Lecture 31 — Term Symbols & Hund's Rules

Reading: Engel 4th ed., Chapter 11 (Sections 11.1–11.3)

Learning Objectives

- Determine the total orbital angular momentum L, total spin S, and total angular momentum J for a multi-electron configuration
- Construct term symbols $^{2S+1}L_J$
- Apply Hund's rules to identify the ground-state term
- Enumerate all possible terms for common electron configurations

1. Angular Momentum Coupling

For a multi-electron atom, individual angular momenta couple to give totals. Under **Russell-Saunders (LS) coupling** (valid for light atoms):

$$\hat{L} = \sum_i \hat{l}_i, \quad \hat{S} = \sum_i \hat{s}_i, \quad \hat{J} = \hat{L} + \hat{S}$$

Total Orbital Angular Momentum

$$L = |l_1 - l_2|, |l_1 - l_2| + 1, \ldots, l_1 + l_2$$

$$|L| = \hbar\sqrt{L(L+1)}, \quad M_L = -L, \ldots, +L$$

Total Spin

$$S = |s_1 - s_2|, \ldots, s_1 + s_2$$

For two electrons: $S = 0$ (singlet) or $S = 1$ (triplet).

Total Angular Momentum

$$J = |L - S|, |L - S| + 1, \ldots, L + S$$

2. Term Symbols

$$^{2S+1}L_J$$

Component	Meaning
$2S + 1$	Spin multiplicity (number of M_S values)
L	Total orbital angular momentum (letter: $S = 0$, $P = 1$, $D = 2$, $F = 3$, ...)
J	Total angular momentum quantum number

Examples

Term	S	L	J	Multiplicity
$^1S_0$	0	0	0	Singlet
$^3P_2$	1	1	2	Triplet
$^2D_{3/2}$	1/2	2	3/2	Doublet
$^4F_{3/2}$	3/2	3	3/2	Quartet

> [!NOTE] **Concept Check 31.1** In the term symbol $^{2S+1}L_J$, what does the superscript $2S + 1$ represent? If $S = 1$, how many possible values can the magnetic spin quantum number M_S take?

3. Finding Terms for a Configuration

Method: Microstate Counting

For carbon ($2p^2$):

1. List all possible (m_l, m_s) assignments for 2 electrons in the p subshell
2. Obey Pauli exclusion (no two electrons with same m_l and m_s)
3. Tabulate $M_L = \sum m_l$ and $M_S = \sum m_s$ for each microstate
4. Extract terms from the M_L, M_S table

Carbon $2p^2$ Terms

Total microstates: $\binom{6}{2} = 15$

The 15 microstates decompose into:

^1S_0, \quad ^1D_2, \quad ^3P_{0,1,2}

Count check: $1 + 5 + (1 + 3 + 5) = 15$ ✓

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4. Hund's Rules

For the **ground state** of a given configuration:

Rule 1 — Maximize S

The term with the **largest spin multiplicity** $(2S + 1)$ is lowest in energy.

Physical basis: Parallel spins → antisymmetric spatial wavefunction → electrons avoid each other → lower repulsion (exchange stabilization).

Rule 2 — Maximize L (for same S)

Among terms with the same S, the one with **largest L** is lowest.

Physical basis: Higher L means electrons orbit in the same direction → more effectively avoid each other.

Rule 3 — J value (for same S and L)

- Subshell **less than half full**: lowest J is ground state ($J = |L - S|$)
- Subshell **more than half full**: highest J is ground state ($J = L + S$)
- Subshell **exactly half full**: $L = 0$, so $J = S$ (only one possibility)

Carbon Ground State

^3P: $S = 1, L = 1$ → $J = 0, 1, 2$

$2p^2$ is less than half full → ground state is $^3P_0$.

> [!NOTE] **Concept Check 31.2** Describe the physical reason behind Hund's first rule (maximizing S). How does a higher total spin affect the spatial distribution of electrons and their mutual repulsion?

5. Ground-State Terms Across the Periodic Table

Atom	Config	Ground Term	Rule applied
H	$1s^1$	$^2S_{1/2}$	One electron
He	$1s^2$	$^1S_0$	Filled shell
C	$2p^2$	$^3P_0$	Rules 1–3
N	$2p^3$	$^4S_{3/2}$	Half-filled: max S
O	$2p^4$	$^3P_2$	More than half: max J
F	$2p^5$	$^2P_{3/2}$	One hole
Fe	$3d^6$	$^5D_4$	Rules 1–3

Key Equations Summary

Equation	Expression
Term symbol	$^{2S+1}L_J$
Total L range	$\|l_1 - l_2\| \le L \le l_1 + l_2$
Total S range	$\|s_1 - s_2\| \le S \le s_1 + s_2$
Total J range	$\|L - S\| \le J \le L + S$
Hund's rules	Max S → Max L → Min/Max J
Microstates	$\binom{2(2l+1)}{N_e}$

Recent Literature Spotlight

This comprehensive review covers L–edge X-ray absorption spectroscopy (XAS) of first-row transition metals and its interpretation using ligand field multiplet theory. L–edge spectra probe 2p → 3d transitions, making them sensitive to the d-orbital splitting, electronic configuration, and oxidation state of metal centres — the same crystal field parameters ($10Dq$, Racah B and C) taught in this lecture.

Practice Problems

1. **Term symbols.** Find all possible term symbols for the $3d^2$ configuration (e.g., Ti). Identify the ground-state term.

2. **Equivalent electrons.** Show that a filled subshell always gives $^1S_0$. (Hint: what are M_L and M_S for a full subshell?)

3. **Ground-state terms.** Determine the ground-state term symbol for (a) V ($[Ar]\,3d^3\,4s^2$), (b) Co ($[Ar]\,3d^7\,4s^2$), (c) Cl ($[Ne]\,3s^2\,3p^5$).

Next lecture: Spin-Orbit Coupling & Fine Structure