

Electron configurations, PES and periodic trends

AP Chemistry · Lesson

Quick answer: Electrons fill subshells in order of energy, giving each atom a configuration. Photoelectron spectroscopy shows these subshells as peaks: position gives binding energy and height gives the number of electrons. Coulomb's law, with effective nuclear charge and distance, explains periodic trends in radius and ionisation energy.

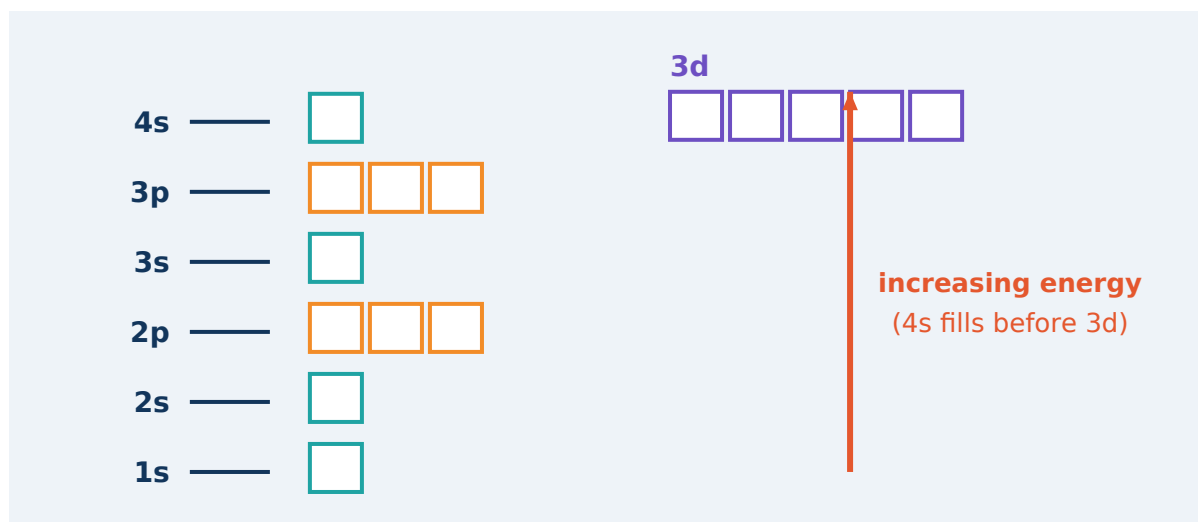
Level: AP Chemistry · **Curriculum:** AP Chem Unit 1

How do electrons fill orbitals?

Definition

An electron configuration lists the subshells occupied by an atom's electrons and how many electrons each holds, for example $1s^2 2s^2 2p^6 3s^2$ for magnesium. Valence electrons are those in the outermost shell.

Three rules decide the order. The aufbau principle fills the lowest-energy subshell first. The Pauli exclusion principle allows two electrons per orbital, with opposite spins. Hund's rule puts one electron in each orbital of a subshell before pairing any of them.



Orbital filling order: each box is an orbital that holds two electrons of opposite spin.

Chromium and copper break the simple pattern. A half-full or full 3d subshell is slightly more stable, so chromium is $[\text{Ar}] 4s^1 3d^5$ and copper is $[\text{Ar}] 4s^1 3d^{10}$. When transition metals form cations, the 4s electrons leave before the 3d ones.

Worked example

Write the configuration of Fe^{3+} . Iron has 26 electrons: $[\text{Ar}] 4s^2 3d^6$. Remove the two 4s

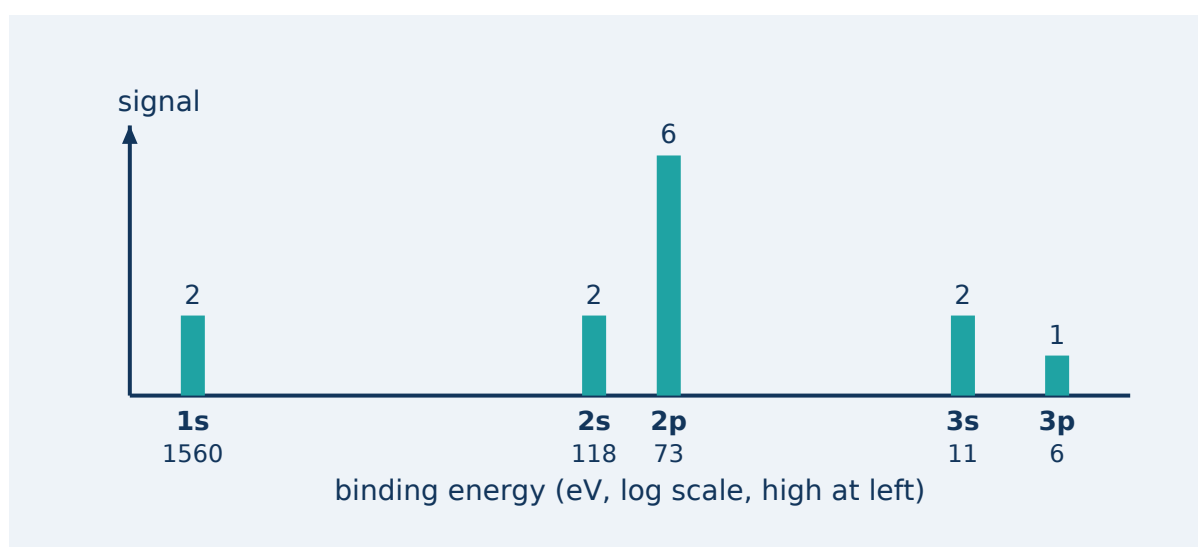
electrons and then one 3d electron. Fe^{3+} is **[Ar] 3d⁵**, with five unpaired electrons.

What does a photoelectron spectrum show?

In photoelectron spectroscopy a beam of high-energy photons knocks electrons out of atoms. The kinetic energy of each ejected electron tells us how tightly it was held: binding energy = photon energy – kinetic energy.

Key law

Each peak is one subshell. The position gives the binding energy of its electrons. The height is proportional to the number of electrons in it. Core electrons have higher binding energies than valence electrons.



PES of aluminium (approximate energies): peak heights show $1s^2 2s^2 2p^6 3s^2 3p^1$.

Worked example

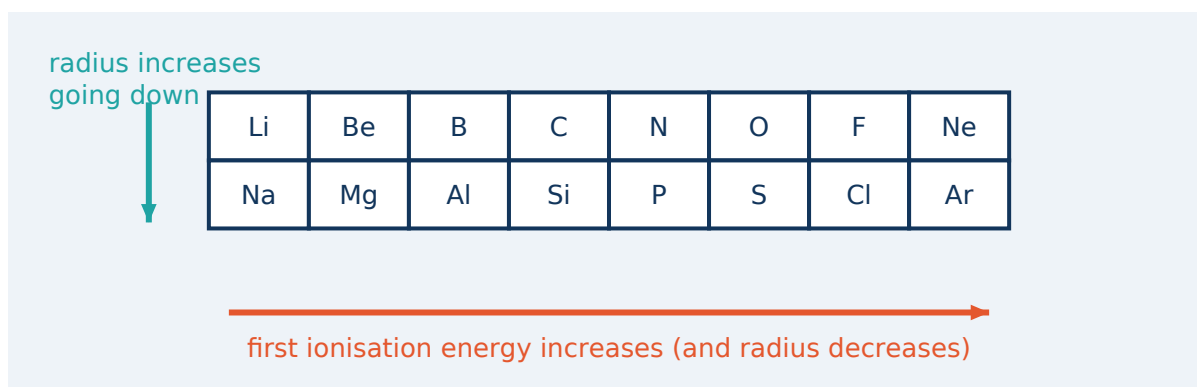
A spectrum has five peaks at about 1560, 118, 73, 11 and 6 eV with relative heights 2 : 2 : 6 : 2 : 1. Matching the heights to subshells gives $1s^2 2s^2 2p^6 3s^2 3p^1$, which is **aluminium**.

How does Coulomb's law explain periodic trends?

Formula

$F = k q_1 q_2 / r^2$, where F is the force in newtons, $k = 8.99 \times 10^9 \text{ N}\cdot\text{m}^2/\text{C}^2$, q_1 and q_2 are the charges in coulombs and r is the separation in metres. The attraction grows with charge and falls quickly with distance.

A valence electron feels the nucleus reduced by the inner electrons that shield it. The effective nuclear charge is roughly $Z_{\text{eff}} \approx Z - \text{number of core electrons}$. For magnesium it is $12 - 10 = 2$, and for chlorine it is $17 - 10 = 7$.



Periodic trends across a period and down a group.

Trend	Across a period	Down a group	Reason
Atomic radius	decreases	increases	Z_{eff} rises across; more shells down
First ionisation energy	generally increases	decreases	stronger pull; electron farther away
Electronegativity	increases	decreases	same as ionisation energy

Worked example

The distance between a valence electron and the nucleus triples while Z_{eff} doubles. Since $F \propto Z_{\text{eff}}/r^2$, the force changes by $2/3^2 = 2/9 \approx \mathbf{0.22 \text{ of its old value}}$, so the electron is much easier to remove.

Successive ionisation energies show the shell structure. Magnesium needs 738 and 1451 kJ/mol for its first two electrons, but 7733 kJ/mol for the third. The big jump shows the third electron comes from an inner shell, so magnesium has two valence electrons.

Common mistake

Students say atomic size increases across a period because there are more electrons. The electrons enter the same shell, but the nuclear charge increases, so the radius shrinks.

Lina's tip

For any trend question, say three things: which charge, which distance, which shielding. Then connect them with Coulomb's law.

Key points to remember

- Fill order: 1s 2s 2p 3s 3p 4s 3d 4p, two electrons per orbital
- PES: peak position = binding energy, height = number of electrons
- Coulomb's law: $F = k q_1 q_2 / r^2$
- $Z_{\text{eff}} \approx Z - \text{core electrons}$
- Radius falls across a period; IE_1 rises across a period

Electron configurations, PES and periodic trends: frequently asked questions

What is the electron configuration of chromium?

It is $[\text{Ar}] 4s^1 3d^5$. A half-filled 3d subshell gives extra stability, so one 4s electron moves into 3d.

What do the peaks in a PES spectrum mean?

Each peak is a subshell. Its position shows the binding energy and its height shows how many electrons are in it.

Why does ionisation energy increase across a period?

The nuclear charge rises while the electrons enter the same shell and shield little. The valence electrons are pulled in more strongly and are harder to remove.

Why is there a large jump in successive ionisation energies?

The jump appears when the next electron must come from an inner shell. This shell is closer to the nucleus and less shielded, so it is held far more strongly.

How does Coulomb's law apply to atoms?

The attraction between nucleus and electron is proportional to the charges and inversely proportional to the distance squared. More charge or less distance means a stronger attraction.