparrow \\ -1 \end{array}
 \quad M_L = 0 \quad M_S = -1/2$$

$$\begin{array}{c} \downarrow \\ m_\ell = 0 \end{array}
 \begin{array}{c} \uparrow \\ m_\ell = +1 \end{array}
 \begin{array}{c} \downarrow \\ 0 \end{array}
 \begin{array}{c} \downarrow \\ -1 \end{array}
 \quad M_L = -1 \quad M_S = -1/2$$

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## Russell-Saunders Coupling

- Construct a Matrix of  $M_L$  and  $M_S$  showing Number of Times each Combination occurs

$M_L$	+1	1	1	$M_S$	Highest $M_L$ are $\pm 1$ , these belong to a state with $L = 1$
	0	2	2		
	-1	1	1		
		+1/2	-1/2		Highest $M_S$ are $\pm 1/2$ , which belong to a state with $S = 1/2$

The state with  $L = 1$  and  $S = 1/2$  is  $^2P$ .

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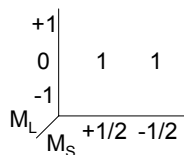
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## Russell-Saunders Coupling



Remove microstates of  $^2P$ .

Highest remaining  $M_L$  is 0, this means  $L = 0$  with corresponding  $M_S = \pm 1/2$ , so  $S = 1/2$ .

This is a  $^2S$  state.

- If  $2s$  and  $2p$  are degenerate can have either a  $^2S$  or a  $^2P$  ground state!

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## Aufbau Principle

- Experimentally Li Ground State is  $^2S$ 
  - Conclude that degeneracy of orbitals with same  $n$  is lifted by electron-electron interactions
- Experimental Energy Ordering of Orbitals in Multi-Electron Systems
  - $1s < 2s < 2p < 3s < 3p < 4s \geq 3d < 4p < 5s \geq 4d < 5p < 6s \approx 4f \approx 5d < 6p \dots$
  - Aufbau Principle

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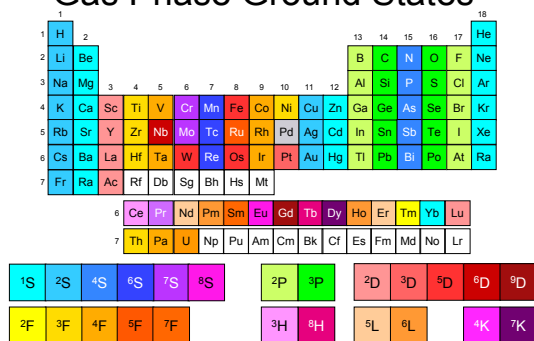
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## Gas Phase Ground States




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## Differences in Potential Energy lifts Orbital Degeneracy

- Shielding ( $Z^* = Z - \sigma$ )
  - Decrease in  $Z$  for electrons in orbitals with higher  $n$
  - *Shielding parameter* ( $\sigma$ ) estimated by Slater's rules
- Penetration Effect
  - Increase in  $Z^*$  in order:  $s > p > d > f$
  - Caused by behavior of  $\psi(r)$  for small  $r$

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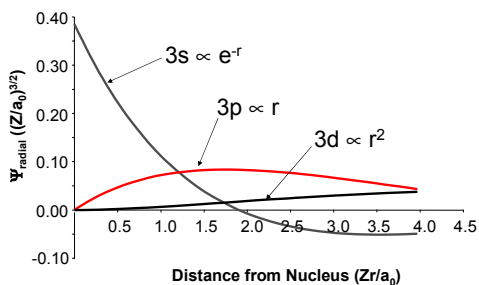
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## Penetration Effect




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## Hund's Rules

- What happens when we fill p Orbitals?
  - Consider C ( $1s^2 2s^2 2p^2$ )
  - For C there are 15 microstates

- 1  $m_\ell = \begin{array}{c} \uparrow \\ +1 \end{array} \begin{array}{c} \uparrow \\ 0 \end{array} \begin{array}{c} \uparrow \\ -1 \end{array} \quad 2p \quad M_L = +1, M_S = +1$
- 2  $m_\ell = \begin{array}{c} \uparrow \\ +1 \end{array} \begin{array}{c} \uparrow \\ 0 \end{array} \begin{array}{c} \uparrow \\ -1 \end{array} \quad 2p \quad M_L = 0, M_S = +1$
- 3  $m_\ell = \begin{array}{c} \uparrow \\ +1 \end{array} \begin{array}{c} \uparrow \\ 0 \end{array} \begin{array}{c} \uparrow \\ -1 \end{array} \quad 2p \quad M_L = -1, M_S = +1$

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### Hund's Rules

$$4 \quad m_\ell = \begin{array}{|c|} \hline \downarrow \\ \hline +1 \\ \hline \end{array} \begin{array}{|c|} \hline \downarrow \\ \hline 0 \\ \hline \end{array} \begin{array}{|c|} \hline \phantom{\downarrow} \\ \hline -1 \\ \hline \end{array} \quad 2p \quad M_L = +1, M_S = -1$$

$$5 \quad m_\ell = \begin{array}{|c|} \hline \downarrow \\ \hline +1 \\ \hline \end{array} \begin{array}{|c|} \hline \phantom{\downarrow} \\ \hline 0 \\ \hline \end{array} \begin{array}{|c|} \hline \downarrow \\ \hline -1 \\ \hline \end{array} \quad 2p \quad M_L = 0, M_S = -1$$

$$6 \quad m_\ell = \begin{array}{|c|} \hline \phantom{\downarrow} \\ \hline +1 \\ \hline \end{array} \begin{array}{|c|} \hline \downarrow \\ \hline 0 \\ \hline \end{array} \begin{array}{|c|} \hline \downarrow \\ \hline -1 \\ \hline \end{array} \quad 2p \quad M_L = -1, M_S = -1$$

$$7 \quad m_\ell = \begin{array}{|c|} \hline \uparrow\downarrow \\ \hline +1 \\ \hline \end{array} \begin{array}{|c|} \hline \phantom{\downarrow} \\ \hline 0 \\ \hline \end{array} \begin{array}{|c|} \hline \phantom{\downarrow} \\ \hline -1 \\ \hline \end{array} \quad 2p \quad M_L = +2, M_S = 0$$

$$8 \quad m_\ell = \begin{array}{|c|} \hline \uparrow \\ \hline +1 \\ \hline \end{array} \begin{array}{|c|} \hline \downarrow \\ \hline 0 \\ \hline \end{array} \begin{array}{|c|} \hline \phantom{\downarrow} \\ \hline -1 \\ \hline \end{array} \quad 2p \quad M_L = +1, M_S = 0$$

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### Hund's Rules

$$9 \quad m_\ell = \begin{array}{|c|} \hline \uparrow \\ \hline +1 \\ \hline \end{array} \begin{array}{|c|} \hline \phantom{\downarrow} \\ \hline 0 \\ \hline \end{array} \begin{array}{|c|} \hline \downarrow \\ \hline -1 \\ \hline \end{array} \quad 2p \quad M_L = 0, M_S = 0$$

$$10 \quad m_\ell = \begin{array}{|c|} \hline \downarrow \\ \hline +1 \\ \hline \end{array} \begin{array}{|c|} \hline \uparrow \\ \hline 0 \\ \hline \end{array} \begin{array}{|c|} \hline \phantom{\downarrow} \\ \hline -1 \\ \hline \end{array} \quad 2p \quad M_L = +1, M_S = 0$$

$$11 \quad m_\ell = \begin{array}{|c|} \hline \phantom{\downarrow} \\ \hline +1 \\ \hline \end{array} \begin{array}{|c|} \hline \uparrow\downarrow \\ \hline 0 \\ \hline \end{array} \begin{array}{|c|} \hline \phantom{\downarrow} \\ \hline -1 \\ \hline \end{array} \quad 2p \quad M_L = 0, M_S = 0$$

$$12 \quad m_\ell = \begin{array}{|c|} \hline \phantom{\downarrow} \\ \hline +1 \\ \hline \end{array} \begin{array}{|c|} \hline \uparrow \\ \hline 0 \\ \hline \end{array} \begin{array}{|c|} \hline \downarrow \\ \hline -1 \\ \hline \end{array} \quad 2p \quad M_L = -1, M_S = 0$$

$$13 \quad m_\ell = \begin{array}{|c|} \hline \downarrow \\ \hline +1 \\ \hline \end{array} \begin{array}{|c|} \hline \phantom{\downarrow} \\ \hline 0 \\ \hline \end{array} \begin{array}{|c|} \hline \uparrow \\ \hline -1 \\ \hline \end{array} \quad 2p \quad M_L = 0, M_S = 0$$

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### Hund's Rules

$$14 \quad m_\ell = \begin{array}{|c|} \hline \phantom{\downarrow} \\ \hline +1 \\ \hline \end{array} \begin{array}{|c|} \hline \downarrow \\ \hline 0 \\ \hline \end{array} \begin{array}{|c|} \hline \uparrow \\ \hline -1 \\ \hline \end{array} \quad 2p \quad M_L = -1, M_S = 0$$

$$15 \quad m_\ell = \begin{array}{|c|} \hline \phantom{\downarrow} \\ \hline +1 \\ \hline \end{array} \begin{array}{|c|} \hline \phantom{\downarrow} \\ \hline 0 \\ \hline \end{array} \begin{array}{|c|} \hline \uparrow\downarrow \\ \hline -1 \\ \hline \end{array} \quad 2p \quad M_L = -2, M_S = 0$$

		1		
+2				
+1	1	2	1	
0	1	3	1	
-1	1	2	1	
-2		1		
	$M_L$	+1	0	-1
		$M_S$		

States arising from two electrons in three p orbitals are:  $^1D$ ,  $^3P$ ,  $^1S$ .

Which one is ground state?

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## Hund's Rules

- Experimentally C's Ground State is  $^3P_0$
- Based on Experimental Data Hund Proposed these Rules
  - Ground state is term with largest S (and largest L)
  - State with minimum J is usually lowest for less than half-filled subshell, but usually highest for greater than half-filled subshell
- Hole Formalism ( $p^2 = p^4$ , etc.)
- Caveat with Excited States

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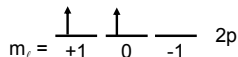
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## Hund's Rules

- Simplification:
  - The ground state can be written by filling all orbitals singly before any are filled doubly, if the orbitals are written in order of decreasing  $m_\ell$
- Example: C



$M_L = +1$  and  $M_S = +1$ , which is a component of  $^3P$ .

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## Spin-Orbit Coupling

- Energy of Spin-Orbit Coupling given by

$$E_{\text{spin-orbit}} = \frac{A\hbar^2}{2} [J(J+1) - L(L+1) - S(S+1)]$$

- A is a constant for each element or ion
- For  $A > 0$ , lowest J is lowest in energy, "regular", usually less than half-filled
- For  $A < 0$ , highest J is lowest in energy, "inverted", usually greater than half-filled

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## Spin-Orbit Coupling

- Example: C with  $^3P$  Ground State

$$E(J=0) = \frac{A\hbar^2}{2} [0(0+1) - 1(1+1) - 1(1+1)] = -2A\hbar^2$$

$$E(J=1) = \frac{A\hbar^2}{2} [1(1+1) - 1(1+1) - 1(1+1)] = -A\hbar^2$$

$$E(J=2) = \frac{A\hbar^2}{2} [2(2+1) - 1(1+1) - 1(1+1)] = +A\hbar^2$$

- Electronic configuration is less than half-filled, expect  $A > 0$  and  $J = 0$  is lowest
- Note that oxygen has a  $^3P_2$  ground state ( $p^4$  is same as  $p^2$ , but  $J$  order is reversed)

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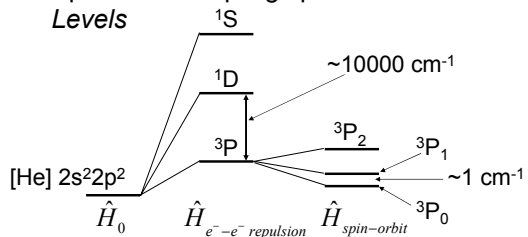
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## Spin-Orbit Coupling

- Electron-Electron Interactions split *Electronic Configurations* into *Terms*
- Spin-Orbit Coupling splits *Terms* into *Levels*




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## Electronic Structure of the Elements

- Using Hund's Rules can derive all Term Symbols for all States of all Elements
- Anomalies
  - Spin-orbit coupling (heavy elements)
  - Spin-spin interactions (partially-filled shells)
  - Spin-pairing energy compared to orbital energy differences
  - Decreasing energy differences for orbitals with increasing  $n$

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## Anomalous Ground States of Copper and Chromium

- Predict
  - Cr [Ar] 4s<sup>2</sup>3d<sup>4</sup> (<sup>5</sup>D)
  - Cu [Ar] 4s<sup>2</sup>3d<sup>9</sup> (<sup>2</sup>D)
- Reality
  - Cr [Ar] 4s<sup>1</sup>3d<sup>5</sup> (<sup>7</sup>S<sub>2</sub>)
  - Cu [Ar] 4s<sup>1</sup>3d<sup>10</sup> (<sup>2</sup>S<sub>1/2</sub>)
- Caused by
  - Spin-pairing energy (Cr, Cu)
  - Spin-spin interactions (Cr)

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## Electronic Anomalies of Heavier Elements

- Arise Primarily as Result of
  - Decreasing energy differences as  $n$  increases
  - Increase in spin orbit coupling
  - Relativistic effects
- Relativistic Effects
  - Contraction of  $s$  orbitals
  - Changes shielding of core  $s$  electrons and properties of outer  $s$  orbitals

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## Trends in Elemental Properties

- All depend on Interplay of  $n$  and  $\sigma$ 
  - $n$  determines size and primary determinant of energy
  - $\sigma$  modifies energy and size
- Down a Group both  $n$  and  $\sigma$  increase
  - $Z^*$  for valence electrons decreases
- Across a Period  $n$  is constant and  $\sigma$  relatively constant within a Subshell
  - $Z^*$  for valence electrons increases

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## Atomic Radius

- Trends
  - Increases down a group
  - Decreases across a period
- Result of opposing Tendencies of  $Z^*$  and  $n$  (Shielding vs. Orbital Size)
  - Down group  $Z^*$  shows small increase
  - Across period  $Z^*$  shows larger increase

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## Ionization Energy ( $IE_n$ )

- General Trends
  - IE increases across a period
  - IE decreases down a group
- Anomalies
  - Filled subshells ( $^1S$  ground state) have higher IE (decreases down group)
  - Half-filled subshells ( $^mS, m \neq 1$ , ground state) have higher IE (decreases down group)
  - Small variation in IE across transition metals and lanthanides

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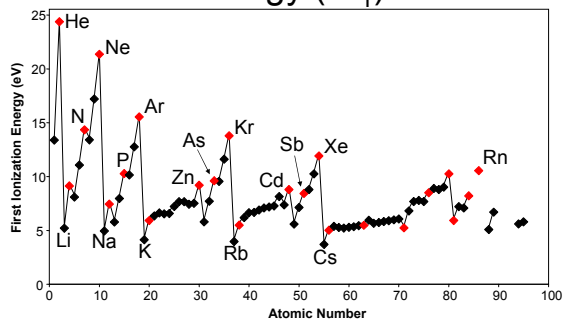
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## Trends in First Ionization Energy ( $IE_1$ )



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## Ionization Energy

- Define Second, Third, etc. IE
  - Removing additional electrons
  - Subsequent IE are always greater than first as result of Coulomb's law
  - Energy of core electrons
- Some Subsequent IE are very Large
  - Example: third IE >> second IE for Mg
  - Disrupting a stable configuration (1S)

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## Electron Affinity (EA<sub>n</sub>)

- General Trends (weaker than for IE)
  - EA decreases down a group
  - EA increases across a period
- Anomalies
  - Group 2: EA<sub>1</sub> ≈ 0, *increases* down group
  - Groups 13 - 17: second period
  - Nitrogen, noble gases: EA<sub>1</sub> < 0
- Can also define subsequent EAs
  - Show similar trends to IE

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## Electronegativity

- Measure of how strongly an Atom pulls Electrons to Itself
  - Pauling Electronegativity
  - Semi-empirical scale based on  $\chi_F = 4.0$
- Absolute (Mullikan) Electronegativity
  - Average "desire" of an atom to accept or donate an electron

$$\chi = \frac{(IE + EA)}{2}$$

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## Hardness

- Measure of the Polarizability of Atom's Electron Cloud
  - Small and/or highly charged  $\Rightarrow$  "hard"
  - Large and/or small charge  $\Rightarrow$  "soft"
- Absolute Hardness
  - Large IE, small EA, large  $\eta \Rightarrow$  "hard"
  - Small IE relative to EA, small  $\eta \Rightarrow$  "soft"

$$\eta = \frac{(IE - EA)}{2}$$

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## Monatomic Ions

- Anions larger than Cations with Same Electronic Configuration
- Size Trends for Ions follow Elemental Trends
- Electronic Configuration can be determined by
  - Follow aufbau principle for anions
  - Reverse aufbau for cations removing electrons in order p, s, d, f

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## Spectroscopy of Multi-Electron Atoms and Ions

- Electron-Electron Interactions cause Electronic Configuration to split into States
  - Ground state and low-lying excited states
- Complete Picture considers all Possible Electron States
- Procedure: if electrons are
  - Equivalent, same as for ground state
  - Non-equivalent, a bit more complicated

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## Spectroscopy of Multi-Electron Atoms and Ions

- For Non-equivalent Electrons, determine Term Symbols for each Electron and then Vector-Couple
  - $S = (S_1 + S_2), (S_1 + S_2 - 1), \dots |S_1 - S_2|$
  - $L = (L_1 + L_2), (L_1 + L_2 - 1), \dots |L_1 - L_2|$
- Example:  $s^1p^1$ 
  - $s^1 \Rightarrow ^2S, p^1 \Rightarrow ^2P (S_1=S_2=1/2, L_1=0, L_2=1)$
  - New  $S = 1, 0$ ; new  $L = 1$
  - Gives states  $^1P$  and  $^3P$

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## Spectroscopy

- Interaction of Light with Electrons, which may be in Presence of a Field
- Electric field  $\Rightarrow$  Stark effect
- Magnetic field  $\Rightarrow$  Zeeman effect
- Photons are Fermions with  $s = 1$ 
  - $m_s = +1$  is left-circularly polarized
  - $m_s = -1$  is right-circularly polarized
- In Absorption Angular Momentum is transferred from a Photon to an Electron

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## Selection Rules

- Not all Transitions Predicted are observed or have the same Intensity
  - Allowed
  - Forbidden
- For Atomic Spectroscopy Selection Rules are
  - $\Delta S = 0$
  - $\Delta L = 0, \pm 1, \Delta \ell = \pm 1$
  - $\Delta J = 0, \pm 1, J = 0 \nrightarrow J = 0$

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## Notation

- In Atomic Spectroscopy Electronic Transitions are denoted
  - Higher energy state  $\leftarrow$  lower energy state (absorption) e. g.  ${}^2P_{1/2} \leftarrow {}^2S_{1/2}$
  - Higher energy state  $\rightarrow$  lower energy state (emission) e. g.  ${}^2P_{1/2} \rightarrow {}^2S_{1/2}$
- This Convention is often ignored and reverse Notation is used!

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## Energy of States

- When Light is absorbed Atom moves between *States*
  - Usually result of moving one electron
  - But must consider all electrons
- Energy of Excited States not easily predicted
  - Assumptions valid in ground state break down in excited states

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## Grotian Diagrams

- Graphical Representation of Spectroscopic Data showing
  - Energies of states
  - Intensities of transitions (line thickness)
- Special Notation
  - Designation "I" is for neutral atom
  - Designation "II" is for the +1 ion
  - Etc.

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