Lecture 32 — Spin-Orbit Coupling & Fine Structure

Reading: Engel 4th ed., Chapter 11 (Sections 11.4–11.5)

Learning Objectives

- Explain the physical origin of spin-orbit coupling
- Calculate spin-orbit energy corrections for hydrogen-like atoms
- Interpret fine structure in atomic spectra
- Distinguish between LS (Russell-Saunders) and jj coupling
- Apply selection rules that include J

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1. Spin-Orbit Interaction

Physical Origin

An electron orbiting a nucleus "sees" the nucleus as a moving charge — creating a magnetic field in the electron's rest frame. This field interacts with the electron's magnetic spin moment.

$\hat{H}_{SO} = \xi(r)\,\hat{L} \cdot \hat{S}$

where $\xi(r)$ is the **spin-orbit coupling constant**, which increases rapidly with Z:

$\xi \propto Z^4$

This is why spin-orbit effects are small for light atoms (C, N, O) but large for heavy atoms (Pb, Bi, actinides).

> [!NOTE] **Concept Check 32.1** Spin-orbit coupling strength ξ is proportional to Z^4. Qualitatively, why would a larger nuclear charge Z lead to a stronger interaction between the electron's spin and its orbital motion?

Energy Correction

Using $\hat{J} = \hat{L} + \hat{S}$:

$\hat{L} \cdot \hat{S} = \frac{1}{2}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2)$

$\langle \hat{L} \cdot \hat{S} \rangle = \frac{\hbar^2}{2}[J(J+1) - L(L+1) - S(S+1)]$

The spin-orbit energy correction:

$$\boxed{E_{SO} = \frac{A}{2}[J(J+1) - L(L+1) - S(S+1)]}$$

where A is the spin-orbit coupling parameter for the specific term.

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2. Fine Structure

Spin-orbit coupling splits each ${}^{2S+1}L$ term into J levels. This splitting produces **fine structure** in atomic spectra.

Example: Carbon ${}^3P$ Term

$L = 1$, $S = 1$ → $J = 0, 1, 2$

$E({}^3P_J) = E_0 + \frac{A}{2}[J(J+1) - 1(2) - 1(2)]$

J	$J(J+1)$	$E - E_0$
0	0	$-2A$
1	2	$-A$
2	6	A

For carbon ($2p^2$, less than half-filled): $A > 0$, so $J = 0$ is lowest → ground state ${}^3P_0$. ✓

Landé Interval Rule

The energy spacing between adjacent J levels is proportional to the larger J:

$E(J) - E(J-1) = AJ$

This can be used to determine A experimentally.

> [!NOTE] **Concept Check 32.2** The Landé interval rule states that $E(J) - E(J-1) = AJ$. If A is positive, which value of J will correspond to the lowest energy state for a given term?

Example: Sodium D-line Doublet

The sodium "D line" at 589 nm is actually a **doublet**:

- D_1: ${}^2P_{1/2} \to^2 S_{1/2}$ at 589.59 nm
- D_2: ${}^2P_{3/2} \to^2 S_{1/2}$ at 589.00 nm

The splitting (0.59 nm, 17 cm^{-1}) arises from spin-orbit coupling in the ${}^2P$ state.

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3. LS vs. jj Coupling

LS Coupling (Russell-Saunders)

Valid for light atoms ($Z \lesssim 30$):

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

Good quantum numbers: L, S, J, M_J

jj Coupling

For heavy atoms ($Z \gtrsim 70$), spin-orbit coupling for individual electrons is stronger than electron-electron repulsion:

$$\hat{j}_i = \hat{l}_i + \hat{s}_i, \quad \hat{J} = \sum \hat{j}_i$$

Good quantum numbers: j_1, j_2, J, M_J (but not L or S individually)

Intermediate Coupling

Most atoms fall in between — neither scheme is perfect, and configuration interaction mixes terms. Numerical computation is required.

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4. Zeeman Effect (Brief)

In an external magnetic field B, each J level splits into $2J+1$ levels ($M_J = -J, \ldots, +J$):

$$E_{M_J} = g_J \mu_B B\, M_J$$

where g_J is the **Landé g-factor**:

$$g_J = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$$

and $\mu_B = e\hbar/(2m_e) = 9.274 \times 10^{-24}$ J/T is the Bohr magneton.

Key Equations Summary

Equation	Expression
Spin-orbit energy	$E_{SO} = \frac{A}{2}[J(J+1) - L(L+1) - S(S+1)]$
Landé interval rule	$E(J) - E(J-1) = AJ$
Landé g-factor	$g_J = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$
Zeeman splitting	$E_{M_J} = g_J \mu_B B\, M_J$
SO coupling strength	$\xi \propto Z^4$

Recent Literature Spotlight

"Skyrmion Hall Effect in Altermagnets" *Z. Jin, Z. Zeng, Y. Cao, P. Yan*, Physical Review Letters, **2024**, 133, 196701. DOI

Altermagnets — a recently discovered class of collinear magnets with spin-split bands but zero net magnetization — exhibit novel spin-orbit-driven phenomena. This paper shows that the skyrmion Hall effect in altermagnets arises from a hidden gauge field tied to the spin-orbit interaction. The spin-orbit coupling that drives this physics is the same $\hat{H}_{SO} = \xi \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ operator treated in this lecture.

Practice Problems

1. **Fine structure.** The ^3P term of silicon ($3p^2$) has levels at: $^3P_0$ = 0 cm⁻¹, $^3P_1$ = 77.1 cm⁻¹, $^3P_2$ = 223.2 cm⁻¹. (a) Verify the Landé interval rule. (b) Determine A.

2. **Sodium D-line.** Calculate the Landé g-factors for the $^2S_{1/2}$, $^2P_{1/2}$, and $^2P_{3/2}$ states of sodium.

3. **Heavy atom.** Explain qualitatively why spin-orbit coupling in lead ($Z = 82$) is much larger than in carbon ($Z = 6$), and why LS coupling is a poor description for Pb.

Next lecture: Atomic Spectroscopy & Selection Rules