

# Physical Chemistry

## Lecture 20

Russell-Saunders Terms, Hund's Rules,  
Spin-orbit Coupling, Spectroscopy

# Atomic configurations

- ◆ Means of describing the energy situation of a multi-electron system
- ◆ Independent-electron energy is a sum of hydrogenic energies of the electrons
  - Add first-order correction for electron-electron repulsion
    - Combinations of Coulomb repulsion integrals and exchange integrals
- ◆ Wave functions of indistinguishable electrons are antisymmetric combinations of products of one-electron wave functions
  - Slater-type orbitals
- ◆ Configurations may be parsed into **terms**
  - Terms from the same configuration differ in energy because of the contributions of Coulomb and exchange integrals
  - To specify possible states, must determine
    - All terms arising from a particular configuration
    - Relative energies of terms

# Determining Russell-Saunders terms

- ◆ Angular momentum found by adding angular momenta of subsystems
  - Add orbital and spin angular momentum independently to give total orbital angular momentum and total spin
  - Use Unsöld's theorem to simplify determination
- ◆ Specify terms arising from a configuration
  - Use Roman letters for total orbital angular momentum
  - Use superscripts for total spin
  - Apply Pauli's principle to determine whether certain combinations are disallowed

# Terms arising from various configurations

Configuration	S	L	Term
$s^1$	1/2	0	$^2S$
$s^2$	0	0	$^1S$
$s^1s^1$	0 or 1	0	$^1S, ^3S$
$s^1p^1$	0 or 1	1	$^1P, ^3P$
$p^1p^1$	0 or 1	0, 1, or 2	$^1D, ^1S, ^3D, ^3P, ^3S$
$p^2$	0 or 1	0, 1, or 2	$^1S, ^3P, ^1D$

# Example: N-atom configurations

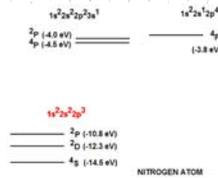
- ◆ Generally find excited configurations by excitation of a **single electron**
- ◆ Ground configuration:  $1s^22s^22p^3$ 
  - Terms:  $^4S, ^2D, ^2P$
- ◆ First excited configuration:  $1s^22s^22p^23s^1$ 
  - Terms:  $^4P, ^2P$
- ◆ Another configuration:  $1s^22s^12p^4$

# Hund's rules

- ◆ Hund discovered relationships that allow prediction of the ordering of terms from a configuration.
  - The ground term of the lowest-energy configuration is the term with maximum spin multiplicity.
  - If several terms have the same maximum multiplicity, then the term of largest orbital angular momentum will be of lowest energy.
- ◆ To determine the ground state, seek the highest spin and the highest orbital angular momentum.

## The Grotrian diagram of N atom

- Energies determined spectroscopically
  - Can estimate by IE energies and Coulomb integrals
- Ordering obeys Hund's rules
- Not all terms from upper configurations shown



## Spin-orbit coupling

- Extra term in the Hamiltonian
- Energy depends on relative orientation of the orbital and spin angular momenta

$$\hat{H}_{so} = \xi \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{\xi}{2} (\hat{J}^2 - \hat{L}^2 - \hat{S}^2)$$

- Arises from magnetic coupling of electronic spin to field due to relative circulation of nuclear charge

$$\hat{H}_{so}(^{2S+1}L_J) = \frac{\xi \hbar^2}{2} [J(J+1) - L(L+1) - S(S+1)](^{2S+1}L_J)$$

## Spin-orbit coupling

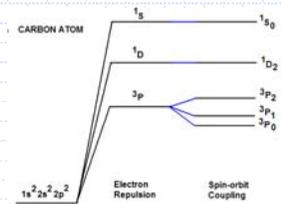
- Energy of states in a term depend on the total angular momentum
- Total angular momentum is combination of orbital and spin angular momenta

$$|L - S| \leq J \leq L + S$$

- Indicate different values of J as a subscript
  - Example:  $^2P$  breaks into  $^2P_{1/2}$  and  $^2P_{3/2}$
  - Spin-orbit contributions:  $E_{so}(^2P_{1/2}) = -\xi \hbar^2$
  - $E_{so}(^2P_{3/2}) = \frac{\xi \hbar^2}{2}$

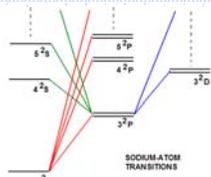
## Example: carbon-atom energy levels

- Sequentially add terms to the energy
  - Electron-electron interaction
  - Spin-orbit coupling
- Carbon ground state is  $1s^2 2s^2 2p^2$ 
  - Three terms
  - Only one split by spin-orbit coupling



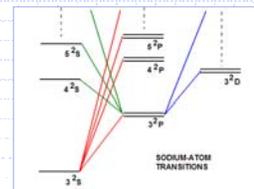
## Spectroscopic transitions

- Absorption or emission of energy measures energy differences
- Only certain transitions possible
- Example: sodium atom spectroscopy



## Spectroscopic selection rules

- $\Delta S = 0$
- $\Delta L = \pm 1$
- $\Delta J = 0, \pm 1$ 
  - $J=0 \leftrightarrow J'=0$  not allowed
- Laporte's rule: Transitions among terms derived from the same configuration are forbidden.



## Forbidden transitions

- ◆ Transitions that occur in violation of these rules are called **forbidden transitions**.
- ◆ States are not pure, so there is always some violation of rules.
- ◆ States labeled as triplets may have some singlet quality
  - Also true of other states
- ◆ Example: Hg atom
  - Strong  $7\ ^1S_0 \leftrightarrow 6\ ^3P_1$  transition

## Summary

- ◆ Terms arise from configurations
  - Labeled in the Russell-Saunders scheme by orbital and spin angular momentum
- ◆ Presence of spin-orbit coupling changes the energy
  - Labeled by J
- ◆ Spectroscopic transitions determine energy differences
  - Spectroscopic selection rules determine connectivity of possible state
  - Forbidden transitions sometimes occur
    - ◆ Transitions that nominally violate the spectroscopic selection rules