Lecture 30 — Electron Spin, Pauli Exclusion & the Aufbau Principle

Reading: Engel 4th ed., Chapter 10 (Sections 10.6–10.8)

Learning Objectives

- Describe electron spin and the quantum numbers s and m_s
- State the Pauli exclusion principle in terms of the antisymmetry requirement
- Apply the aufbau principle, Hund's rules, and the Pauli principle to predict electron configurations
- Explain shielding, penetration, and the $(n+l)$ rule for orbital filling
- Determine the ground-state configuration of any atom in the periodic table

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1. Electron Spin

Discovery

The Stern-Gerlach experiment (1922) showed that silver atoms are deflected into exactly **two** beams by an inhomogeneous magnetic field — implying a two-valued angular momentum.

Spin Quantum Numbers

Electron spin is an **intrinsic** angular momentum with no classical analog:

Quantity	Symbol	Value
Spin quantum number	s	$1/2$ (always, for electrons)
Spin magnetic quantum number	m_s	$+1/2$ (↑ or α) or $-1/2$ (↓ or β)
Spin angular momentum	$\|\|S\|\|$	$\hbar\sqrt{s(s+1)} = \frac{\sqrt{3}}{2}\hbar$
z-component	S_z	$m_s\hbar = \pm\frac{\hbar}{2}$

Spin Operators

$\hat{S}^2|\alpha\rangle = \frac{3}{4}\hbar^2|\alpha\rangle, \quad \hat{S}_z|\alpha\rangle = +\frac{\hbar}{2}|\alpha\rangle$

$\hat{S}^2|\beta\rangle = \frac{3}{4}\hbar^2|\beta\rangle, \quad \hat{S}_z|\beta\rangle = -\frac{\hbar}{2}|\beta\rangle$

Spin-Orbitals

A complete single-electron state (spin-orbital):

$\chi(\mathbf{x}) = \phi_{nlm_l}(\mathbf{r}) \cdot \sigma(s)$

where $\sigma = \alpha$ or β. Each spatial orbital holds at most **two electrons** (with opposite spin).

> [!NOTE] **Concept Check 30.1** In the Stern-Gerlach experiment, the beam of silver atoms split into two. If the electron spin quantum number s were 1 (instead of 1/2), how many beams would have been observed?

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2. The Pauli Exclusion Principle

Statement (Antisymmetry version)

> The total wavefunction (including spin) for a system of identical fermions (particles with half-integer spin, including electrons) must be **antisymmetric** under exchange of any two particles: $\Psi(\ldots, \mathbf{x}_i, \ldots, \mathbf{x}_j, \ldots) = -\Psi(\ldots, \mathbf{x}_j, \ldots, \mathbf{x}_i, \ldots)$

Consequence

No two electrons can have the **same set of four quantum numbers** (n, l, m_l, m_s). If two electrons occupy the same spatial orbital (n, l, m_l the same), they must have opposite spin.

Maximum per Subshell

Subshell	l	m_l values	Max electrons
s	0	0	2

Subshell	l	m_l values	Max electrons
p	1	$-1, 0, +1$	6
d	2	$-2, \dots, +2$	10
f	3	$-3, \dots, +3$	14

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3. Helium: Singlet and Triplet States

For excited helium ($1s^1 2s^1$), we can construct symmetric and antisymmetric spatial wavefunctions:

Symmetric spatial (paired with antisymmetric spin = singlet): $\psi_+ = \frac{1}{\sqrt{2}}[\phi_{1s}(1)\phi_{2s}(2) + \phi_{1s}(2)\phi_{2s}(1)]$

Antisymmetric spatial (paired with symmetric spin = triplet): $\psi_- = \frac{1}{\sqrt{2}}[\phi_{1s}(1)\phi_{2s}(2) - \phi_{1s}(2)\phi_{2s}(1)]$

The **triplet** ($S = 1$) is lower in energy because:

1. Antisymmetric spatial function → electrons avoid each other → reduced repulsion
2. Additional exchange stabilization ($-K$)

This illustrates **Hund's first rule**.

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4. The Aufbau Principle

Orbital Filling Order

Fill orbitals in order of increasing energy, placing at most 2 electrons per orbital:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < \dots$$

The $(n + l)$ Rule (Madelung)

Orbitals fill in order of increasing $n + l$. For equal $n + l$, lower n fills first.

Hund's Rules (for degenerate orbitals)

1. **Maximize total spin** S: Fill degenerate orbitals singly (with parallel spin) before pairing
2. **Maximize total orbital angular momentum** L: Among states with the same S, the one with highest L is lowest
3. **Spin-orbit coupling**: For less-than-half-filled subshells, lowest J is lowest; for more-than-half-filled, highest J is lowest

> [!NOTE] **Concept Check 30.2** According to the $(n + l)$ rule, which orbital fills first: $4s$ or $3d$? Justify your answer using the sum of n and l.

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5. Electron Configurations

Building Up the Periodic Table

Atom	Z	Configuration	Notes
H	1	$1s^1$	
He	2	$1s^2$	Filled shell
Li	3	$[He]\,2s^1$	
Be	4	$[He]\,2s^2$	
B	5	$[He]\,2s^2\,2p^1$	
C	6	$[He]\,2s^2\,2p^2$	Hund: ↑ ↑ _
N	7	$[He]\,2s^2\,2p^3$	Half-filled: ↑ ↑ ↑
O	8	$[He]\,2s^2\,2p^4$	↑↓ ↑ ↑
F	9	$[He]\,2s^2\,2p^5$	
Ne	10	$[He]\,2s^2\,2p^6$	Filled shell

Notable Exceptions

Atom	Expected	Actual	Reason
Cr	$[Ar]\,3d^4\,4s^2$	$[Ar]\,3d^5\,4s^1$	Half-filled d shell stability

Atom	Expected	Actual	Reason
Cu	$[Ar]\,3d^9\,4s^2$	$[Ar]\,3d^{10}\,4s^1$	Filled d shell stability

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6. Periodic Trends from Quantum Mechanics

Property	Trend across period	Trend down group	QM Explanation
Z_{eff}	Increases	Roughly constant	Imperfect shielding
Atomic radius	Decreases	Increases	Z_{eff} vs. n
IE	Increases	Decreases	Orbital energy vs. size
Electron affinity	Generally increases	Decreases	Same reasoning

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Key Equations Summary

Equation	Expression
Spin angular momentum	$\|S\| = \hbar\sqrt{s(s+1)} = \frac{\sqrt{3}}{2}\hbar$
S_z	$m_s\hbar = \pm\hbar/2$
Max electrons per subshell	$2(2l+1)$
Max electrons per shell	$2n^2$
Antisymmetry requirement	$\Psi(\ldots x_i \ldots x_j \ldots) = -\Psi(\ldots x_j \ldots x_i \ldots)$

Recent Literature Spotlight

"Topological Insulators and Superconductors" *X.-L. Qi, S.-C. Zhang*, Reviews of Modern Physics, **2011**, 83, 1057–1110. DOI

This seminal review explains how the quantum mechanics of electrons in periodic potentials — band theory, taught in this lecture — gives rise to topological insulators: materials that are bulk insulators but have conducting surface states protected by time-reversal symmetry. The topological classification of electronic bands demonstrates that quantum mechanics can produce robust, dissipationless conduction without magnetic fields.

Practice Problems

1. **Electron configurations.** Write ground-state electron configurations for (a) Si, (b) Fe, (c) Br, (d) Ag.
2. **Hund's rule.** For the nitrogen atom ($1s^2 2s^2 2p^3$), show that the ground-state configuration has $S = 3/2$ rather than $S = 1/2$. How many exchange pairs does each configuration have?
3. **Effective nuclear charge.** Using Slater's rules, calculate Z_{eff} for (a) a $2p$ electron in F, (b) a $3d$ electron in Fe. Explain why the $3d$ electron is much more effectively shielded.

Next week: Quantum States for Many-Electron Atoms & Atomic Spectroscopy