

# Lecture 27 — The Hydrogen Emission Spectrum & Selection Rules

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

## Learning Objectives

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- 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

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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- $\alpha$ (121.6 nm)

Series	$n_f$	$n_i$	Region	Notable lines
Balmer	2	3, 4, 5, ...	Visible	H- $\alpha$ (656.3 nm, red), H- $\beta$ (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  $\Delta n$**  (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  $\pm 1$ :

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

### 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

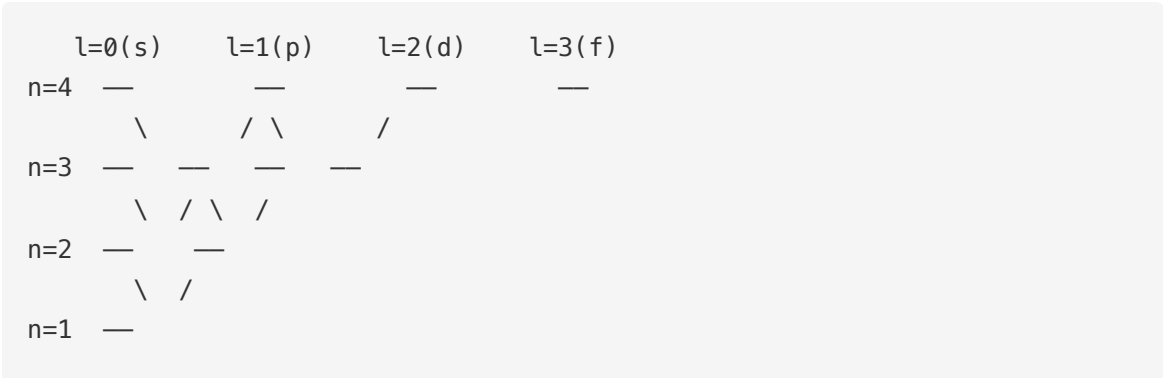
Transition	$\Delta l$	Allowed?
$2s \rightarrow 1s$	0	× (forbidden)
$2p \rightarrow 1s$	−1	✓
$3s \rightarrow 2p$	+1	✓
$3d \rightarrow 1s$	−2	×
$3d \rightarrow 2p$	−1	✓
$3s \rightarrow 1s$	0	×

[!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)

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## 4. Emission vs. Absorption

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- **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).

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## 5. Beyond Hydrogen: Preview

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### 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

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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

- 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?
- 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?
- 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?

*Next week: Many-Electron Atoms*