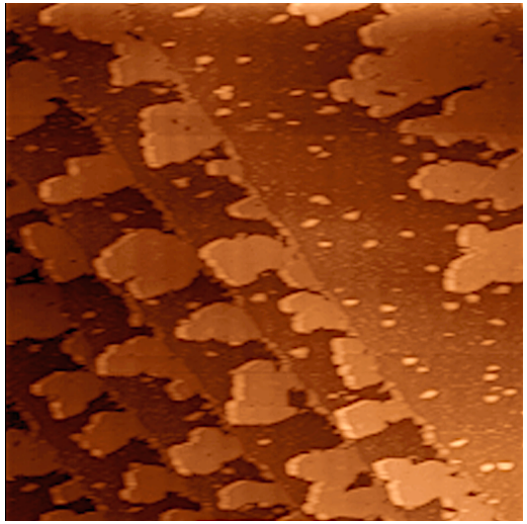
Atomic structure

A-Level Chemistry

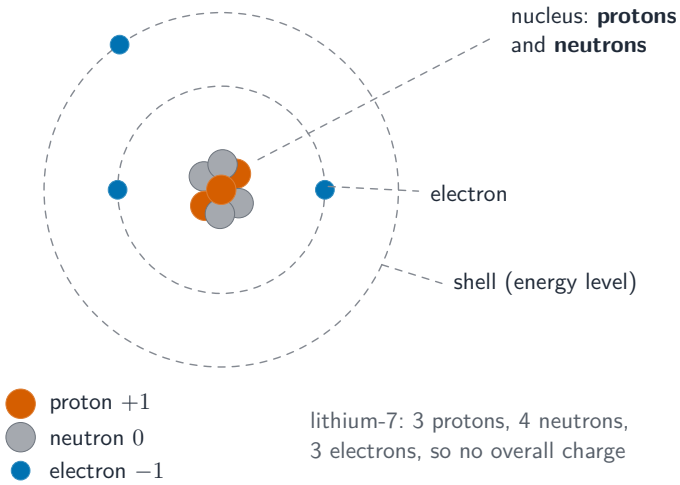
What an atom is made of



A scanning tunnelling microscope can image individual atoms.

Everything is made of **atoms**. An atom is mostly empty space. At its centre is a tiny, heavy **nucleus**. The nucleus holds two kinds of particle: **protons** and **neutrons**. Around the nucleus, in the empty space, move the **electrons**. The electrons stay in **shells** – layers at set distances from the nucleus.

The nucleus is very small but holds almost all the mass. The electrons take up almost all the space but have almost no mass.



An atom is mostly empty space: protons and neutrons sit in the tiny central nucleus, while electrons move in shells around it

Relative charge and relative mass

We compare the three particles using **relative charge** and **relative mass**. These are simple numbers, not real units.

Particle	Relative charge	Relative mass
proton	+1	1
neutron	0	1
electron	−1	$\frac{1}{1836}$ (about 0)

A proton and a neutron have almost the same mass. An electron is about 1836 times lighter. The proton is positive, the electron is negative, and the neutron has no charge – it is **neutral**.

Proton number and nucleon number

Two numbers describe the nucleus:

- the **proton number** (also called the **atomic number**), symbol Z – the number of protons.
- the **nucleon number** (also called the **mass number**), symbol A – the total number of protons and neutrons. Protons and neutrons are both **nucleons**.

So the number of neutrons is $A - Z$.

Counting particles in an atom or ion

For a neutral atom, the number of electrons equals the number of protons, which equals Z.

An **ion** is an atom that has lost or gained electrons, so it has a charge:

- a positive ion has fewer electrons than protons.
- a negative ion has more electrons than protons.

Example: $^{27}_{13}\mathrm{Al}^{3+}$ has 13 protons, $27 - 13 = 14$ neutrons, and $13 - 3 = 10$ electrons (it lost 3 electrons to become 3+).

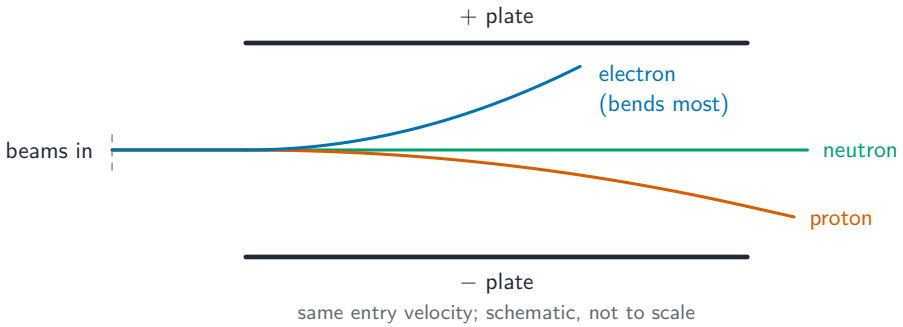
How mass and charge are spread out

Almost all the mass sits in the nucleus, because protons and neutrons are heavy and electrons are very light. All the positive charge is in the nucleus (the protons). The negative charge is spread out in the shells (the electrons).

Beams of particles in an electric field

Imagine beams of protons, neutrons and electrons moving at the same speed into an **electric field** between two charged plates:

- the proton beam bends towards the negative plate (protons are positive).
- the electron beam bends the other way, towards the positive plate. It bends much more, because the electron is far lighter – the same force gives a bigger **deflection** to a smaller mass.
- the neutron beam goes straight through. It has no charge, so the field gives it no force.



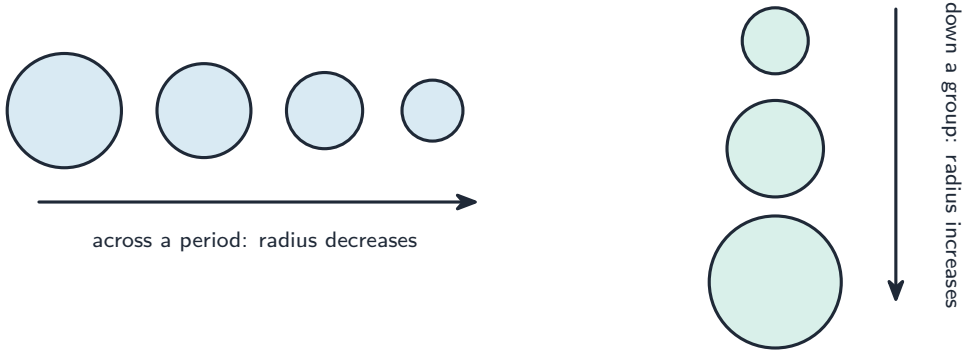
In an electric field the proton bends towards the − plate and the electron bends the opposite way and far more (it is much lighter); the neutron passes straight through

Atomic radius and ionic radius

The **atomic radius** is the size of an atom. The **ionic radius** is the size of an ion.

Across a **period** (left to right), the atomic radius gets **smaller**. The **nuclear charge** (the pull from the protons) rises, but the electrons go into the same outer shell, so the **shielding** by inner shells stays about the same. The stronger pull draws the outer shell inwards.

Down a **group** (top to bottom), the atomic radius gets **larger**. Each step down adds a new shell, so the outer electrons are further out and feel more shielding from the nucleus.



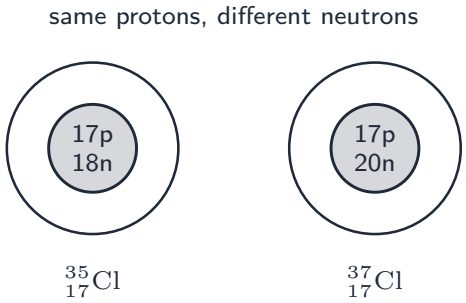
Across a period the atoms shrink (stronger nuclear pull on the same outer shell); down a group they grow (each step adds a shell)

For ions:

- a positive ion (**cation**) is smaller than its atom. Electron loss reduces electron-electron repulsion and increases the attraction for the remaining electrons. The whole outer occupied shell may be lost, but not every electron loss empties a shell.
- a negative ion (**anion**) is larger than its atom. It has gained electrons, so there is more **repulsion** between the electrons.
- among ions that have the same number of electrons, the one with more protons is smaller.

Isotopes

Isotopes are atoms of the same element with the same number of protons but a different number of neutrons. So isotopes have the same proton number Z but a different nucleon number A.



Two chlorine isotopes: same protons, different neutrons

We write an isotope as $^{A}_{Z}$X: the nucleon number A on top, the proton number Z below. For example, chlorine has two main isotopes, $^{35}_{17}$Cl and $^{37}_{17}$Cl.

Same chemical properties

Chemical properties depend on the electrons, especially the outer electrons. Isotopes of one element have the same number of electrons arranged in the same way. So they react in exactly the same way – they have the same chemical properties.

Different physical properties

Some **physical properties** depend on mass, so they differ between isotopes. A heavier isotope has more neutrons, so more mass, and therefore a higher **density**. (The syllabus limits this difference to mass and density.)

Electrons, energy levels and orbitals

Hydrogen emits light only at discrete, characteristic wavelengths – its line emission spectrum.

Electrons are arranged in shells, sub-shells and orbitals.

Shells and the principal quantum number

Each shell is labelled by the **principal quantum number** $n = 1, 2, 3, \ldots$ A larger n generally means greater spatial extent, but n alone does not put all sub-shells of a multi-electron atom into energy order. The configurations and ionisation processes assessed in these sections are ground-state species from hydrogen to krypton.

Sub-shells and orbitals

Each shell is split into **sub-shells**, named s, p and d. Each sub-shell is built from **orbitals**. An orbital is a small region that can hold up to two electrons.

Sub-shell	Number of orbitals	Maximum electrons
s	1	2
p	3	6
d	5	10

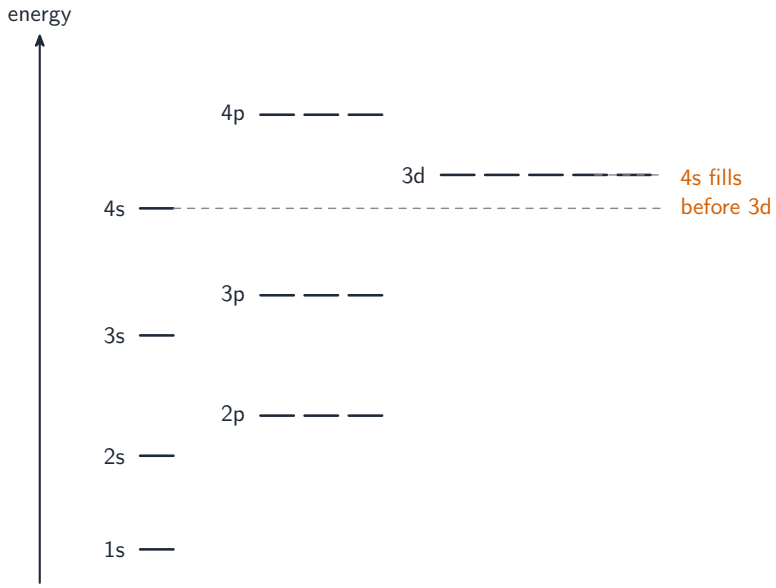
So an s sub-shell holds 2 electrons, a p sub-shell holds 6, and a d sub-shell holds 10.

Order of increasing energy

Electrons occupy the lowest-energy available arrangement. The usual neutral-atom filling sequence for the sub-shells studied here is:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p$$

4s is reached before 3d in this usual construction sequence. The ordering is not fixed in every occupied atom or ion; apply the separate 4s-first removal rule for transition-metal cations.



The usual neutral filling order; it must not be used to claim that 4s is always lower than occupied 3d levels

Electronic configuration

The **electronic configuration** lists how many electrons are in each sub-shell. The lowest-energy arrangement is the **ground state**.

For iron (Fe, $Z = 26$):

$$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^6\,4s^2$$

You can write a shorthand using the nearest **noble gas** in square brackets:

$$[\mathrm{Ar}]\,3d^6\,4s^2$$

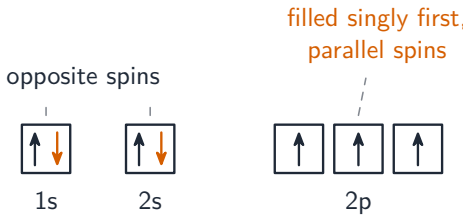
Here [Ar] stands for the full configuration of argon. Chromium and copper are exceptions to mechanically placing two electrons in 4s: Cr is $[\mathrm{Ar}]3d^5 4s^1$ and Cu is $[\mathrm{Ar}]3d^{10}4s^1$. Both totals and ground-state occupations matter.

For ions, you add or remove electrons. One key rule: when a transition metal forms a positive ion, it loses its 4s electrons **before** its 3d electrons. So Fe^{3+} is $[\mathrm{Ar}]\,3d^5$.

Electrons in boxes

The **electrons in boxes** notation draws each orbital as a box and each electron as an arrow. Two electrons in the same orbital must point opposite ways, because each electron has a property called **spin**, and a shared orbital needs opposite spins.

Within a sub-shell, electrons fill empty orbitals one at a time, with parallel arrows, before any orbital gets a second electron. Spreading out like this keeps the electrons apart and lowers the repulsion between them.



Electrons in boxes for nitrogen ($1s^2\,2s^2\,2p^3$): paired electrons point opposite ways, and the 2p orbitals fill singly with parallel spins

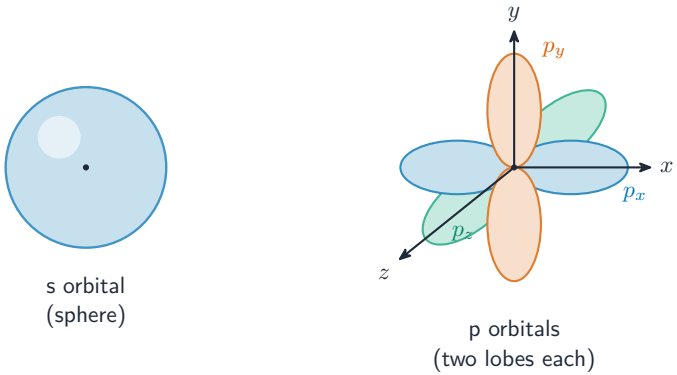
For oxygen, $2p^4$ has one pair and two singly occupied orbitals. The n = 2 shell also contains the 2s pair, so it contains two pairs altogether. A whole-shell question and a named-sub-shell question have different counting boundaries.

Why the configuration takes this shape

Electrons fill from low energy to high energy because that gives the most stable (lowest-energy) atom. Within a sub-shell they spread out singly first to reduce the repulsion between the negative electrons.

Shapes of s and p orbitals

- an s orbital is a **sphere** centred on the nucleus.
- a p orbital has two lobes, like a dumbbell, pointing along one axis. The three p orbitals point along three directions at right angles (the x, y and z axes).



An s orbital is a sphere; each p orbital is a dumbbell, and the three p orbitals point along the x, y and z axes

Free radicals

A **free radical** is a species with one or more **unpaired electrons**. Many free radicals are reactive, but the defining feature is an unpaired electron, not reactivity alone or a net charge.

Ionisation energy

First ionisation energy

The **first ionisation energy** (IE) is the energy needed to remove one electron from each atom in one mole of gaseous atoms, forming one mole of gaseous +1 ions.

Starting from separate gaseous atoms isolates electron removal without adding energy for breaking a solid or molecule into atoms. The unit is kJ mol^{-1}. As an equation, for an element X:

$$\mathrm{X(g)} \rightarrow \mathrm{X^+(g)} + \mathrm{e^-}$$

The (g) shows the species is a gas.

Successive ionisation energies

After removing one electron, you can remove another. The second ionisation energy removes one electron from each +1 ion:

$$X^+(g) \rightarrow X^{2+}(g) + e^-$$

You can keep going. These are the **successive ionisation energies** . Each is larger than the one before, because every electron is pulled away from a more positive ion.

What ionisation energy depends on

Ionisation energy comes from the attraction between the positive nucleus and the outer electron. Three main factors set how strong that attraction is:

- **nuclear charge**: more protons pull the electrons more strongly, so the ionisation energy is higher.
- **atomic radius**: the further the outer electron sits from the nucleus, the weaker the pull, so the ionisation energy is lower.
- **shielding**: inner shells block some of the pull on the outer electron. More inner shells mean more shielding and a lower ionisation energy.

There is a smaller effect too – **spin-pair repulsion** . When two electrons share one orbital, they push each other a little, so one is easier to remove.

Trends in first ionisation energy

Across a period, the first ionisation energy generally **rises**. The nuclear charge grows while shielding stays about the same, so the outer electrons are held more tightly.

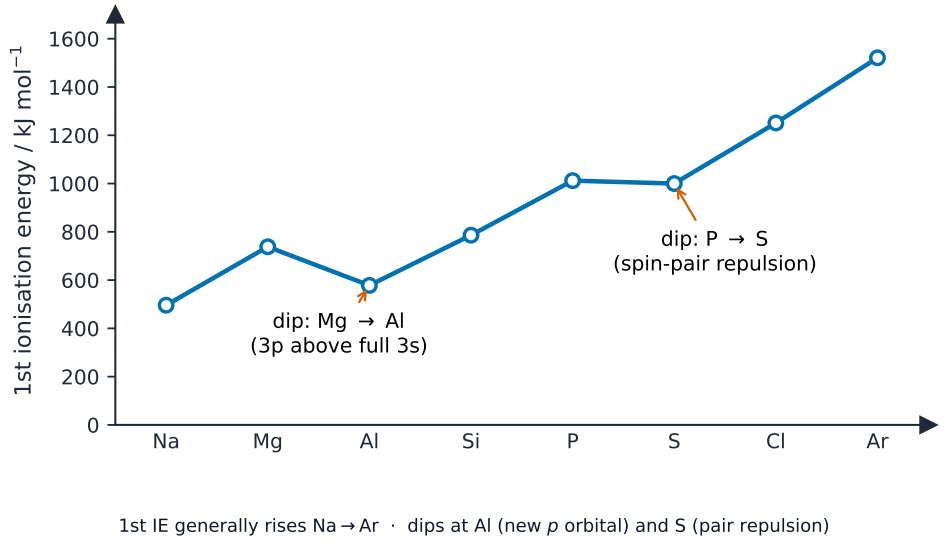
Down a group, the first ionisation energy **falls**. Lower elements have more shells, so more shielding and a larger radius, and the outer electron is easier to remove.

The dips are evidence for sub-shells

The rise across a period is not smooth. Two small dips appear, and you should be able to explain both:

- **Group 2 to Group 13** (for example Mg to Al): the electron removed from Al comes from a 3p sub-shell, which is higher in energy than the full 3s sub-shell in Mg. A 3p electron is easier to remove, so the value dips.
- **Group 15 to Group 16** (for example P to S): in S, one 3p orbital now holds a pair of electrons. Spin-pair repulsion makes one of them easier to remove, so the value dips.

These dips are evidence that sub-shells exist.

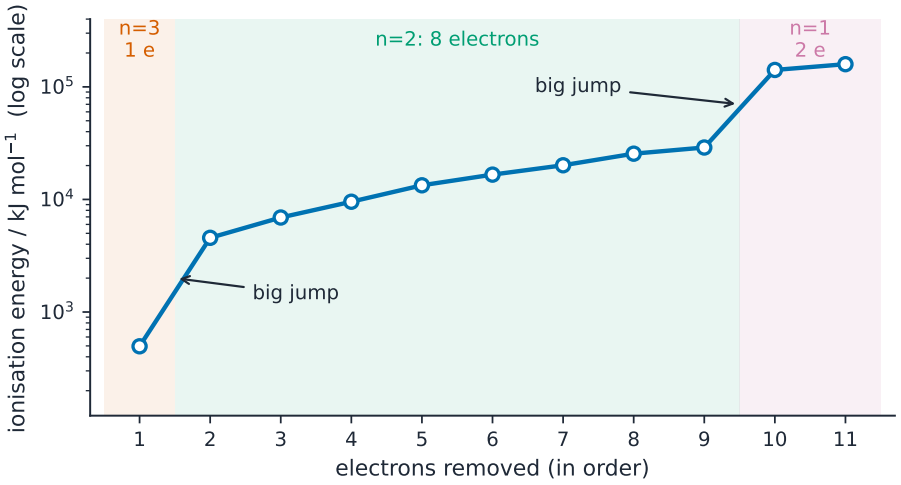


First ionisation energy rises across Period 3 but dips at Al and at S – evidence that sub-shells exist

Successive ionisation energies are evidence for shells

If you plot the successive ionisation energies of one element, the values rise, with **big jumps** at certain points. A big jump happens when the next electron must come from a shell closer to the nucleus.

For main-group atoms, count the electrons removed before the first inner-shell jump to find the outer-shell count. Counts 1 and 2 correspond to Groups 1 and 2; counts 3–8 correspond to Groups 13–18, with helium as the two-electron Group 18 exception. The first jump alone does not establish the period: use the number of occupied shells from fuller data or additional information about the atom.



big jump = next electron from a shell closer to the nucleus (shell structure)

Successive ionisation energies of sodium (log scale): the big jumps reveal the $2, 8, 1$ *shell structure*

Electrons removed before the first big jump	Group
1	Group 1
2	Group 2
3	Group 13

Worked example. The first five successive ionisation energies of an element are 590, 1150, 4940, 6480 and 8120 kJ mol^{-1}. Which group is it in? Look for the **big jump**, not the biggest number. From the 1st to the 2nd the value roughly doubles, which is a normal rise. From the 2nd (1150) to the 3rd (4940) it more than quadruples: that is the jump. So **two** electrons come off easily before it, the outer shell holds 2 electrons, and the element is in **Group 2**. Count the electrons removed **before** the jump, and explain the jump properly: the next electron is being pulled from a shell **closer to the nucleus**, not from a different element.

Common mistakes.

- Leaving out the state symbols in an ionisation-energy equation. The atoms and ions are **gaseous**: $\mathrm{Na(g)} \rightarrow \mathrm{Na^+(g)} + \mathrm{e^-}$.
- Writing the equation as $\mathrm{X(g)} + \mathrm{e^-} \rightarrow \mathrm{X^-(g)}$. That is electron **gain**; ionisation **removes** an electron.
- Removing 3d electrons before 4s when a transition metal forms an ion. The **4s** electrons go first: $\mathrm{Fe^{2+}}$ is $[\mathrm{Ar}]\,3\mathrm{d}^6$, not $[\mathrm{Ar}]\,3\mathrm{d}^4\,4\mathrm{s}^2$.
- Writing chromium as $[\mathrm{Ar}]\,3\mathrm{d}^4\,4\mathrm{s}^2$ or copper as $[\mathrm{Ar}]\,3\mathrm{d}^9\,4\mathrm{s}^2$. Both are exceptions: Cr is $3\mathrm{d}^5\,4\mathrm{s}^1$ and Cu is $3\mathrm{d}^{10}\,4\mathrm{s}^1$.
- Explaining the Mg $\rightarrow$ Al dip by spin-pair repulsion. The Al electron is removed from a **3p** sub-shell, higher in energy than Mg's 3s; spin-pair repulsion explains the **P $\rightarrow$ S** dip.
- Saying successive ionisation energies rise "because there are fewer electrons". Each electron is removed from an increasingly **positive ion**, so it is held more strongly; a big jump shows a new, inner **shell**.
- Saying the electron beam bends towards the negative plate. Electrons are negative, so they bend towards the **positive** plate, and more sharply than protons because their mass is far smaller.

Exam tips

- Define **isotopes** in full: atoms of the same element with the same number of protons but a different number of neutrons – the mark scheme wants both halves.
- 4s fills **before** 3d, but electrons are **removed from 4s first** when forming ions, so $\mathrm{Fe^{3+}}$ is $[\mathrm{Ar}]3\mathrm{d}^5$ (not $[\mathrm{Ar}]3\mathrm{d}^3 4\mathrm{s}^2$).
- In successive ionisation energies, a **big jump** marks the start of a new (inner) shell – use the jumps to place the element in its group.
- Explain every ionisation-energy trend with the same three factors: **nuclear charge, distance and shielding**, plus sub-shell effects for the small dips.
- Learn the exact reason first ionisation energy of oxygen is **below** nitrogen: oxygen's **paired 2p electrons repel**, so one is easier to remove.