

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

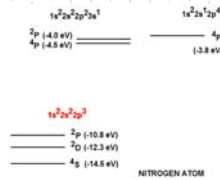
- ◆ Generally find excited configurations by excitation of a **single electron**
- ◆ Ground configuration: $1s^22s^22p^3$
 - Terms: $^4S, ^2D, ^2P$
- ◆ First excited configuration: $1s^22s^22p^23s^1$
 - Terms: $^4P, ^2P$
- ◆ Another configuration: $1s^22s^12p^4$

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

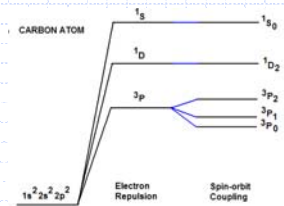
- Energy of states in a term depend on the total angular momentum
- Total angular momentum is combination of orbital and spin angular momenta

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

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

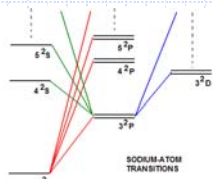
Example: carbon-atom energy levels

- 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



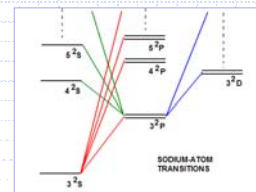
Spectroscopic transitions

- 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