Atomic structure

Protons, neutrons and electrons, isotopes, shells, sub-shells and orbitals, electronic configurations, free radicals, and ionisation energies and what they tell you.

1.1 Particles in the atom and atomic radius

An atom is mostly empty space. Almost all the mass is in a very small, dense, positively charged **nucleus** of protons and neutrons. Electrons occupy shells in the space around it.

Particle	Relative charge	Relative mass
Proton	+1	1
Neutron	0	1
Electron	−1	1/1836 (negligible)

- The **proton (atomic) number**, Z, is the number of protons. The **nucleon (mass) number**, A, is the number of protons plus neutrons.
- In an atom, electrons = protons. For an ion, electrons = Z − charge. $^{27}_{13}Al^{3+}$ has 13 protons, 14 neutrons and 10 electrons.
- In an electric field a beam of protons is deflected towards the negative plate and a beam of electrons towards the positive plate (much more, because of their tiny mass). Neutrons are not deflected.

Atomic and ionic radius

- **Across a period** atomic radius **decreases**: the nuclear charge increases but the shielding is almost unchanged (same shell), so the outer electrons are pulled in more strongly.
- **Down a group** atomic radius **increases**: more shells and more shielding, so the outer electrons are further from the nucleus.
- A **cation is smaller** than its atom (it has lost its outer shell, or has less electron repulsion). An **anion is larger** than its atom (more electron repulsion, same nuclear charge). Across Period 3 the ions Na^+ to Si^{4+} get smaller, then P^{3-} to Cl^- (which have an extra shell) are much larger and also get smaller.

Using particle counts rather than memorised examples

The identity of an element depends on its proton number, not its mass number or charge. Chemical reactions rearrange electrons; they do not turn an aluminium nucleus into a different element. Ion formation therefore changes the electron count while leaving proton and neutron counts unchanged. For

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a positive ion subtract electrons; for a negative ion add them. A superscript 2− means two **extra** electrons, not two fewer.

Worked example: $^{56}_{26}Fe^{2+}$ contains 26 protons, $56 - 26 = 30$ neutrons and $26 - 2 = 24$ electrons. The neutral atom of the same isotope has 26 electrons but the same nucleus. Conversely, a species with 16 protons, 18 neutrons and 18 electrons is $^{34}_{16}S^{2-}$: calculate its mass number by adding nucleons and its charge by comparing protons with electrons.

In field-deflection questions, separate **direction** from **extent**. Charge determines which plate attracts the beam. At the same speed and field strength, a larger charge-to-mass ratio gives a larger acceleration and deflection. Equal and opposite charges do not imply equal deflections if the masses differ. A neutron beam continues straight because it has no net electric charge.

For radius explanations, name both competing effects. Increasing nuclear charge strengthens attraction; increased distance and inner-electron shielding weaken it. In an **isoelectronic series**, all species have the same electron configuration, so nuclear charge provides a particularly clear comparison. O^{2-}, F^{-}, Na^{+} and Mg^{2+} each have ten electrons; their radii decrease in that order as proton number increases. Do not claim the smaller species has fewer occupied shells when all four have the same shells.

> **TRY IT**
>
> Give the particle counts in $^{37}_{17}Cl^{-}$ and explain why it is larger than a neutral chlorine atom.

Answer: 17 protons, 20 neutrons and 18 electrons. Adding an electron increases electron–electron repulsion within the occupied outer shell, while nuclear charge remains 17+. The cloud expands; a new principal shell is not created.

1.2 Isotopes

Isotopes are atoms of the same element with the same number of protons but different numbers of neutrons. They are written $^{A}_{Z}X$, for example $^{35}_{17}Cl$ and $^{37}_{17}Cl$.

- They have the **same chemical properties**, because chemical properties depend on the electron arrangement, which is set by the number of protons.
- They have **different physical properties** (mass, density) because their masses differ.

What remains the same between isotopes?

Neutral isotopes of an element have the same number and arrangement of electrons. Consequently, their bonding patterns and usual reactions are essentially the same at this level. Their nuclei contain different neutron numbers, changing mass and mass-dependent physical properties. Avoid writing that isotopes have “the same mass but different electrons”: that describes neither isotopes nor ion formation correctly.

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Worked example: chlorine has two illustrative isotopic abundances, 75.0% chlorine-35 and 25.0% chlorine-37. Its weighted relative atomic mass is $(35 \times 75.0 + 37 \times 25.0)/100 = 35.5$. The non-integer average does not mean an individual atom has half a neutron. Each atom has an integer nucleon count; the average describes the sample.

> **TRY IT**
>
> Why do two isotopes of magnesium form ions with the same charge even though their masses differ?

Answer: Their neutral atoms have the same electron configuration, including two outer-shell electrons. Each normally loses those two electrons to form a 2+ ion. Different neutron numbers do not change this outer-electron arrangement.

1.3 Electrons, energy levels and atomic orbitals

Electrons are in **shells** (principal quantum number $n = 1, 2, 3 \ldots$), which contain **sub-shells** (s, p, d), which contain **orbitals**. An orbital holds at most two electrons, which must have opposite spins.

Sub-shell	Orbitals	Maximum electrons
s	1	2
p	3	6
d	5	10

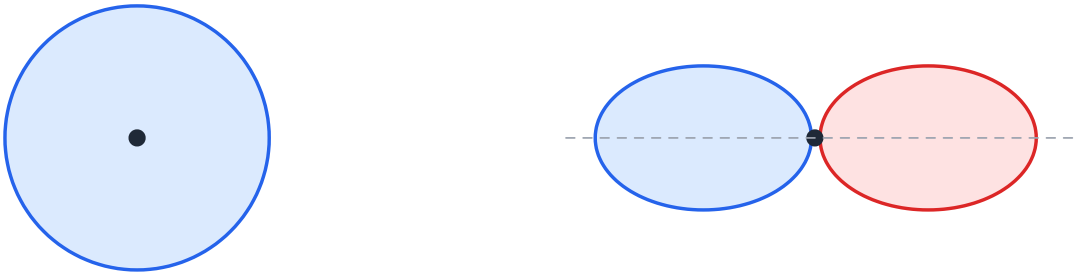
- An s **orbital** is spherical. A p **orbital** is dumb-bell shaped; there are three, along the x, y and z axes.
- The order of increasing energy is 1s, 2s, 2p, 3s, 3p, **4s**, 3d, 4p. The 4s fills before the 3d, but is **lost first** when a transition element forms an ion.
- Electrons occupy orbitals of equal energy singly before pairing (**Hund's rule**), which minimises electron–electron repulsion.
- Ground state configurations, in the full and shorthand forms: Fe is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$ or $[Ar]\,3d^6 4s^2$. Fe^{3+} is $[Ar]\,3d^5$.
- Two exceptions: Cr is $[Ar]\,3d^5 4s^1$ and Cu is $[Ar]\,3d^{10} 4s^1$ (a half-full or full 3d is more stable).
- In the **electrons-in-boxes** notation each orbital is a box and each electron an arrow; paired electrons have opposite arrows.

A free radical is a species with one or more unpaired electrons, for example $Cl\cdot$ and $\cdot CH_3$.

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Building and checking an electronic configuration

Orbitals are probability regions, not circular electron paths



s orbital: spherical | **p orbital: two lobes; nucleus at node**

Different lobe colours indicate wavefunction phase, not positive/negative charge.

An orbital is a region in which there is a high probability of finding an electron; it is not a fixed circular path. A shell contains sub-shells of different energies, and each sub-shell contains its allowed number of orbitals. Keep the hierarchy clear: the **2p sub-shell** contains three orbitals, not three shells. A filled 2p sub-shell holds six electrons because each orbital can hold two.

To construct a configuration, establish the total electron count, fill the lower-energy orbitals first, and check that the superscripts add to that count. Within three equal-energy p orbitals, put one electron into each before pairing. Nitrogen's $2p^3$ has three unpaired electrons; oxygen's $2p^4$ has one pair and two unpaired electrons. Pairing all four into just two orbitals would leave an equal-energy orbital unnecessarily empty.

Worked example: neutral iron has 26 electrons, $[Ar]3d^6 4s^2$. Forming Fe^{2+} removes the two 4s electrons to give $[Ar]3d^6$; forming Fe^{3+} removes one further 3d electron to give $[Ar]3d^5$. Do not remove 3d electrons first just because 3d is written before 4s. The relative orbital energies change as these sub-shells become occupied and ions form.

Chromium and copper are important configuration exceptions; learn their observed ground states rather than forcing them into a mechanical filling rule. Also distinguish an unpaired-electron species from an electrically charged species: a radical can be neutral, while an ion need not contain an unpaired electron.

> **TRY IT**
>
> Write the configurations of S^{2-} and Cu^{2+}, and count unpaired electrons in each.

Answer: S^{2-} is $1s^2 2s^2 2p^6 3s^2 3p^6$, with none. Cu^{2+} is $[Ar]3d^9$, with one unpaired electron. Remove the single 4s electron from neutral Cu first, then one 3d electron.

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1.4 Ionisation energy

The **first ionisation energy** is the energy needed to remove one mole of electrons from one mole of gaseous atoms to form one mole of gaseous 1+ ions.

$$Mg(g) \rightarrow Mg^{+}(g) + e^{-} \qquad \Delta H = +738 \text{ kJ mol}^{-1}$$

The second ionisation energy is for $Mg^{+}(g) \rightarrow Mg^{2+}(g) + e^{-}$, and so on. Each is endothermic, and each is larger than the one before, because the electron is removed from a more positive ion.

Factors

Ionisation energy increases with greater **nuclear charge** and smaller **atomic radius**, and decreases with more **shielding** by inner shells and sub-shells. It is due to the attraction between the nucleus and the outer electron.

Trends

- **Down a group** it decreases: the outer electron is further away and better shielded.
- **Across a period** it generally increases: more nuclear charge, the same shielding, a smaller radius.
- Two dips occur in Periods 2 and 3. **Be to B and Mg to Al:** the outer electron is in a p sub-shell, which is higher in energy and slightly shielded by the s electrons. **N to O and P to S:** the electron is removed from a doubly occupied p orbital, and **spin-pair repulsion** makes it easier to remove.

Successive ionisation energies

A large jump in successive ionisation energies shows that the next electron comes from an inner shell. The number of electrons removed before the jump gives the **group** of the element. The pattern also tells you how many electrons are in each shell, so the **electronic configuration** can be deduced.

> **TRY IT**
>
> Successive ionisation energies of an element (kJ mol^{-1}): 738, 1451, 7733, 10543. Which group?

The big jump comes after the second, so there are two outer electrons: **Group 2**.

Turning a trend into an explanation

A good comparison identifies the electron being removed, its shell or sub-shell, and the balance of nuclear attraction and shielding. “More protons” alone is insufficient down a group: the outer electron is

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also in a more distant, more shielded shell. “A full shell is stable” alone does not explain the Mg-to-Al dip; the crucial change is from a 3s electron to a higher-energy 3p electron.

For successive ionisations, a large jump indicates crossing into a more strongly bound inner shell. The energies before that jump still increase because electrons are being removed from increasingly positive ions. For main-group atoms, two removals before the first very large jump support Group 2; seven support Group 17. Do not apply this simple outer-shell rule uncritically to transition-metal sequences.

> **TRY IT**
>
> Explain why the first ionisation energy of sulfur is lower than that of phosphorus, despite sulfur having more protons.

Answer: Both lose an electron from a 3p sub-shell, with similar shielding. Phosphorus has three singly occupied p orbitals; sulfur has a paired electron in one of them. Extra repulsion within that pair makes sulfur's electron easier to remove and outweighs the increase in nuclear attraction for this comparison.

Chapter check: distinguish isotope from ion, shell from orbital, and nuclear charge from ionic charge. In every ionisation equation, show a gaseous starting species, a gaseous product ion and an electron on the product side. Link these ideas to **periodicity** and **transition elements**.

References and further reading

Scope follows section 1 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide’s Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

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