

Lecture 33 — Atomic Spectroscopy & Selection Rules

Reading: Engel 4th ed., Chapter 11 (Sections 11.6–11.8)

Learning Objectives

- State and apply the selection rules for multi-electron atoms ($\Delta L, \Delta S, \Delta J$)
 - Interpret Grotrian diagrams for multi-electron atoms
 - Predict allowed and forbidden transitions from term symbols
 - Describe the features of atomic emission and absorption spectra
 - Explain the singlet-triplet distinction in helium and its spectroscopic implications
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1. Selection Rules for Multi-Electron Atoms

Electric Dipole Selection Rules (LS coupling)

$$\Delta S = 0, \quad \Delta L = 0, \pm 1, \quad \Delta J = 0, \pm 1 \text{ (but not } J = 0 \rightarrow J = 0 \text{)}$$

$$\Delta M_J = 0, \pm 1$$

Additionally, for a single-electron transition: $\Delta l = \pm 1$ (the electron that "jumps" still must change l by 1).

Physical Justification

- $\Delta S = 0$: the photon carries no spin; it cannot flip electron spin
- $\Delta L = 0, \pm 1$: from the triangle rule for coupling photon angular momentum ($l = 1$) with the atom
- $\Delta J = 0, \pm 1$: from the triangle rule for J

Forbidden Transitions

Transitions violating these rules are "**forbidden**" — they can still occur but at rates $\sim 10^6$ times slower (via magnetic dipole, electric quadrupole, or spin-orbit-induced mixing).

[!NOTE] **Concept Check 33.1** Explain why $\Delta S = 0$ is a strict selection rule for electric dipole transitions. What is it about the interaction between light and the atom that makes spin-flips highly unlikely?

2. Helium: Singlet-Triplet Separation

Two "Independent" Systems

Because $\Delta S = 0$, singlet ($S = 0$) and triplet ($S = 1$) states of helium form **separate spectral systems** with no electric dipole transitions between them.

Historically: "**parahelium**" (singlets) and "**orthohelium**" (triplets) — once thought to be different elements!

Singlet States

$^1S_0, ^1P_1, ^1D_2, \dots$ — only one M_S value \rightarrow single lines

Triplet States

$^3S_1, ^3P_{0,1,2}, ^3D_{1,2,3}, \dots$ — three M_S values \rightarrow fine structure multiplets

The Metastable $2\text{p}^1\text{D}_2$ State

The $2\text{p}^1\text{D}_2$ state cannot decay to $1\text{s}^1\text{S}_0$ because:

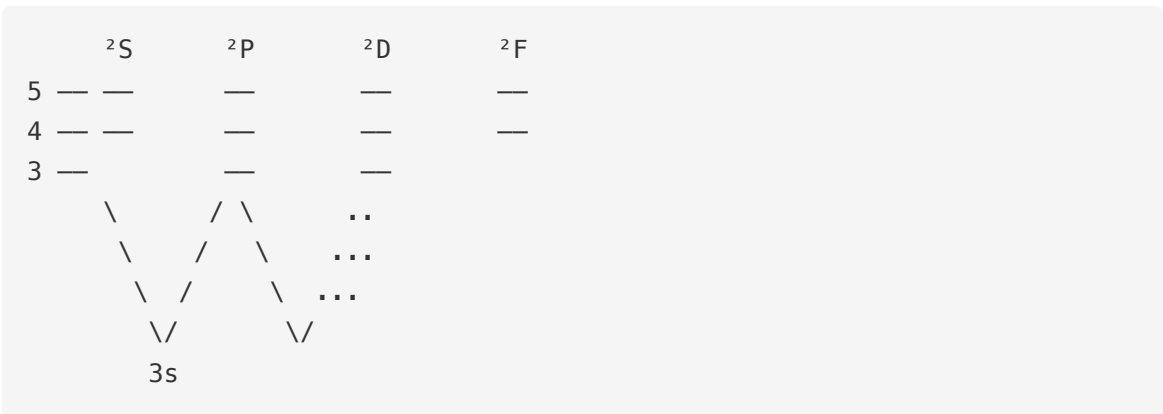
- $\Delta S = 1$ (forbidden)
- $\Delta L = 0$ (allowed but $S = s$)

This makes it **metastable** with a lifetime of ~ 7900 s (> 2 hours!) — compared to $\sim 10^{-8}$ s for allowed transitions.

[!NOTE] **Concept Check 33.2** Why did early scientists believe that "parahelium" and "orthohelium" were two different gases? How does the $\Delta S = 0$ selection rule explain

the lack of transitions between singlet and triplet states?

- Columns: different L values (S, P, D, F, \dots)
- Separate panels: different multiplicities (singlets, doublets, triplets)
- Allowed transitions: arrows connecting terms following selection rules



- **Sharp:** $n_l^2S \rightarrow 3_l^2P$
- **Principal:** $n_l^2P \rightarrow 3_l^2S$ (includes the D-line)
- **Diffuse:** $n_l^2D \rightarrow 3_l^2P$
- **Fundamental (Bergmann):** $n_l^2F \rightarrow 3_l^2D$

For alkali metals (one valence electron outside a closed core):

$$E_{n,l} = -\frac{R_H}{(n-\delta_l)^2}$$

where δ_l is the **quantum defect** — larger for s electrons (more penetrating) than for d or f electrons:

Li	δ_s	δ_p	δ_d
	0.41	0.04	0.00

Na	δ_s	δ_p	δ_d
	1.37	0.88	0.01

5. X-Ray Spectroscopy

Characteristic X-Rays

When a high-energy electron knocks out a core electron (e.g., $1s$), an outer electron fills the vacancy, emitting an X-ray photon.

Moseley's Law (1913):

$$\sqrt{\nu} = a(Z - b)$$

where a and b are constants for each spectral series. This established that **atomic number** (not atomic weight) determines chemical identity.

X-Ray Lines

Transition	Name	Typical energy
$L \rightarrow K$	K_α	keV range
$M \rightarrow K$	K_β	Slightly higher
$M \rightarrow L$	L_α	Lower energy

Selection rules still apply within each shell.

Key Equations Summary

Equation	Expression
Selection rules (LS)	$\Delta S = 0, \Delta L = 0, \pm 1, \Delta J = 0, \pm 1$ (not $0 \rightarrow 0$)
Quantum defect	$E = -R_H / (n - \delta_l)^2$
Moseley's law	$\sqrt{\nu} = a(Z - b)$

Recent Literature Spotlight

"Radiative Lifetimes and Transition Probabilities of Vanadium and Chromium Ions"

A. Kramida, G. Nave, *Physical Review A*, **2023**, 109, 022813. [DOI](#)

State-of-the-art measurements of radiative lifetimes and oscillator strengths for transition-metal ions require careful accounting of electronic configuration mixing and term symbol assignments. This paper presents benchmark-quality data for V and Cr ions, using the same Russell-Saunders coupling scheme and selection rules ($\Delta L = \pm 1, \Delta S = 0$) derived in this lecture to classify the observed spectral lines.

Practice Problems

- Allowed transitions.** Which of the following transitions in calcium are allowed? (a) $^1S_0 \rightarrow ^1P_1$, (b) $^3P_1 \rightarrow ^1S_0$, (c) $^3D_2 \rightarrow ^3P_1$, (d) $^1D_2 \rightarrow ^1S_0$, (e) $^3P_0 \rightarrow ^3P_1$.
- Sodium spectrum.** The first four lines of the principal series of sodium (transitions $n, ^2P_{1/2,3/2} \rightarrow 3, ^2S_{1/2}$) are observed at 589.0/589.6, 330.2/330.3, 285.3/285.3, and 268.0/268.0 nm. Why does the doublet splitting decrease for higher n ?
- Moseley's law.** The K_α X-ray frequencies for several elements are: Ti ($Z = 22, \nu = 1.09 \times 10^{18}$ Hz), Fe ($Z = 26, \nu = 1.65 \times 10^{18}$ Hz), Cu ($Z = 29, \nu = 2.18 \times 10^{18}$ Hz). Verify Moseley's law by plotting $\sqrt{\nu}$ vs. Z , and determine the screening constant b .

Next week: The Chemical Bond in Diatomic Molecules