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Tutorial 1: Atomic Structure — Detailed Answer Key
Academic Year 2026/2027

How to use this sheet: This is not a course summary. It is a **problem-solving accelerator**. Each section answers the question: *"What reflex should I have when I see this type of problem?"* Read it the night before the exam, redo the exercises, and memorise the flash formulas.

1 Universal Calculation Tools

1.1 Working in electron-volts (eV)

Constant	Value
1 eV	1.602×10^{-19} J
h	4.136×10^{-15} eV·s or 6.626×10^{-34} J·s
hc	**1240 eV·nm** or **12400 eV·Å**
R_H	1.097×10^{7} m^{-1}
a_0 (Bohr radius)	0.53 Å $= 5.3 \times 10^{-11}$ m

❖ **Tip: The** 1240 **reflex:** Whenever a question mixes energy (eV) and wavelength (nm), write:

$$\lambda(\text{nm}) = \frac{1240}{\Delta E(\text{eV})} \qquad \Delta E(\text{eV}) = \frac{1240}{\lambda(\text{nm})}$$

Example: A photon of 3.40 eV has a wavelength $\lambda = 1240/3.40 = 365$ nm.

❖ **Caution:** $hc = 1240$ works **only** if ΔE is in eV and λ is in nm.

2 Energy Levels of Hydrogen (Bohr)

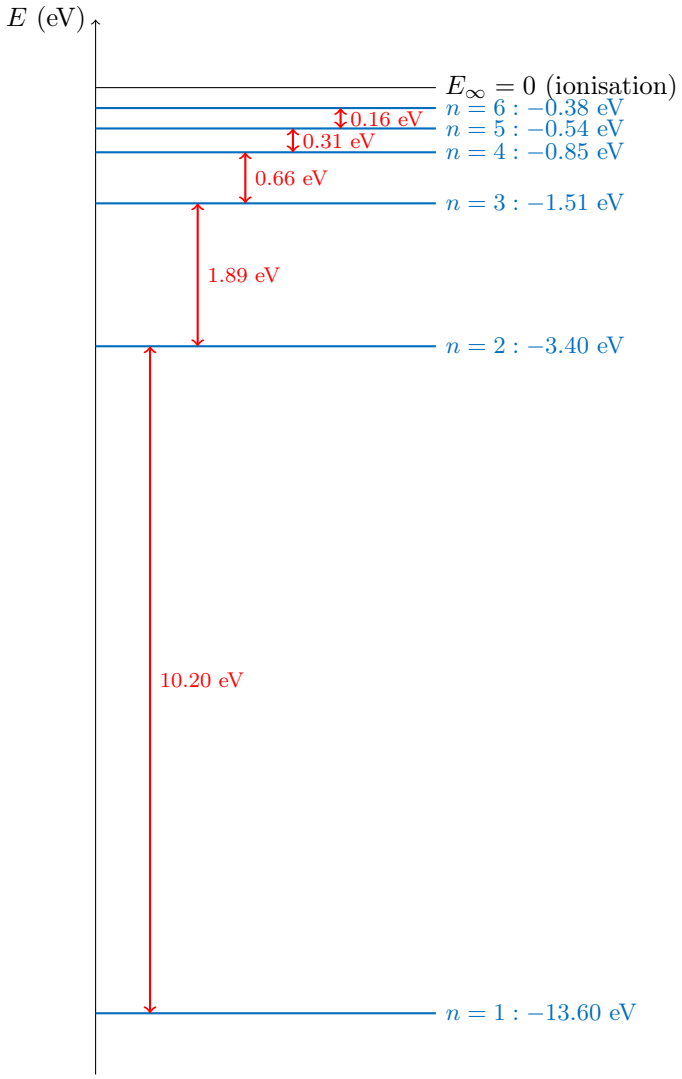
2.1 The Master Formula

$$E_n = -\frac{\mathcal{R}}{n^2} = -\frac{13.6}{n^2} \quad \text{(eV)} \qquad , \qquad r_n = a_0 \cdot n^2 = 0.53 \cdot n^2 \quad \text{(Å)}$$

With: $\mathcal{R}$: Rydberg energy a_0 : Bohr radius

n	E_n (eV)	Gap from previous level
1	-13.60	—
2	-3.40	10.20 eV
3	-1.51	1.89 eV
4	-0.85	0.66 eV
5	-0.54	0.31 eV
∞	0	—

❖ **Tip:** The levels **bunch up** towards the top. The larger n is, the smaller the gap to the next level. This is why spectral lines crowd together near the series limit.



2.2 Ionisation Energy

$$E_{\text{ion}} = E_\infty - E_1 = 0 - (-13.6) = +\mathbf{13.6}\ \text{eV}$$

❖ **Caution: Do not confuse E_1 and E_{ion}!** **($|E_{\text{ion}}| = |E_1|$).**

- $E_1 = -13.6$ eV: this is the **ground state energy** of the hydrogen atom.
  - It is **negative** because the electron is **bound** to the nucleus.
  - The electron is in a **potential well**: energy must be supplied to remove it.
  - The more negative the energy, the more **stable** the state.
- $E_{\text{ion}} = +13.6$ eV: this is the **ionisation energy**.
  - It is **positive** because it is the energy that must be **supplied** to the atom to remove the electron.
  - It is the **work** required to overcome the electrostatic attraction of the nucleus.
  - Once ionised, the electron is free: $E_\infty = 0$ eV.

Relationship between the two:

$$E_{\text{ion}} = |E_1| = 13.6\ \text{eV}$$

Quantity	Symbol	Value	Sign
Ground state energy	E_1	-13.6 eV	Negative (bound state)
Ionisation energy	E_{ion}	$+13.6$ eV	Positive (energy to be supplied)

3 Spectral Series

3.1 The p and n Notation

The classic pitfall: The Rydberg formula uses n_1 and n_2. Students mix them up constantly.
The solution: Use p (final level, **fixed** for the series) and n (initial level, **variable**).

- p: series index (arrival level). $p = 1$ (Lyman), 2 (Balmer), 3 (Paschen)...
- n: line index (departure level). $n = p + 1,\ p + 2,\ p + 3, \ldots$

A transition is written: $\mathbf{n} \to \mathbf{p}$ with $\mathbf{n} > \mathbf{p}$ **always**.

Series	p	**Region**	λ_∞ **(nm)**	λ_i **(nm)**
Lyman	1	UV	91	121
Balmer	2	Visible	364	656
Paschen	3	Near IR	820	1875
Brackett	4	IR	1458	4051
Pfund	5	Far IR	2278	7460

❖ **Tip:** Mnemonic: **LBPBP** — "**L**azy **B**ears **P**lay **B**anjo **P**oorly" (**L**yman, **B**almer, **P**aschen, **B**rackett, **P**fund).

3.2 Classic Pitfalls on Spectral Series

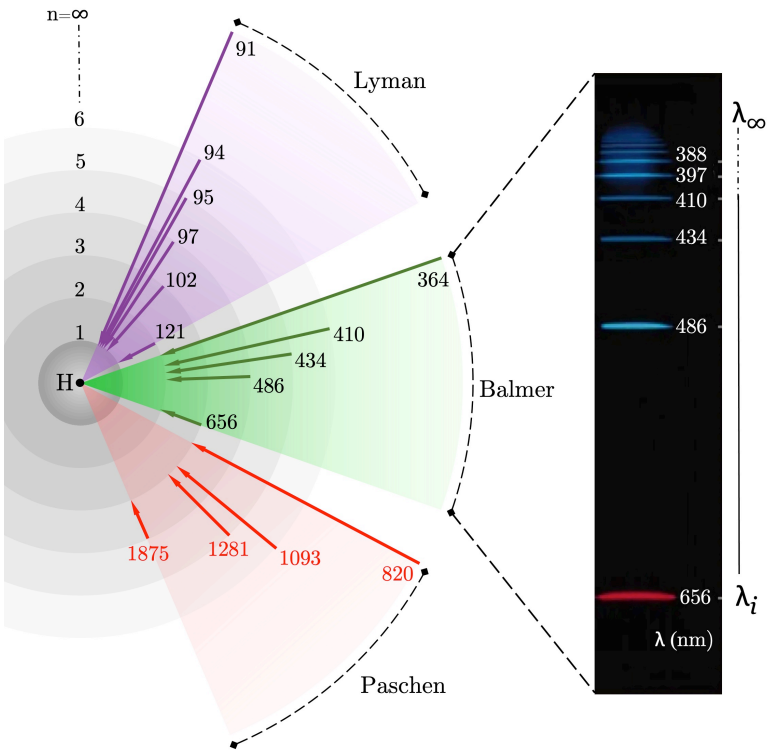


Figure 1: Spectral series of the hydrogen atom and their associated spectrum.

To decode this figure of hydrogen spectral series without error, it is essential to understand that the adjectives "upper" and "lower" never refer to the wavelength value, but to the energy gap between the atomic levels.

Look at the Balmer series (in green) on the diagram:

n	**Transition**	**Name**	λ **(nm)**
3	$3 \to 2$	H_α (1st line, λ_i)	656.3
4	$4 \to 2$	H_β	486.1
5	$5 \to 2$	H_γ	434.0
6	$6 \to 2$	H_δ	410.2
∞	$\infty \to 2$	Limit (λ_∞)	364.6

- **The lower series limit λ_i (or fundamental line)**:
  This is the first line of the series, the one with the longest wavelength and therefore the lowest energy.
  In concrete terms: the electron makes the shortest possible jump for the series: it leaves from the **first excited level** ($n = p+1$) and falls to the series base level ($n = p$). This is the transition requiring the **least energy**.
  Example for Balmer ($p = 2$): the line $\lambda_i = 656$ nm corresponds to the transition $n = 3 \to n = 2$ (the famous red line visible in the hydrogen spectrum).
  Key point: it is the line **furthest** from the ionisation zone.

- **The upper series limit λ_∞ (or series limit)**:
  This is the end of the series, the line with the shortest wavelength and therefore the highest energy.
  In concrete terms: the electron comes from the **highest energy level** ($n = \infty$, the ionised state) and falls to the series base level ($n = p$). This is the **most energetic** transition of the series.
  Example for Balmer ($p = 2$): $\lambda_\infty = 364$ nm. This is the limit where the lines are so close together that they **merge** before entering the ionisation zone.
  Key point: this is the **maximum** energy the electron can absorb **without** being ejected from the atom for this series.

Mathematically, remember that $\lambda_\infty < \lambda_i$. To avoid any vocabulary trap, you must distinguish between the nature of the transition and the appearance of the spectrum:

- The **"upper limit"** (λ_∞) is the **end-of-series** limit (where lines crowd together and merge upon entering the **ionisation zone**).
- The **"lower limit"** (λ_i) is the **first line** of the series (the furthest from the ionisation zone).

Beware of linguistic pitfalls

Pitfall #1: "upper" does not mean "larger"

Understanding the vocabulary

$$\underbrace{\text{Upper series limit}}_{\substack{\text{the electron comes from level } \infty \\ \text{(the upper level)}}} \iff \lambda_\infty \qquad \underbrace{\text{Lower series limit}}_{\substack{\text{the electron comes from level } p+1 \\ \text{(the first excited level)}}} \iff \lambda_i$$

- The **"Upper wavelength limit"** (λ_i) is the **first line** of the series. It is the **largest wavelength value** in the series ($\lambda_i > \lambda_\infty$).
- The **"Lower wavelength limit"** (λ_∞) is the **end-of-series** limit. It is the **smallest wavelength value** in the series ($\lambda_\infty < \lambda_i$).

Pitfall #2: "Wavelength limit" and "Series limit"

$$\underbrace{\text{Lower wavelength limit}}_{\substack{\text{corresponds to the end of the series} \\ (\infty \to p)}} = \lambda_\infty \qquad \underbrace{\text{Upper wavelength limit}}_{\substack{\text{corresponds to the first line} \\ (p+1 \to p)}} = \lambda_i$$

3.3 Novel Formulas with p and n

Quantity	Formula
Generalised Rydberg	$\frac{1}{\lambda} = R_H \left(\frac{1}{p^2} - \frac{1}{n^2} \right)$
Series limit ($\infty \to p$)	$\lambda_\infty = \frac{p^2}{R_H}$
First line ($p+1 \to p$)	$\lambda_i = \frac{p^2(p+1)^2}{R_H(2p+1)} = \lambda_\infty \cdot \frac{(p+1)^2}{2p+1}$
Invariant ratio	$\frac{\lambda_i}{\lambda_\infty} = \frac{(p+1)^2}{2p+1}$

❖ **Tip: The Key Formula:**

$$\lambda = \frac{\lambda_\infty}{1 - \left(\frac{p}{n}\right)^2}$$

It allows you to find n in two lines when you know λ and p. A precious time-saver in exams.

4 Hydrogen-like Ions: the Z^2 Rule

$$E_n(Z) = Z^2 \times E_n(\mathrm{H}) \qquad \lambda(Z) = \frac{\lambda(\mathrm{H})}{Z^2} \qquad r_n(Z) = \frac{r_n(\mathrm{H})}{Z}$$

Ion	Z	E_1 (eV)	r_1
H	1	-13.6	a_0
He^+	2	-54.4	$a_0/2$
Li^{2+}	3	-122.4	$a_0/3$
Be^{3+}	4	-217.6	$a_0/4$

❖ **Tip: Quick check:** For a hydrogen-like ion, λ is ALWAYS divided by Z^2.
If $\lambda(\mathrm{H}) = 656$ nm, then $\lambda(He^+) = 656/4 = 164$ nm, $\lambda(Li^{2+}) = 656/9 = 72.9$ nm.

❖ **Caution:** For He^+, $Z = 2$ (not 1). For Li^{2+}, $Z = 3$. The factor Z^2 is the #**1 careless mistake** in exams.

5 Slater's Model: Screening

5.1 The Algorithm for Calculating σ

Note: Question 1: Is the electron under study in an s **or** p group, or a d **or** f group?

Case: s or p

1. Same group: 0.35 per electron (except 0.30 for $1s$)
2. Group $n-1$: 0.85 per electron
3. Groups $\leq n-2$: 1.00 per electron
4. Higher groups ($> n$): **0**

Case: d or f

1. Same group (d or f): 0.35 per electron
2. All other inner groups: 1.00 per electron
3. Higher groups: **0**

$$\boxed{Z^* = Z - \sigma}$$

n	1	2	3	4	5	6
n^*	1.0	2.0	3.0	3.7	4.0	4.2

5.2 Energy in Slater's Model

$$E_n = -13.6 \times \left(\frac{Z^*}{n^*}\right)^2 \quad \text{eV}$$

5.3 The Brain-Teaser: Filling and Ionisation

Property	Order	Reason
Filling	$4s \to 3d$	Klechkowski rule ($n+l$: $4s$ is $4+0=4$, $3d$ is $3+2=5$)
Ionisation	$4s \to 3d$	In the constructed atom, the 4s electron has a lower Z^* (3.75) than the 3d electron (6.25). It is less tightly bound: it leaves first.

Note: The order is the same ($4s$ before $3d$), but for **different reasons**. This is a classic pitfall.

5.4 Atomic Radius via Slater (the Bohr-Slater Bridge)

$$r_{\text{atom}} \approx \frac{n^{*2}}{Z^*} \times a_0$$

Example: Na ($Z^* = 2.20$, $n^* = 3$): $r \approx \dfrac{9}{2.20} \times 53 \approx 217$ pm (exp.: 186 pm). The trend is respected.

6 Frequent Transitions to Know by Heart

Transition	ΔE (eV)	λ (nm)
$2 \to 1$ (Lyman α)	10.20	121.6
$3 \to 1$	12.09	102.6
$3 \to 2$ (Balmer α)	1.89	656.3
$4 \to 2$ (Balmer β)	2.55	486.0
$4 \to 3$ (Paschen α)	0.66	1875

❖ **Tip:** These values serve as **reference points** to check your calculations in 2 seconds. If you find 500 nm for Lyman α, there is a mistake.

7 Number of Lines and Orders of Magnitude

$N_{\max}$: Maximum number of lines observable from a level n

$$N_{\max} = (n-1) + (n-2) + \cdots + 2 + 1 = \sum_{k=1}^{n-1} k = \frac{n(n-1)}{2}$$

Why this formula?

Imagine the atom has n energy levels (from level 1 up to level n). To create a spectral line, two different levels must be chosen (a departure level and an arrival level).

The total number of possible pairs of levels is given by:

$$N_{\max} = \frac{n \times (n-1)}{2}$$

What is this formula used for?

This formula is an **enormous time-saver in exams** for two reasons:

- It instantly gives the total number of lines that will be emitted.
- It serves to **validate your calculations**. If you have found 3 lines for an atom excited to level $n = 4$, and the formula gives $N_{\max} = 6$, you have definitely missed some transitions!

The pitfall to avoid:

The formula gives the **maximum number** of lines **emitted** during complete de-excitation to level $n = 1$. Do not confuse this with the number of lines in a **specific series** (such as Balmer, which only contains transitions to $n = 2$).

Worked examples with both methods:

n	**Sum** $\sum_{k=1}^{n-1} k$	**Formula** $\frac{n(n-1)}{2}$	$N_{\max}$
2	1	$\frac{2 \times 1}{2}$	1
3	$2+1$	$\frac{3 \times 2}{2}$	3
4	$3+2+1$	$\frac{4 \times 3}{2}$	6
5	$4+3+2+1$	$\frac{5 \times 4}{2}$	10
6	$5+4+3+2+1$	$\frac{6 \times 5}{2}$	15
7	$6+5+4+3+2+1$	$\frac{7 \times 6}{2}$	21

Spectral regions:

This second table allows you to know whether a line is visible to the naked eye or not.

Spectral Region	**Wavelength** λ
X-rays	< 10 nm
Ultraviolet (UV)	10 – 400 nm
Visible	400 – 800 nm
Infrared (IR)	> 800 nm

Combined application example: If an atom is excited to level $n = 5$, it can emit 10 lines in total. Thanks to the spectral region table, the student knows that only the Balmer series lines (between 400 and 800 nm) will be visible to the naked eye.

End of the revision sheet — Good luck with your revision!