Ahmed Ben Bella University, Oran 1
Faculty of Medicine
Dr. Belarbi Hichem — Senior Lecturer
Tutorial Work — First Year Medicine & Dental Medicine
Chemistry Module — Academic Year 2026/2027

Tutorial 1: Atomic Structure — From the Bohr Model to Polyelectronic Atoms

Objectives of this Tutorial: Master the entire atomic structure chapter in a single robust handout:
- Bohr's postulates, energy levels, absorption/emission.
- Spectral lines, series, upper and lower series limits.
- Generalisation to hydrogen-like ions.
- Polyelectronic model: Slater's rules, effective nuclear charge Z^*, screening constant σ.
- Evolution of atomic properties across the periodic table.

General Data: $R_H = 1.097 \times 10^7\,\text{m}$ | $h = 6.626 \times 10^{-34}\,\text{J}\cdot\text{s}$ | $c = 3.00 \times 10^8\,\text{m/s}$ | $1\,\text{eV} = 1.602 \times 10^{-19}\,\text{J}$
$e = 1.602 \times 10^{-19}\,\text{C}$ | $m_e = 9.109 \times 10^{-31}\,\text{kg}$ | $\varepsilon_0 = 8.854 \times 10^{-12}\,\text{F/m}$ | $a_0 = 0.53\,\text{Å} = 5.3 \times 10^{-11}\,\text{m}$

I. The Bohr Model

1. State the three fundamental postulates of the Bohr model as applied to the hydrogen atom.

2. Guided derivation.

(a) Write Bohr's quantisation condition using the de Broglie relation:

$$2\pi r = n\lambda \quad \text{with} \quad \lambda = \frac{h}{m_e v}$$

Deduce the expression for the velocity v as a function of r and n.

(b) Write the equality between the Coulomb electrostatic force and the centripetal force:

$$\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2} = \frac{m_e v^2}{r}$$

(c) By combining the two previous equations, deduce the expression for the orbital radii r_n as a function of n, and show that:

$$r_n = n^2 a_0 \quad \text{with} \quad a_0 = \frac{h^2\varepsilon_0}{\pi m_e e^2} = 0.53\,\text{Å}$$

Hint: From the de Broglie condition, extract $v = \dfrac{nh}{2\pi m_e r}$. *From the force equality, extract* $v^2 = \dfrac{e^2}{4\pi\varepsilon_0 m_e r}$. *Equate the two expressions for* v^2.

3. Deduce that the total energy of the electron in orbit n can be written as:

$$E_n = \frac{E_1}{n^2} \quad \text{with} \quad E_1 = -13.6\ \text{eV}$$

Reminder: *The total energy is* $E = E_c + E_p = \dfrac{1}{2}m_e v^2 - \dfrac{1}{4\pi\varepsilon_0}\dfrac{e^2}{r}$.

4. Calculate numerically E_1, E_2, E_3, E_4 and E_∞. Schematically draw the energy level diagram, respecting the relative scales.

5. Define ionisation energy. Calculate its value in eV and in J for the hydrogen atom starting from the ground state. Justify the positive sign.

II. Generalisation to Hydrogen-like Ions

A hydrogen-like ion is a single-electron system orbiting a nucleus of charge $+Ze$.

1. Write the generalised expressions for r_n and E_n for a hydrogen-like ion of atomic number Z:

$$r_n = \frac{n^2 a_0}{Z} \qquad E_n = -13.6 \times \frac{Z^2}{n^2}\ (\text{eV})$$

2. Calculate the ground state energy ($n = 1$) for the ions He^+ ($Z = 2$) and Li^{2+} ($Z = 3$).

3. Calculate the radius of the first Bohr orbit for He^+. Compare with hydrogen and physically comment on the observed contraction.

4. Calculate the ionisation energy of Li^{2+}. Why are hydrogen-like ions harder to ionise than the hydrogen atom?

III. Electronic Transitions and Spectral Series

1. Recall the Rydberg-Ritz formula giving the wavenumber $\tilde{\nu}$ of radiation emitted during a transition $n_2 \to n_1$ (with $n_2 > n_1$):

$$\tilde{\nu} = \frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

For a hydrogen-like ion of charge Z: $\tilde{\nu} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

> **Caution:** We use $\tilde{\nu}$ (nu tilde) for the wavenumber here, to avoid any confusion with the screening constant σ from Slater's model introduced in Part IV.

2. Application. Calculate the wavelength λ (in nm) of the H_α line of the Balmer series, corresponding to the transition $n = 3 \to n = 2$.

3. Calculate the wavelength of the upper series limit of the Lyman series (transition $n = \infty \to n = 1$). What does this series limit physically represent?

4. A photon of energy 12.09 eV is absorbed by a hydrogen atom initially in its ground state.

(a) To which level n is the electron excited? Justify by calculation.

(b) When the electron falls back to the ground state, it can do so directly or in a cascade. What is the maximum number of different spectral lines that can be emitted during this return? Identify them (transitions and corresponding series).

5. An emission spectrum of an unknown hydrogen-like ion shows a line at $\lambda = 30.4\,\text{nm}$, attributed to the transition $n = 2 \to n = 1$. Identify the ion (determine Z).

6. Identifying a transition from λ. A Balmer series line is measured at $\lambda = 486\,\text{nm}$. Identify the corresponding transition (determine n_i).

Summary of Hydrogen Spectral Series:

Series	n_f	Region	Upper Series Limit
Lyman	1	Far UV	91.2 nm
Balmer	2	Visible/Near UV	≈ 365 nm
Paschen	3	Near IR	820 nm
Brackett	4	Mid IR	–
Pfund	5	Far IR	–

Common Pitfall

- **Confusing ionisation energy and electron energy:** Ionisation energy is always **positive** (energy supplied), the bound electron energy is **negative**.
- **Forgetting the factor Z^2** for hydrogen-like ions in Rydberg formulae.
- **Lower and upper series limits:** The **lower** limit of a series corresponds to $n_i = n_f + 1$ (longest λ), the **upper** limit to $n_i = \infty$ (shortest λ, ionisation threshold from n_f).
- **Do not confuse $\tilde{\nu}$ (wavenumber) and σ (Slater screening constant)**: two completely different concepts that sometimes use the same Greek symbol.

IV. Polyelectronic Atoms — Screening and Slater's Rules

In a polyelectronic atom, each electron experiences an **effective** nuclear charge Z^* lower than the actual nuclear charge Z, due to the **screening effect** (or shielding) exerted by the other electrons. Slater's rules allow estimation of the screening constant σ and hence $Z^* = Z - \sigma$.

Reminder: Slater's Rules for Calculating σ

For a given electron, electrons are grouped as: $(1s), (2s, 2p), (3s, 3p), (3d), (4s, 4p), (4d), (4f)$, etc.
The screening constant σ is the sum of the contributions from all other electrons:

- Electrons in **higher groups** (further out) → **zero** contribution.
- Electrons in the **same group** → 0.35 each (except 0.30 for the 1s group if the electron under study is also in 1s).
- If the electron under study is in an s **or** p group:
  - Electrons in the **immediately lower** shell $(n-1)$ → 0.85 each.
  - Electrons in **even deeper** shells $(\leq n-2)$ → 1.00 each.
- If the electron under study is in a d **or** f group:
  - Electrons in the **same** d **or** f **group** → 0.35 each.
  - All electrons in **inner groups** → 1.00 each.

The effective nuclear charge is then: $Z^* = Z - \sigma$

Effective Principal Quantum Number n^*

Calculating energies with Slater's rules requires using the effective principal quantum number n^* rather than the principal quantum number n for shells $n \geq 4$. The values adopted in this tutorial are as follows[1]:

n	1	2	3	4	5	6	7
n^*	1.0	2.0	3.0	3.7	4.0	4.2	4.3

1. Study of the sodium atom ($Z = 11$).

(a) Give the full electronic configuration of sodium in its ground state. Specify which is the valence electron.

(b) Rigorously applying Slater's rules, group the electrons, then calculate σ and Z^* for the valence electron $3s^1$.

(c) Using the Slater model energy formula:

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

with $n^* = 3$ for $n = 3$, calculate the energy of the $3s$ orbital of sodium. Compare with the experimental ionisation energy (-5.14 eV) and comment on the discrepancy.

2. Trend across the 3rd period: Sodium ($Z = 11$) → Magnesium ($Z = 12$) → Aluminium ($Z = 13$).

(a) For magnesium ($1s^2 2s^2 2p^6 3s^2$), calculate σ and Z^* for a $3s$ electron. Explain why the ionisation energy of Mg (7.65 eV) is higher than that of Na (5.14 eV).

(b) For aluminium ($1s^2 2s^2 2p^6 3s^2 3p^1$), calculate σ and Z^* for the $3p$ electron. The experimental ionisation energy of Al is 5.99 eV. Why is it lower than that of Mg, even though Z has increased?

3. Trend down the 1st group: Sodium ($Z = 11$) → Potassium ($Z = 19$).

(a) For potassium ($1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$), calculate σ and Z^* for the $4s$ valence electron. Use $n^* = 3.7$ for the 4s orbital.

(b) Explain why the atomic radius of potassium is larger than that of sodium, and why its ionisation energy is lower (4.34 eV vs. 5.14 eV), despite a higher Z. Support your answer with the values of Z^* and n^*.

4. Screening of a core electron. For the sodium atom ($Z = 11$), calculate the effective nuclear charge Z^* experienced by a $1s$ electron. What can be concluded about the ability of outer electrons to screen the inner shells?

5. Link with atomic radius. In Slater's model, the atomic radius can be estimated using a formula analogous to Bohr's, replacing Z with Z^* and n with n^*:

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

where $a_0 = 0.53\,\text{Å} = 53\,\text{pm}$ is the Bohr radius.

(a) Using the values of Z^* and n^* found previously, calculate the estimated atomic radius of sodium ($Z = 11$, valence electron $3s^1$) and potassium ($Z = 19$, valence electron $4s^1$).

(b) Compare with experimental values: $r_{\text{exp}}(\text{Na}) = 186\,\text{pm}$ and $r_{\text{exp}}(\text{K}) = 227\,\text{pm}$.

(c) Does the model correctly account for the observed trend down the first group? Qualitatively discuss any discrepancies.

V. Synthesis Exercises — Deeper Study and Cross-Topic Links

[1] *Approximate values used in this tutorial.* These values are pedagogical simplifications. For a more complete table, see Zheng, N. W., *A new formula for the effective principal quantum number and its application to the calculation of ionization energies of atoms*, *J. Chem. Phys.* **1990**, 92, 2497–2501. Zheng's table gives $n^* = 1.00; 1.99; 2.89; 3.45; 3.85; 4.36$ for $n = 1$ to 6, but the simplified values here are adapted for tutorial use.

These additional exercises link the Bohr model, hydrogen-like ions and Slater's model. They are designed for students aiming for complete and robust mastery of the chapter.

Exercise A: Upper and Lower Series Limits, Absorption

1. **Balmer series ($n_f = 2$).**
   (a) Calculate the wavelength of the lower series limit (first line, $n_i = 3$) and the upper series limit ($n_i \to \infty$).
   (b) Schematically represent the Balmer emission spectrum, indicating the positions of the H_α (656 nm), H_β (486 nm), H_γ (434 nm) lines and the series limit.
2. **Absorption from an excited state.** A hydrogen atom is initially in the $n = 2$ level. It absorbs a photon of wavelength $\lambda = 656$ nm.
   (a) Is this absorption possible? Justify.
   (b) Same question for a photon of $\lambda = 365$ nm. What phenomenon then occurs?
3. **Paschen series ($n_f = 3$).** Calculate the wavelength of the first line ($n_i = 4$) and the upper series limit of the Paschen series.

Exercise B: Hydrogen-like Ions — Deeper Study

1. **Li^{2+} ($Z = 3$).**
   (a) Calculate the wavelength of the first line of the Balmer series ($n = 3 \to n = 2$) for Li^{2+}.
   (b) Compare with hydrogen (656 nm) and explain the shift.
   (c) Determine the upper series limit of the Lyman series for Li^{2+}.
2. **Be^{3+} ($Z = 4$).** The ionisation energy of Be^{3+} from $n = 1$ is 217.6 eV. Confirm this value. What is the wavelength of the ionising photon?
3. **Transition energy and nuclear charge.** Show that for a given transition, the energy of the emitted photon is proportional to Z^2. Deduce that $\lambda(Z)/\lambda(\mathrm{H}) = 1/Z^2$.

Exercise C: Slater's Rules — Deeper Study and Transition Elements

1. **Study of calcium ($Z = 20$).**
   (a) Calculate σ and Z^* for a $4s$ electron of calcium. Compare with potassium ($Z^* = 2.20$) and explain the evolution of E_i.
   (b) Calculate σ and Z^* for a $3p$ electron of calcium. Why is $Z^*(3p) > Z^*(4s)$? What does this imply?
2. **Study of iron ($Z = 26$).**
   (a) Calculate σ and Z^* for a $3d$ electron of iron.
   (b) Calculate σ and Z^* for a $4s$ electron of iron.
   (c) Are your calculations consistent with the fact that $4s$ electrons are removed before $3d$ electrons?
3. **Energy of a $3d$ electron of iron.** Calculate E_{3d} and E_{4s} of iron using Slater's model. Conclude on the filling order and the ionisation order.

Exercise D: Synthesis Problem — From Hydrogen to Heavy Atoms

We consider the sequence: H ($Z = 1$), He ($Z = 2$), Li ($Z = 3$), Na ($Z = 11$), K ($Z = 19$).

1. **Experimental ionisation energies:**

H	He	Li	Na	K
13.6 eV	24.6 eV	5.39 eV	5.14 eV	4.34 eV

   (a) Justify 13.6 eV (H) and 54.4 eV (He^+) using the Bohr model.
   (b) Qualitatively explain the Li, Na, K trend using Slater's model.
   (c) Why is $E_i(\mathrm{He}) = 24.6$ eV lower than $E_i(He^+) = 54.4$ eV?
2. **Atomic radii:** $r(\mathrm{Na}) = 186$ pm, $r(\mathrm{K}) = 227$ pm. Explain this increase using Z^* and n^*. Qualitatively estimate $r(\mathrm{Li})$.

Synthesis of Key Concepts

Bohr Model	Slater Model
Single electron, no screening.	Multiple electrons, mutual screening.
$E_n = -\dfrac{13.6Z^2}{n^2}$ (eV)	$E_n = -13.6\left(\dfrac{Z^*}{n^*}\right)^2$ (eV)
$r_n = \dfrac{n^2 a_0}{Z}$	$Z^* = Z - \sigma$ (Slater's rules)
Transitions: $\Delta E = 13.6Z^2\left(\dfrac{1}{n_f^2} - \dfrac{1}{n_i^2}\right)$	σ depends on group and shell
Applicable to H and hydrogen-like ions.	Applicable to all polyelectronic atoms.

Periodic trends:

• Across a **period** (same n): Z increases $\Rightarrow$ Z^* increases $\Rightarrow$ E_i increases, r decreases.

• Down a **group**: n and n^* increase $\Rightarrow$ E_i decreases, r increases.

Bohr-Slater link: $r_{\text{atom}} \approx \dfrac{n^{*2}}{Z^*}a_0$. Formula analogous to $r_n = \dfrac{n^2 a_0}{Z}$ with $Z \to Z^*$ and $n \to n^*$.

Glossary

Hydrogen-like ion

A single-electron system orbiting a nucleus of charge $+Ze$ (e.g. He^+, Li^{2+}).

Effective nuclear charge (Z^*)

Nuclear charge actually "seen" by an electron after accounting for screening by other electrons.

Screening constant (σ)

Quantitative measure of the screening effect. $Z^* = Z - \sigma$.

Wavenumber ($\tilde{\nu}$)

Inverse of wavelength ($\tilde{\nu} = 1/\lambda$), expressed in m^{-1}. Allows the Rydberg-Ritz formula to be written compactly. Do not confuse with the screening constant σ!

Upper series limit

Line corresponding to the transition $n = \infty \to n_f$. This is the ionisation threshold from the n_f level.

Lower series limit

First line of a series, corresponding to $n = n_f + 1 \to n_f$. This is the longest-wavelength line of the series.

Ionisation energy

Minimum energy (positive) required to remove an electron from a neutral atom at rest.

Effective principal quantum number (n^*)

Semi-empirical parameter of Slater's model, different from n, which accounts for orbital penetration.

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

How to use this answer key: Do not just read the answers. Redo each calculation yourself, then compare. The "Note" and "Tip" boxes are to be memorised. The "Caution" boxes highlight the most common exam mistakes.

I. The Bohr Model

1. The three postulates of Bohr (1913):

(a) **Quantisation of orbits:** the electron can only orbit on certain well-defined circular orbits, called "stationary".

(b) **Absence of radiation:** in these stationary orbits, the electron does not radiate energy, contrary to what classical electromagnetism would predict.

(c) **Quantum jumps:** emission or absorption of energy occurs only when an electron passes from one orbit to another. The energy of the emitted or absorbed photon is: $\Delta E = h\nu = |E_{\text{final}} - E_{\text{initial}}|$.

Note: These three postulates break with classical physics. Bohr formulated them to explain the line spectrum of hydrogen, which classical theory could not justify.

2. Guided derivation of the Bohr radius:

Step 1 — Quantisation according to de Broglie. The wave associated with the electron must form a standing wave on the circular orbit. The condition is that the circumference contains an integer number of wavelengths:

$$2\pi r = n\lambda \quad \text{with} \quad \lambda = \frac{h}{m_e v}$$

From this we extract the velocity:

$$v = \frac{nh}{2\pi m_e r} \tag{1}$$

Step 2 — Force equality. The Coulomb electrostatic force acts as the centripetal force:

$$\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2} = \frac{m_e v^2}{r}$$

Simplifying by r:

$$v^2 = \frac{e^2}{4\pi\varepsilon_0 m_e r} \tag{2}$$

Step 3 — Synthesis. Square (1) and equate to (2):

$$\frac{n^2h^2}{4\pi^2 m_e^2 r^2} = \frac{e^2}{4\pi\varepsilon_0 m_e r}$$

Simplify by m_e and r:

$$\frac{n^2h^2}{4\pi^2 m_e r} = \frac{e^2}{4\pi\varepsilon_0}$$

Isolate r:

$$r_n = \frac{n^2h^2\varepsilon_0}{\pi m_e e^2} = n^2 a_0$$

with:

$$a_0 = \frac{h^2\varepsilon_0}{\pi m_e e^2} \approx 0.53\,\text{Å} = 5.3 \times 10^{-11}\,\text{m}$$

Solution: Orbital radii are quantised: $r_n = n^2 a_0$. The first orbit ($n = 1$) has a radius of 0.53 Å.

Note: a_0 is called the **Bohr radius**. It is the natural unit of distance in atomic physics.

3. **Total energy of the electron:**
The total energy is the sum of kinetic and potential energy:

$$E_n = E_c + E_p = \frac{1}{2} m_e v^2 - \frac{1}{4\pi\varepsilon_0} \frac{e^2}{r_n}$$

From the force equality: $m_e v^2 = \dfrac{e^2}{4\pi\varepsilon_0 r_n}$.

Hence: $E_c = \dfrac{1}{2} m_e v^2 = \dfrac{e^2}{8\pi\varepsilon_0 r_n}$.

The total energy becomes:

$$E_n = \frac{e^2}{8\pi\varepsilon_0 r_n} - \frac{e^2}{4\pi\varepsilon_0 r_n} = -\frac{e^2}{8\pi\varepsilon_0 r_n}$$

Substituting $r_n = n^2 a_0$:

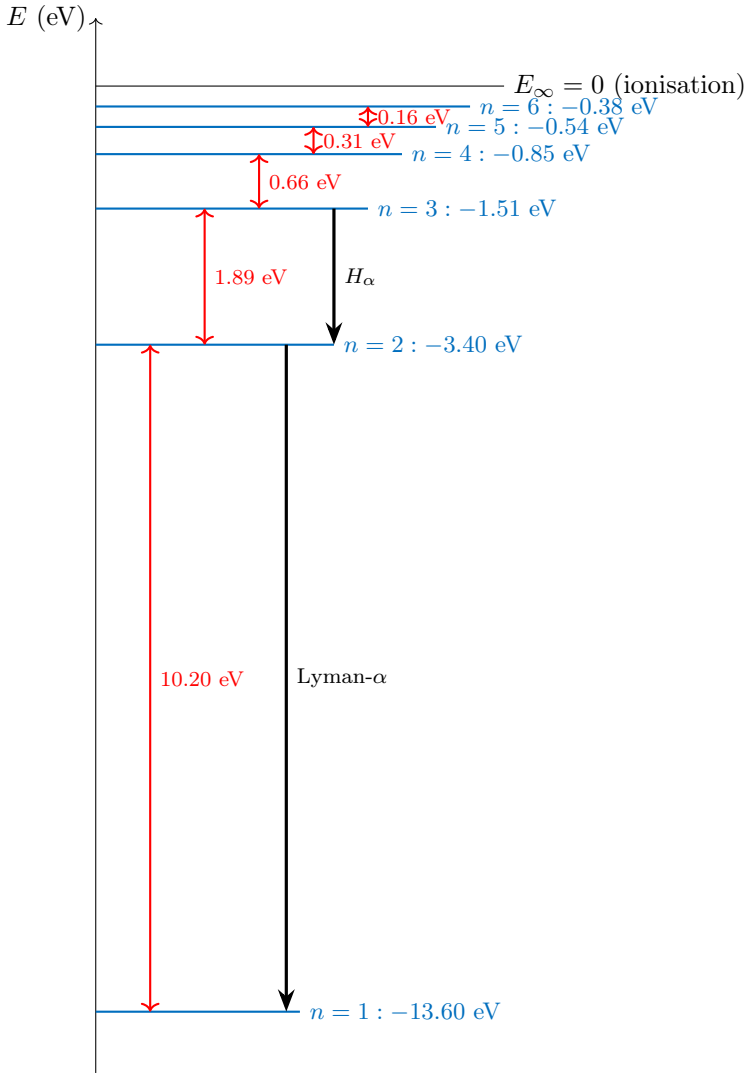
$$E_n = -\frac{e^2}{8\pi\varepsilon_0 a_0} \cdot \frac{1}{n^2} = \frac{E_1}{n^2}$$

with:

$$E_1 = -\frac{e^2}{8\pi\varepsilon_0 a_0} = -13.6 \text{ eV}$$

> **Note:** The negative sign means the electron is **bound** to the nucleus. The larger n is, the closer the energy is to zero (the electron is less bound).

4. **Energy levels:** Energy level diagram:



> **Caution:** The gaps between levels decrease as n increases: the levels are said to "bunch up" towards the top. This is why spectral lines crowd together near the series limit.

> **Note:** Calculation trick: $E_n = -13.6/n^2$. For $n = 2$: $-13.6/4 = -3.40$ eV. For $n = 3$: $-13.6/9 \approx -1.51$ eV.

5. **Ionisation energy:**
Definition: The ionisation energy E_i is the minimum energy required to remove an electron from a neutral atom in its ground state (to take it from $n = 1$ to $n = \infty$).

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

In joules: $E_i = 13.6 \times 1.602 \times 10^{-19} = 2.18 \times 10^{-18}$ J.

Solution: The ionisation energy is **positive** (+13.6 eV) because it is energy **supplied** to the system. The energy of the bound electron itself is **negative** (-13.6 eV).

II. Generalisation to Hydrogen-like Ions

1. **Generalised expressions:**
For a nucleus of charge $+Ze$, the electrostatic force is multiplied by Z. Repeating the previous derivation with $e^2 \to Ze^2$ in the numerator of the Coulomb force, we obtain:

$$r_n(Z) = \frac{n^2 a_0}{Z} \qquad E_n(Z) = -13.6 \times \frac{Z^2}{n^2} \text{ eV}$$

Note: The radius is **divided** by Z: the electron is closer to the nucleus. The energy is **multiplied** by Z^2: the electron is much more tightly bound.

2. **Ground state energies:**
- He^+ $(Z = 2)$: $E_1 = -13.6 \times 2^2 = -13.6 \times 4 = -54.4$ eV.
- Li^{2+} $(Z = 3)$: $E_1 = -13.6 \times 3^2 = -13.6 \times 9 = -122.4$ eV.

Note: Key fact: He^+ has an energy 4 times more negative than H; Li^{2+} 9 times more. The factor Z^2 must be known by heart.

3. **Radius of He^+:**

$$r_1(He^+) = \frac{a_0}{Z} = \frac{0.53}{2} = 0.265 \text{ Å}$$

Physical interpretation: The helium nucleus has a charge of $+2e$, twice that of hydrogen. The Coulomb attraction is therefore twice as strong, which "pulls" the electron closer to the nucleus. The radius is divided by 2.

4. **Ionisation energy of Li^{2+}:**

$$E_i(Li^{2+}) = 0 - E_1 = 0 - (-122.4) = 122.4 \text{ eV}$$

Why is it harder? The ionisation energy grows as Z^2. For Li^{2+} $(Z = 3)$, it is $3^2 = 9$ times larger than for hydrogen. The more charged the nucleus, the more strongly it holds its electron.

III. Electronic Transitions and Spectral Series

1. **Rydberg-Ritz formula:**

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

where n_f is the final level (lowest), n_i the initial level (highest), with $n_i > n_f$.
For a hydrogen-like ion of charge Z:

$$\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

Note: $R_H = 1.097 \times 10^7$ m^{-1}. Be careful with units: λ will be in metres if you use this value.

2. **Balmer H_α line ($n = 3 \to n = 2$):**

$$\frac{1}{\lambda} = 1.097 \times 10^7 \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = 1.097 \times 10^7 \left(\frac{1}{4} - \frac{1}{9} \right)$$

$$\frac{1}{\lambda} = 1.097 \times 10^7 \times \frac{9-4}{36} = 1.097 \times 10^7 \times \frac{5}{36} = 1.524 \times 10^6 \text{ m}^{-1}$$

$$\lambda = \frac{1}{1.524 \times 10^6} = 6.56 \times 10^{-7} \text{ m} = 656 \text{ nm}$$

Solution: H_α is at 656 nm, in the red. It is the most intense line in the visible hydrogen spectrum.

Note: Tip: $\Delta E = \dfrac{hc}{\lambda} = \dfrac{1240}{656} \approx 1.89$ eV. Check: $E_3 - E_2 = (-1.51) - (-3.40) = 1.89$ eV.

3. Lyman series limit ($\infty \to 1$):

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

$$\lambda_\infty = \frac{1}{R_H} = \frac{1}{1.097 \times 10^7} = 9.12 \times 10^{-8} \text{ m} = 91.2 \text{ nm}$$

Physical meaning: This wavelength of 91.2 nm corresponds to the **ionisation threshold** from the ground state. Any photon with a wavelength **shorter** than 91.2 nm (hence energy greater than 13.6 eV) has enough energy to ionise the hydrogen atom. The excess energy is converted to kinetic energy of the ejected electron.

Note: The series limit marks the boundary between the line spectrum (discrete) and the ionisation continuum.

4. Absorption of a 12.09 eV photon:

(a) **Level reached:** The electron starts from $n = 1$ with $E_1 = -13.6$ eV. After absorption, its energy is:

$$E_n = -13.6 + 12.09 = -1.51 \text{ eV}$$

We look for n such that $E_n = -13.6/n^2 = -1.51$:

$$n^2 = \frac{13.6}{1.51} = 9 \Rightarrow n = 3$$

Solution: The electron is excited to level $n = 3$.

Note: Method: $E_n = E_1 + \Delta E$ (absorption). Solve $n = \sqrt{-13.6/E_n}$.

(b) **Lines emitted during the return:** From $n = 3$, the electron can fall directly to $n = 1$ or cascade via $n = 2$. The possible transitions are:

- $3 \to 1$: Lyman series (UV)
- $3 \to 2$: Balmer series, H_α line (visible, 656 nm)
- $2 \to 1$: Lyman series (UV)

Solution: 3 lines in total.

Note: General formula: from level n, the maximum number of lines is $N = \dfrac{n(n-1)}{2}$. For $n = 3$: $N = 3 \times 2/2 = 3$.

Detail of possible transitions:

- **Direct return:** $3 \to 1$ (1 line, Lyman series, UV).
- **Cascade return (2 steps):** $3 \to 2$ then $2 \to 1$ (2 additional lines).

Solution: Hence a total of $1 + 2 = 3$ lines.

Caution: Do not confuse the total number of lines emitted during complete de-excitation from level n with the number of lines in a **specific series** (e.g. Balmer series).

5. Identification of the unknown ion:

$$\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = R_H Z^2 \times \frac{3}{4}$$

$$\lambda = 30.4 \text{ nm} = 30.4 \times 10^{-9} \text{ m} \quad \text{(essential conversion!)}$$

$$Z^2 = \frac{4}{3R_H\lambda} = \frac{4}{3 \times 1.097 \times 10^7 \times 30.4 \times 10^{-9}} = \frac{4}{1.000} = 4 \implies Z = 2$$

Solution: The ion is He^+ (singly ionised helium).

Caution: Always check units: λ must be in metres if R_H is in m^{-1}. 30.4 nm $= 30.4 \times 10^{-9}$ m.

6. Identifying a transition from $\lambda = 486$ nm:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n_i^2} \right) \quad \text{(Balmer series, } n_f = 2\text{)}$$

$$\frac{1}{486 \times 10^{-9}} = 1.097 \times 10^7 \times \left(\frac{1}{4} - \frac{1}{n_i^2} \right)$$

$$2.058 \times 10^6 = 1.097 \times 10^7 \times \left(0.25 - \frac{1}{n_i^2} \right)$$

$$0.1876 = 0.25 - \frac{1}{n_i^2} \quad \Rightarrow \quad \frac{1}{n_i^2} = 0.0625 = \frac{1}{16}$$

$$n_i^2 = 16 \quad \Rightarrow \quad n_i = 4$$

Solution: The line at 486 nm corresponds to the transition $n = 4 \to n = 2$, i.e. the H_β line of the Balmer series.

IV. Polyelectronic Atoms — Screening and Slater's Rules — Answer Key

1. Study of the sodium atom ($Z = 11$).

(a) **Electronic configuration:**

$$\text{Na } (Z = 11) : 1s^2\, 2s^2 2p^6\, 3s^1$$

The valence electron is the $3s^1$ electron.

(b) **Calculation of σ and Z^* for the $3s$ electron:** Grouping: $(1s^2)\,(2s^2 2p^6)\,(3s^1)$

- Same group (3s): 0 other electrons $\to 0$
- Shell $n - 1 = 2$ (2s,2p): 8 electrons $\to 8 \times 0.85 = 6.80$
- Shell $n - 2 = 1$ (1s): 2 electrons $\to 2 \times 1.00 = 2.00$

$$\sigma = 8.80 \quad \Rightarrow \quad Z^* = 11 - 8.80 = 2.20$$

(c) **Energy of the $3s$ orbital:** With $Z^* = 2.20$, $n^* = 3$:

$$E_{3s} = -13.6 \times \left(\frac{2.20}{3} \right)^2 = -13.6 \times (0.733)^2 = -13.6 \times 0.537 = -7.30 \text{ eV}$$

Comparison with experiment: The experimental ionisation energy of sodium is $E_i = 5.14$ eV, so $E_{3s}^{\text{exp}} = -5.14$ eV.

	Slater Model	Experiment
E_{3s}	-7.30 eV	-5.14 eV

Analysis of the discrepancy: The Slater model overestimates the binding of the $3s$ electron. This arises from:

- Slater's rules being semi-empirical and simplified.
- The approximation $n^* = n$ for $n \leq 3$, which is crude for sodium.
- The model not accounting for core orbital penetration.

Note: The Slater model gives correct trends and orders of magnitude, but exact numerical values should be taken with caution.

2. Trend across the 3rd period: Na ($Z = 11$) $\to$ Mg ($Z = 12$) $\to$ Al ($Z = 13$).

(a) **Magnesium ($Z = 12$), $3s$ electron:** Configuration: $1s^2\, 2s^2 2p^6\, 3s^2$.

- Same group (3s): 1 other electron $\to 1 \times 0.35 = 0.35$
- Shell $n - 1 = 2$ (2s,2p): 8 electrons $\to 8 \times 0.85 = 6.80$
- Shell $n - 2 = 1$ (1s): 2 electrons $\to 2 \times 1.00 = 2.00$

$$\sigma = 9.15 \quad \Rightarrow \quad Z^* = 12 - 9.15 = 2.85$$

Solution: $Z^*(\text{Mg}) = 2.85 > Z^*(\text{Na}) = 2.20$. The 3s electron of Mg is therefore more strongly attracted by the nucleus, which explains $E_i(\text{Mg}) = 7.65$ eV $> E_i(\text{Na}) = 5.14$ eV.

(b) **Aluminium ($Z = 13$), $3p$ electron:** Configuration: $1s^2\,2s^2 2p^6\,3s^2 3p^1$.

- Same group (3s,3p): 2 other electrons (the two $3s$) $\rightarrow 2 \times 0.35 = 0.70$
- Shell $n-1=2$: 8 electrons $\rightarrow 8 \times 0.85 = 6.80$
- Shell $n-2=1$: 2 electrons $\rightarrow 2 \times 1.00 = 2.00$

$$\sigma = 9.50 \quad \Rightarrow \quad Z^* = 13 - 9.50 = 3.50$$

Caution: Slater's model gives $Z^*(\mathrm{Al}, 3p) = 3.50 > Z^*(\mathrm{Mg}, 3s) = 2.85$, which would naively suggest that aluminium's 3p electron is more tightly bound. Yet experimentally, $E_i(\mathrm{Al}) = 5.99$ eV is **lower** than $E_i(\mathrm{Mg}) = 7.65$ eV.
Why? The $3p$ orbital is **less penetrating** than the $3s$ orbital: its electron density is more diffuse and less concentrated near the nucleus. Consequently, the $3p$ electron undergoes **more effective screening** from the inner shells than Slater's model predicts, since the model assigns the same screening constant to all electrons in the same group ($3s$ and $3p$ together). This non-distinction of subshells within the same shell n is a known limitation of the simple Slater model.

3. Trend down the 1st group: Na ($Z = 11$) $\rightarrow$ K ($Z = 19$).

(a) **Potassium ($Z = 19$), $4s$ electron:** Configuration: $1s^2\,2s^2 2p^6\,3s^2 3p^6\,4s^1$.

- Same group (4s): 0 other electrons $\rightarrow 0$
- Shell $n-1=3$ (3s,3p): 8 electrons $\rightarrow 8 \times 0.85 = 6.80$
- Shells $\leq n-2$ (1s,2s,2p): 10 electrons $\rightarrow 10 \times 1.00 = 10.00$

$$\sigma = 16.80 \quad \Rightarrow \quad Z^* = 19 - 16.80 = 2.20$$

(b) **Na/K comparison:** $Z^*(\mathrm{Na}) = Z^*(\mathrm{K}) = 2.20$: identical! It is n^* that governs the difference (3.7 vs 3). Since $E \propto (Z^*/n^*)^2$ and $r \propto n^{*2}/Z^*$, a larger n^* for the same Z^* gives a larger radius and a lower binding energy: $r(\mathrm{K}) > r(\mathrm{Na})$, $E_i(\mathrm{K}) = 4.34$ eV $< E_i(\mathrm{Na}) = 5.14$ eV.

4. Screening of a core $1s$ electron of sodium ($Z = 11$):

- Same group (1s): 1 other electron, special coefficient 0.30 $\rightarrow 1 \times 0.30 = 0.30$
- All other electrons (2s,2p,3s) belong to **higher groups** $\rightarrow$ zero contribution

$$\sigma = 0.30 \quad \Rightarrow \quad Z^* = 11 - 0.30 = 10.70$$

Solution: **Result:** $Z^*(1s) = 11 - 0.30 = 10.70$, i.e. $Z^*(1s) \approx Z$. The core $1s$ electron of sodium therefore experiences a nuclear charge almost equal to the true nuclear charge ($Z = 11$): it undergoes almost no screening effect.
Mechanism: This result reflects a simple geometric principle. For one electron to screen another, it must lie **between** that electron and the nucleus. However, the $1s$ electron is, by definition, the closest shell to the nucleus: no other electron can come between it and the nucleus. The outer-shell electrons ($2s, 2p, 3s$) are all **further out** than it — they therefore play no screening role whatsoever, which is exactly what Slater's rules state: zero contribution from higher groups.
Image to remember: a core electron is like a spectator sitting in the front row of a stadium: no matter how many people are behind, none of them block his view of the stage (the nucleus).
Scope of the result: this conclusion is general, not specific to sodium. For **any** polyelectronic atom, the $n = 1$ shell electrons experience an effective nuclear charge very close to Z — which is why their binding energy is always very negative (of the order of hundreds to thousands of eV for heavy atoms), far beyond the typical binding energies of valence electrons (a few tens of eV at most).

5. Atomic radius via Slater

(a) **Sodium ($Z = 11$):** $Z^*(3s) = 2.20$, $n^* = 3$.

$$r(\mathrm{Na}) \approx \frac{3^2}{2.20} \times 53 = \frac{9}{2.20} \times 53 = 4.09 \times 53 \approx 217\,\mathrm{pm}$$

Potassium ($Z = 19$): $Z^*(4s) = 2.20$, $n^* = 3.7$.

$$r(\mathrm{K}) \approx \frac{3.7^2}{2.20} \times 53 = \frac{13.69}{2.20} \times 53 = 6.22 \times 53 \approx 330\,\mathrm{pm}$$

(b) **Comparison:**

Atom	$r_{\mathrm{calculated}}$	$r_{\mathrm{experimental}}$
Na	217 pm	186 pm
K	330 pm	227 pm

(c) **Analysis:** The model overestimates absolute radii (factor ∼1.2 for Na, ∼1.45 for K), which is expected since the formula $r \propto n^{*2}/Z^*$ is a semi-classical approximation. However, the **qualitative trend is perfectly respected**: $r(\text{K}) > r(\text{Na})$ because n^* increases ($3 \to 3.7$) while Z^* remains identical (2.20). The potassium valence electron lies in a more external shell, hence further from the nucleus.

> **Note:** This approximate formula $r \approx \dfrac{n^{*2}}{Z^*} a_0$ directly links the Slater model to periodic properties. It shows that radius increases down a group ($n^* \uparrow$) and decreases across a period ($Z^* \uparrow$).

V. Synthesis Exercises — Answer Key

Exercise A: Series Limits and Absorption

1. Balmer series ($n_f = 2$):

(a) **Lower series limit** ($n_i = 3$) :

$$\frac{1}{\lambda_i} = R_H \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = R_H \times \frac{5}{36}$$

$$\lambda_i = \frac{36}{5R_H} = \frac{36}{5 \times 1.097 \times 10^7} = 6.56 \times 10^{-7} \text{ m} = 656 \text{ nm}$$

Upper series limit ($n_i \to \infty$) :

$$\lambda_\infty = \frac{4}{R_H} = \frac{4}{1.097 \times 10^7} = 3.646 \times 10^{-7} \text{ m} = 364.6 \text{ nm}$$

> **Note:** The lower series limit is the **longest** wavelength of the series (656 nm). The upper series limit is the **shortest** (364.6 nm).

(b) **Spectrum sketch:**

$$\underbrace{364.6 \text{ nm}}_{\text{limit (UV)}} \quad \underbrace{410 \text{ nm}}_{H_\delta} \quad \underbrace{434 \text{ nm}}_{H_\gamma} \quad \underbrace{486 \text{ nm}}_{H_\beta} \quad \underbrace{656 \text{ nm}}_{H_\alpha \text{ (red)}}$$

The lines crowd together as they approach the limit at 364.6 nm.

2. Absorption from $n = 2$:

(a) Photon $\lambda = 656$ nm :

$$E = \frac{hc}{\lambda} = \frac{1240}{656} = 1.89 \text{ eV}$$

Now $E_3 - E_2 = (-1.51) - (-3.40) = 1.89$ eV.

> **Solution:** The photon energy matches exactly the $2 \to 3$ transition. Absorption is possible.

(b) Photon $\lambda = 365$ nm :

$$E = \frac{1240}{365} = 3.40 \text{ eV} = |E_2|$$

This energy is exactly the ionisation energy from $n = 2$.

> **Solution:** The photon ionises the atom. The electron is ejected with zero kinetic energy (this is the threshold). Any photon with $\lambda < 365$ nm (hence more energetic) would ionise the atom with an excess of kinetic energy.

> **Note:** From a level n, the ionisation threshold is $\lambda_{\text{threshold}} = hc/|E_n|$. For $n = 2$: $\lambda = 1240/3.40 = 365$ nm.

3. Paschen series ($n_f = 3$):

$$\lambda_\infty = \frac{9}{R_H} = 820 \text{ nm}$$

$$\lambda_i = \frac{1}{R_H \left(\frac{1}{9} - \frac{1}{16} \right)} = \frac{144}{7R_H} = 1875 \text{ nm}$$

> **Solution:** The Paschen series extends from 820 nm to 1875 nm, entirely in the infrared.

Exercise B: Hydrogen-like Ions — Deeper Study

1. Li^{2+} ($Z = 3$):

(a) **Balmer $3 \to 2$:**

$$\frac{1}{\lambda} = R_H \times 3^2 \times \left(\frac{1}{2^2} - \frac{1}{3^2}\right) = R_H \times 9 \times \frac{5}{36}$$

$$\lambda = \frac{1}{R_H} \times \frac{36}{9 \times 5} = \frac{656}{9} = 72.9 \text{ nm}$$

> **Note:** Tip: start from $\lambda(\text{H}) = 656$ nm and divide by $Z^2 = 9$.

(b) **Comparison:** The line has shifted from 656 nm (visible, red) to 72.9 nm (far UV). The factor $Z^2 = 9$ makes transitions 9 times more energetic, hence wavelengths 9 times shorter.

(c) **Lyman limit for Li^{2+}:**

$$\lambda_\infty = \frac{1}{R_H \times 9} = \frac{91.2}{9} = 10.1 \text{ nm}$$

This is in the **soft X-ray** (or extreme UV) region.

2. Be^{3+} ($Z = 4$):

$$E_i = 13.6 \times Z^2 = 13.6 \times 16 = 217.6 \text{ eV}$$

$$\lambda = \frac{1240}{217.6} = 5.70 \text{ nm}$$

> **Solution:** This photon lies in the **X-ray** region. Ionising Be^{3+} requires X-ray radiation.

3. Proof of proportionality:

$$\Delta E = 13.6 Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

For a given transition (n_f, n_i fixed), everything is constant except Z^2. Hence $\Delta E \propto Z^2$.
For wavelengths:

$$\frac{\lambda(Z)}{\lambda(\text{H})} = \frac{hc/\Delta E(Z)}{hc/\Delta E(\text{H})} = \frac{\Delta E(\text{H})}{\Delta E(Z)} = \frac{1}{Z^2}$$

> **Note:** For any hydrogen-like ion: $\lambda(Z) = \lambda(\text{H})/Z^2$. This simple formula enables very fast calculations.

Exercise C: Slater's Rules — Deeper Study

1. Calcium ($Z = 20$), configuration: $1s^2\,2s^2 2p^6\,3s^2 3p^6\,4s^2$.

(a) **4s electron:**

- Same group ($4s$): 1 other electron $\to 1 \times 0.35 = 0.35$
- Shell $n - 1 = 3$ ($3s, 3p$): 8 electrons $\to 8 \times 0.85 = 6.80$
- Deeper shells ($1s, 2s, 2p$): 10 electrons $\to 10 \times 1.00 = 10.00$

$$\sigma = 0.35 + 6.80 + 10.00 = 17.15$$

$$Z^* = 20 - 17.15 = 2.85$$

Comparison K ($Z^* = 2.20$) $\to$ Ca ($Z^* = 2.85$): Going from K to Ca adds one proton (Z increases by 1) and one 4s electron. The added electron only partially screens (0.35), so Z^* increases significantly. Result: $E_i(\text{Ca}) = 6.11$ eV $> E_i(\text{K}) = 4.34$ eV.

> **Note:** Across a period, Z^* increases because electrons added to the same shell screen each other poorly (0.35). Attraction dominates, so E_i increases.

(b) **3p electron:**

- Same group (3s,3p): 7 other electrons $\to 7 \times 0.35 = 2.45$
- Shell $n - 1 = 2$ (2s,2p): 8 electrons $\to 8 \times 0.85 = 6.80$
- Deeper shell (1s): 2 electrons $\to 2 \times 1.00 = 2.00$
- 4s electrons (higher group): zero contribution.

$$\sigma = 2.45 + 6.80 + 2.00 = 11.25$$

$$Z^* = 20 - 11.25 = 8.75$$

> **Solution:** $Z^*(3p) = 8.75 \gg Z^*(4s) = 2.85$. The $3p$ electrons are much more tightly bound. During successive ionisations, $4s$ electrons are removed first, then $3p$.

2. **Iron ($Z = 26$), configuration:** $1s^2\,2s^2 2p^6\,3s^2 3p^6\,3d^6\,4s^2$.

(a) **3d electron:**

- Same group (3d): 5 others $\rightarrow 5 \times 0.35 = 1.75$
- All inner electrons (1s to 3p): 18 electrons $\rightarrow 18 \times 1.00 = 18.00$
- 4s electrons (higher group): zero contribution.

$$\sigma = 19.75, \quad Z^* = 26 - 19.75 = 6.25$$

(b) **4s electron:**

- Same group (4s): 1 other $\rightarrow 1 \times 0.35 = 0.35$
- Shell $n - 1 = 3$ (3s,3p,3d): 14 electrons $\rightarrow 14 \times 0.85 = 11.90$
- Deeper shells (1s,2s,2p): 10 electrons $\rightarrow 10 \times 1.00 = 10.00$

$$\sigma = 22.25, \quad Z^* = 26 - 22.25 = 3.75$$

(c) **Consistency with experiment:** $Z^*(3d) = 6.25 > Z^*(4s) = 3.75$. The 3d electrons are therefore more tightly bound to the nucleus than the 4s electrons. This explains why, upon ionisation of iron, the 4s electrons are removed before the 3d electrons.

> **Note:** This is an important result: the order of ionisation is not always the same as the order of filling. For transition metals, ns electrons leave before $(n-1)d$ electrons.

3. **Energies of iron orbitals:**

$$E_{3d} = -13.6 \times \left(\frac{6.25}{3}\right)^2 = -13.6 \times 4.34 = -59.0 \text{ eV}$$

$$E_{4s} = -13.6 \times \left(\frac{3.75}{3.7}\right)^2 = -13.6 \times 1.027 = -14.0 \text{ eV}$$

Interpretation:

- **Ionisation order:** In the already-constructed iron atom, the Slater model gives $|E_{3d}| = 59.0$ eV $> |E_{4s}| = 14.0$ eV. The $4s$ electron is therefore **less tightly bound** than the $3d$ electron. Consequently, upon ionisation, $4s$ electrons are removed before $3d$ electrons. This result agrees with experiment.
- **Filling order:** The filling order ($4s$ before $3d$) obeys the Klechkowski rule ($n + l$ increasing: $4s$ has $n + l = 4 + 0 = 4$, $3d$ has $n + l = 3 + 2 = 5$) and is not directly predicted by this Slater calculation on the complete atom. The Slater model applied to the final atom explains the **ionisation** order, not the **filling** order.
- **Consistency of the two orders:** Although the reasons are different, the order is the same in both cases ($4s$ before $3d$), which is a frequent source of confusion among students.

Summary: Filling and Ionisation in Transition Metals

Property	Observed Order	Explanation via Slater's Model
Filling (Atom under construction)	$4s \rightarrow 3d$	The **empty** $4s$ orbital is lower in energy than the empty $3d$. (Klechkowski rule: increasing $n + l$: $4s$: $4 + 0 = 4$; $3d$: $3 + 2 = 5$)
Ionisation (Fully constructed atom)	$4s \rightarrow 3d$	In the complete atom, the $4s$ electron experiences $Z^* = 3.75$, much lower than the $Z^* = 6.25$ of a $3d$ electron. The $4s$ electron is therefore **less tightly bound**: it leaves first.

Key point: In both cases, the order is $4s$ before $3d$, but for **different reasons**!

Exercise D: Synthesis Problem

1. **Ionisation energies:**

(a) **H and He^+ via the Bohr model:**

- H ($Z = 1$): $E_i = |E_1| = 13.6$ eV.
- He^+ ($Z = 2$): $E_i = 13.6 \times 2^2 = 54.4$ eV.

These values are perfectly predicted by the Bohr model. The discrepancy with neutral He (24.6 eV) arises because He is not a hydrogen-like ion: it has two electrons that repel each other.

(b) **Li, Na, K trend via the Slater model:**

- Li ($Z = 3$): $1s^2 2s^1$, $Z^*(2s) \approx 1.3$, $n^* = 2$

- Na ($Z = 11$): $1s^2 2s^2 2p^6 3s^1$, $Z^*(3s) = 2.20$, $n^* = 3$
- K ($Z = 19$): $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$, $Z^*(4s) = 2.20$, $n^* = 3.7$

From Na to K, Z^* is virtually identical (2.20), but n^* increases ($3 \to 3.7$). Since $E \propto (Z^*/n^*)^2$, the binding energy decreases, so E_i decreases. Down a group, it is the increase in n (and n^*) that governs the trend, not the variation in Z^*.

> **Note:** Down a group: E_i **decreases** going down, because the valence electron occupies an increasingly outer shell.

(c) **He and He^+:**

- He^+ is a hydrogen-like ion: a single electron around a $+2e$ nucleus. Exact Bohr model: $E_i = 54.4$ eV.
- Neutral He has two $1s$ electrons. Each electron experiences:
  - Attraction from the $+2e$ nucleus.
  - Repulsion from the other electron.
  - Partial screening: $\sigma = 0.30$ for the other 1s.

  Hence $Z^* = 2 - 0.30 = 1.70$. The calculated ionisation energy is:

$$E_i \approx 13.6 \times \left(\frac{1.70}{1}\right)^2 = 39.3 \text{ eV}$$

The experimental value (24.6 eV) is lower because the Slater model does not perfectly capture electron correlation. But qualitatively, we understand why $E_i(\text{He}) < E_i(\text{He}^+)$: screening and repulsion reduce the effective attraction.

2. Atomic radii:

The atomic radius approximately follows: $r \propto \dfrac{n^{*2}}{Z^*}$.

- Na: $n^* = 3$, $Z^* = 2.20 \Rightarrow r \propto 9/2.20 \approx 4.09$
- K: $n^* = 3.7$, $Z^* = 2.20 \Rightarrow r \propto 13.69/2.20 \approx 6.22$

The ratio $r(\text{K})/r(\text{Na}) \approx 6.22/4.09 \approx 1.52$ is consistent with the experimental ratio $227/186 \approx 1.22$. The increase in radius from Na to K is explained by the increase in n^* (the valence shell is further out), while Z^* remains unchanged.

Estimate for Li: $n^* = 2$, $Z^* \approx 1.3$.

$$r \propto \frac{4}{1.3} \approx 3.08$$

The lithium radius should be smaller than that of sodium (4.09). Experimentally: $r(\text{Li}) \approx 152$ pm, versus 186 pm for Na. The trend is correctly predicted.

> **Note:** Atomic radius increases down a group (Na $\to$ K) because the valence electron occupies a more external shell (larger n).

Summary of Spectral Series:

Series	Final level n_1	Spectral Region	Series Limit
Lyman	1	Ultraviolet	91.2 nm
Balmer	2	Visible / Near UV	364.6 nm
Paschen	3	Near Infrared	820.4 nm
Brackett	4	Infrared	1458 nm
Pfund	5	Far Infrared	2278 nm
Humphreys	6	Very Far Infrared	3280 nm

End of the answer key — Good luck with your revision!