

# Orbitals, configurations and ionisation energy patterns

Chemistry grades 11-12 (A Level · IB · Class 11-12) · Lesson

**Quick answer:** An atomic orbital is a region around a nucleus that holds at most two electrons, and orbitals come as s, p and d types. Electrons fill them from the lowest energy upwards. Ionisation energy is the energy needed to remove one mole of electrons from gaseous atoms, and its successive values reveal the shell structure.

**Level:** Chemistry grades 11-12 (A Level · IB · Class 11-12) · **Curriculum:** A Level 3.1.1, IB S1.3

## What is an atomic orbital?

An electron does not circle the nucleus on a track. Quantum mechanics describes a region of space where the electron is most likely to be found, and that region is an orbital. Each orbital holds at most two electrons, and the two must have opposite spins.

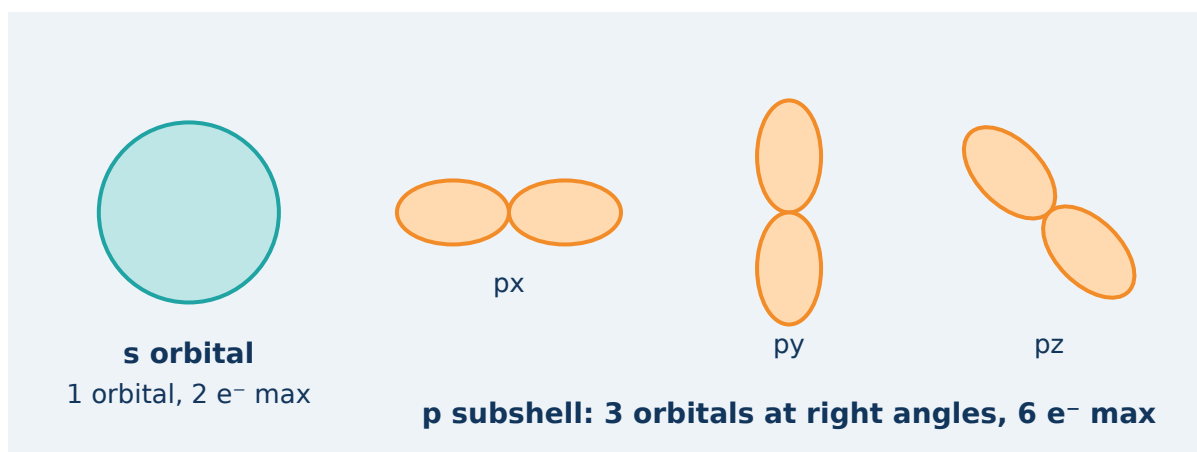
### Definition

An **atomic orbital** is a region around the nucleus that can hold up to two electrons of opposite spin, and in which there is a high probability of finding an electron.

Orbitals are grouped into subshells (s, p, d, f), and subshells are grouped into shells numbered  $n = 1, 2, 3...$

| Subshell | Shape             | Orbitals | Maximum electrons |
|----------|-------------------|----------|-------------------|
| s        | sphere            | 1        | 2                 |
| p        | dumbbell          | 3        | 6                 |
| d        | mostly four lobes | 5        | 10                |
| f        | complex           | 7        | 14                |

Shell  $n$  holds up to  $2n^2$  electrons: 2 in the first shell, 8 in the second, 18 in the third.



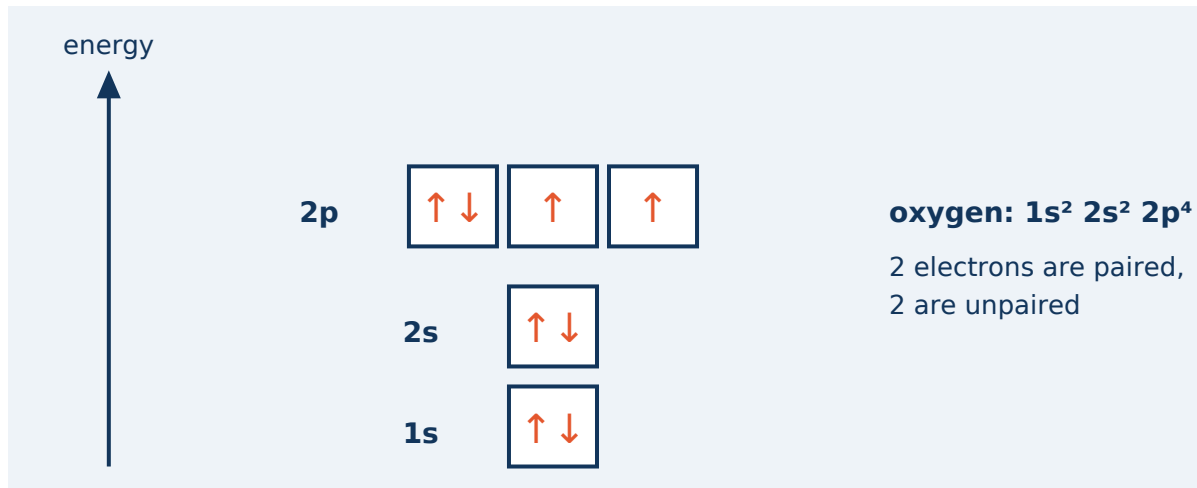
An s orbital is a sphere; the three p orbitals are dumbbells pointing along perpendicular axes.

## How do you write an electron configuration?

### Key law

Three rules build a ground-state configuration. **Aufbau**: fill the lowest energy orbital first. **Pauli**: no more than two electrons per orbital, with opposite spins. **Hund**: electrons occupy orbitals of equal energy singly, with parallel spins, before any pairing.

The filling order is 1s 2s 2p 3s 3p 4s 3d 4p 5s 4d. Note that 4s fills before 3d. Oxygen (8 electrons) is 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>4</sup>, and the shorthand for iron is [Ar] 3d<sup>6</sup> 4s<sup>2</sup>.



Oxygen 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>4</sup>: Hund's rule puts one electron in each 2p box before the fourth electron pairs up.

### Worked example 1

Write the configuration of the Fe<sup>3+</sup> ion (iron has 26 electrons).

Iron atom: [Ar] 3d<sup>6</sup> 4s<sup>2</sup>. Remove the two 4s electrons first, then one 3d electron.

Answer: **Fe<sup>3+</sup> = [Ar] 3d<sup>5</sup>** (23 electrons).

### Common mistake

Transition metals fill 4s before 3d, but they lose 4s electrons first when they form ions. Writing Fe<sup>2+</sup> as [Ar] 3d<sup>4</sup> 4s<sup>2</sup> is wrong; the correct answer is [Ar] 3d<sup>6</sup>.

Two exceptions are worth remembering: chromium is  $[\text{Ar}] 3d^5 4s^1$  and copper is  $[\text{Ar}] 3d^{10} 4s^1$ , because a half-full or full 3d subshell is slightly more stable.

## What is ionisation energy?

### Definition

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

### Formula

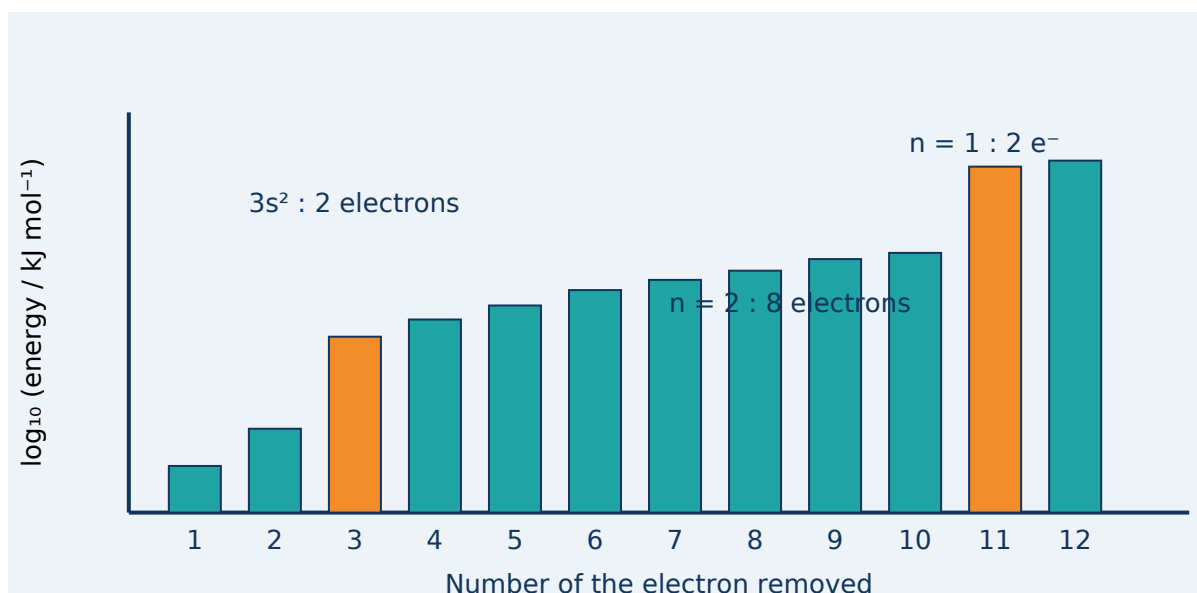
$X(g) \rightarrow X^+(g) + e^-$   $\Delta H = \text{first ionisation energy, in kJ mol}^{-1}$ . The value is always positive because energy is absorbed. The second ionisation energy refers to  $X^+(g) \rightarrow X^{2+}(g) + e^-$ .

Three factors decide the size: the nuclear charge, the distance of the outer electron from the nucleus, and the shielding by inner electrons.

| Observation               | Explanation                                                                                      |
|---------------------------|--------------------------------------------------------------------------------------------------|
| Increases across a period | More protons, same shell and similar shielding, so a stronger pull on a smaller atom             |
| Decreases down a group    | Outer electron is in a higher shell, further away and more shielded                              |
| Dip from Be to B          | The 2p electron has higher energy than the 2s electron and is partly shielded by it              |
| Dip from N to O           | In oxygen the fourth 2p electron shares an orbital, and pair repulsion makes it easier to remove |

## What do successive ionisation energies reveal?

Each successive ionisation removes an electron from a more positively charged ion, so the values always rise. A very large jump shows that the next electron comes from an inner shell, closer to the nucleus. Counting the electrons before the first big jump gives the number of outer electrons, and so the group.



Successive ionisation energies of magnesium. The orange bars mark the first electron taken from a new shell.

### Worked example 2

Element X has successive ionisation energies ( $\text{kJ mol}^{-1}$ ) of 810, 2400, 3700, 25000 and 32800. Find its group.

The ratio  $25000 / 3700 \approx 6.8$  is the first huge jump, after the third electron.

Three outer electrons: **group 13**, forming  $X^{3+}$ .

### Lina's tip

To explain a dip in ionisation energy, sketch the outer electrons in boxes. Ask which electron is highest in energy, or which one is paired. That electron is the easiest to remove.

### Key points to remember

- An orbital holds 2 electrons; s, p, d subshells have 1, 3, 5 orbitals
- Shell n holds up to  $2n^2$  electrons
- Fill order: 1s 2s 2p 3s 3p 4s 3d; Cr and Cu are exceptions
- First ionisation energy:  $X(g) \rightarrow X^+(g) + e^-$ , in  $\text{kJ mol}^{-1}$
- A big jump in successive values marks a new inner shell

## Orbitals, configurations and ionisation energy patterns: frequently asked questions

### What is the difference between a shell and an orbital?

A shell is a group of subshells with the same principal quantum number n. An orbital is a single region that holds at most two electrons. Shell 3 contains nine orbitals: one 3s, three 3p and five 3d.

### Why does 4s fill before 3d?

In a neutral atom the 4s orbital has slightly lower energy than 3d as the shells fill, so it is occupied first. Once 3d holds electrons it drops below 4s, which is why 4s electrons leave first in ions.

**Why is the first ionisation energy of oxygen lower than that of nitrogen?**

The fourth 2p electron in oxygen is paired with another electron in the same orbital. Repulsion between the pair makes it easier to remove, even though oxygen has one more proton.

**Why do successive ionisation energies always increase?**

After each removal the ion has the same number of protons but one fewer electron. The remaining electrons are held more tightly, so each next electron needs more energy.

**How do you find the group from ionisation energy data?**

Look for the first very large jump between successive values. The number of electrons removed before that jump equals the number of outer electrons, which gives the group number for s and p block elements.