

Lecture 27 — The Hydrogen Emission Spectrum & Selection Rules

Reading: Engel 4th ed., Chapter 9 (Sections 9.7–9.8)

Learning Objectives

- Derive the Rydberg formula from the hydrogen energy eigenvalues
 - Identify the Lyman, Balmer, Paschen, and Brackett series and their spectral regions
 - State and justify the selection rules for electric dipole transitions in hydrogen
 - Explain the connection between selection rules and angular momentum conservation
 - Discuss the limitations of the hydrogen model and preview multi-electron effects
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1. The Hydrogen Emission Spectrum

When hydrogen atoms are excited (by electrical discharge, heat, etc.), they emit light at discrete wavelengths. These form the **line spectrum** of hydrogen.

The Rydberg Formula

From $E_n = -13.6 \text{ eV}/n^2$, the photon emitted in a $n_i \rightarrow n_f$ transition has:

$$\tilde{\nu} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right), \quad n_i > n_f$$

where the **Rydberg constant** is:

$$R_H = \frac{\mu e^4}{8\epsilon_0^2 h^3 c} = 109,677 \text{ cm}^{-1}$$

Spectral Series

Series	n_f	n_i	Region	Notable lines
Lyman	1	2, 3, 4, ...	UV	Ly- α (121.6 nm)

Series	n_f	n_i	Region	Notable lines
Balmer	2	3, 4, 5, ...	Visible	H- α (656.3 nm, red), H- β (486.1 nm, cyan)
Paschen	3	4, 5, 6, ...	Near-IR	
Brackett	4	5, 6, 7, ...	IR	
Pfund	5	6, 7, 8, ...	Far-IR	

Series Limit

As $n_i \rightarrow \infty$, the lines converge to the **series limit**:

$$\tilde{\nu}_{\text{limit}} = R_H / n_f^2$$

Beyond this, the spectrum becomes continuous (ionization).

[!NOTE] **Concept Check 27.1** Which series of the hydrogen spectrum—Lyman or Balmer— involves higher energy photons? Explain your answer in terms of the initial and final principal quantum numbers.

2. Selection Rules for Hydrogen

Not all transitions between energy levels are allowed. The electric dipole selection rules for the hydrogen atom are:

$$\Delta l = \pm 1, \quad \Delta m_l = 0, \pm 1$$

There is **no restriction on Δn** (any change in n is allowed).

Physical Justification

A photon carries one unit of angular momentum ($l_{\text{photon}} = 1$). Conservation of angular momentum requires that the atom's angular momentum change by exactly ± 1 :

$$|l_i - 1| \leq l_f \leq l_i + 1, \quad l_f \neq l_i \implies \Delta l = \pm 1$$

Symmetry Justification

The transition dipole moment integral:

$$\mu_{fi} = \langle n_f, l_f, m_f | \hat{\mathbf{r}} | n_i, l_i, m_i \rangle$$

The position operator $\hat{\mathbf{r}}$ has angular parts that transform as $l = 1$ (like the p orbitals). By the triangle rule for angular momentum coupling:

$$\Gamma_{l_f} \otimes \Gamma_1 \otimes \Gamma_{l_i} \supseteq \Gamma_0 \iff \Delta l = \pm 1$$

Allowed and Forbidden Transitions

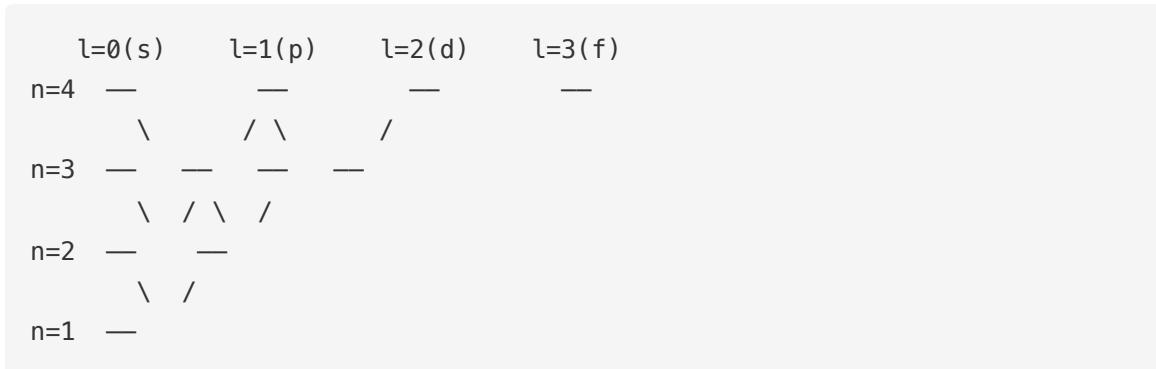
Transition	Δl	Allowed?
$2s \rightarrow 1s$	0	✗ (forbidden)
$2p \rightarrow 1s$	-1	✓
$3s \rightarrow 2p$	+1	✓
$3d \rightarrow 1s$	-2	✗
$3d \rightarrow 2p$	-1	✓
$3s \rightarrow 1s$	0	✗

[!NOTE] **Concept Check 27.2** According to the selection rules ($\Delta l = \pm 1$), is the transition from a $3d$ orbital to a $2s$ orbital allowed? Why or why not?

The $2s$ state is **metastable** — it cannot decay to $1s$ by electric dipole radiation.

3. Grotrian Diagram

A Grotrian (energy level) diagram shows allowed transitions as arrows connecting energy levels, arranged by l :



(arrows only connect adjacent l columns)

4. Emission vs. Absorption

- **Emission:** atom in excited state \rightarrow lower state; photon emitted
- **Absorption:** atom in lower state + photon \rightarrow excited state
- Same selection rules apply to both

In practice, the hydrogen **absorption spectrum** shows primarily the Lyman series (from $n = 1$, since at room temperature virtually all atoms are in the ground state).

5. Beyond Hydrogen: Preview

Fine Structure

The actual hydrogen spectrum shows closely spaced **doublets** due to:

- **Spin-orbit coupling:** interaction between electron spin and orbital angular momentum
- **Relativistic corrections:** electron velocity is significant fraction of c near the nucleus

These effects are small ($\sim \alpha^2 E$, where $\alpha \approx 1/137$ is the fine-structure constant) and will be revisited in Weeks 10–11.

Multi-Electron Atoms

For atoms with more than one electron:

- The n^2 -fold degeneracy is **broken** — energy depends on both n and l
 - Electron-electron repulsion makes the problem analytically unsolvable
 - We need approximate methods (Hartree-Fock, DFT) — coming in Weeks 10 and 13–14
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Key Equations Summary

Equation	Expression
Rydberg formula	$\tilde{\nu} = R_H(1/n_f^2 - 1/n_i^2)$
Rydberg constant	$R_H = 109,677 \text{ cm}^{-1}$
Selection rules	$\Delta l = \pm 1, \Delta m_l = 0, \pm 1$
Photon energy	$E = hc\tilde{\nu}$
Series limit	$\tilde{\nu}_\infty = R_H/n_f^2$

Recent Literature Spotlight

"Tentative Detection of Helium in the Atmosphere of the Hot Jupiter HD 189733 b"

K. Paragas, M. W. McElwain, G. Fu, K. B. Stevenson, et al., The Astronomical Journal, **2022**, 164, 59. [DOI](#)

Metastable helium (2^3S_1) is emerging as a powerful probe of exoplanet atmospheric escape. This study reports the detection of helium absorption at 10,833 Å in the transmission spectrum of a hot Jupiter — matching the $n = 2$ triplet-to-triplet transition of the helium atom. Each spectral line corresponds directly to the hydrogen-like energy levels and selection rules taught in this lecture.

Practice Problems

- 1. Balmer series.** Calculate the wavelengths (in nm) of the first four lines of the Balmer series. In what region of the spectrum does each appear?
 - 2. Selection rules.** For a hydrogen atom in the $4d$ state, list all allowed transitions and the series each belongs to. Which transition produces the longest wavelength photon?
 - 3. Ionization from excited states.** How much energy (in eV) is needed to ionize a hydrogen atom from (a) the ground state, (b) the $n = 2$ state, (c) the $n = 5$ state? What wavelength of light would be needed in each case?
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Next week: Many-Electron Atoms