Cambridge (CIE) A Level Chemistry

Your notes

Electrons, Energy Levels & Atomic Orbitals

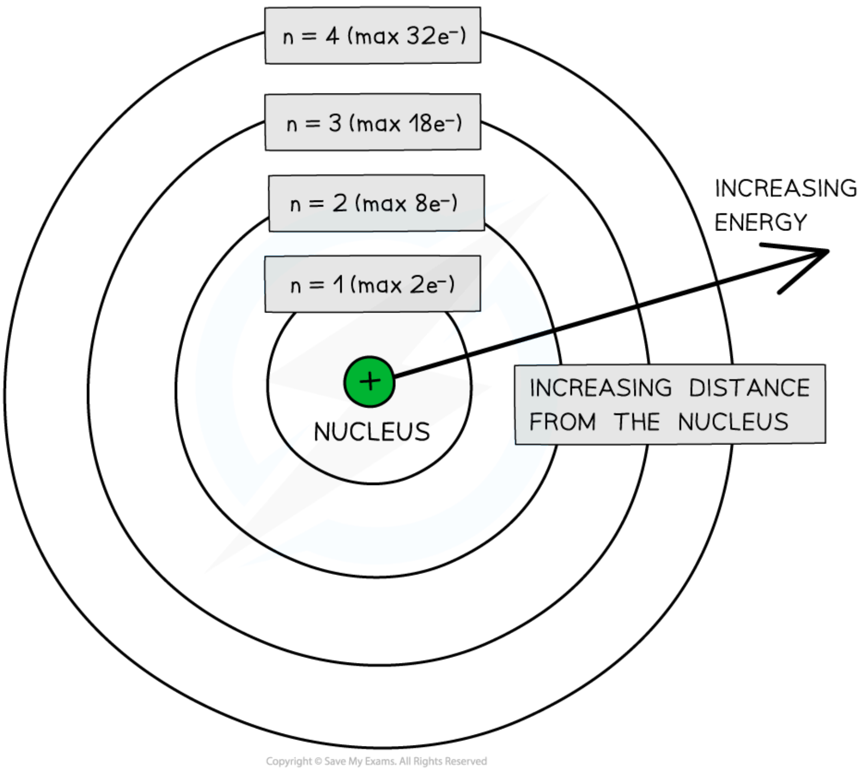
Contents

Basic Electronic Structure

Shells

- The arrangement of electrons in an atom is called the **electronic configuration**
- Electrons are arranged around the nucleus in **principal energy levels** or **principal quantum shells**
- **Principal quantum numbers** (**n**) are used to number the energy levels or quantum shells
  - The **lower** the principal quantum number, the closer the shell is to the nucleus
  - The **higher** the principal quantum number, the higher the energy of the shell
- Each principal quantum number has a **fixed** number of electrons it can hold
  - n = 1 : up to 2 electrons
  - n = 2 : up to 8 electrons
  - n = 3 : up to 18 electrons
  - n = 4 : up to 32 electrons

Principal quantum shells



Electrons are arranged in principal quantum shells, which are numbered by principal quantum numbers

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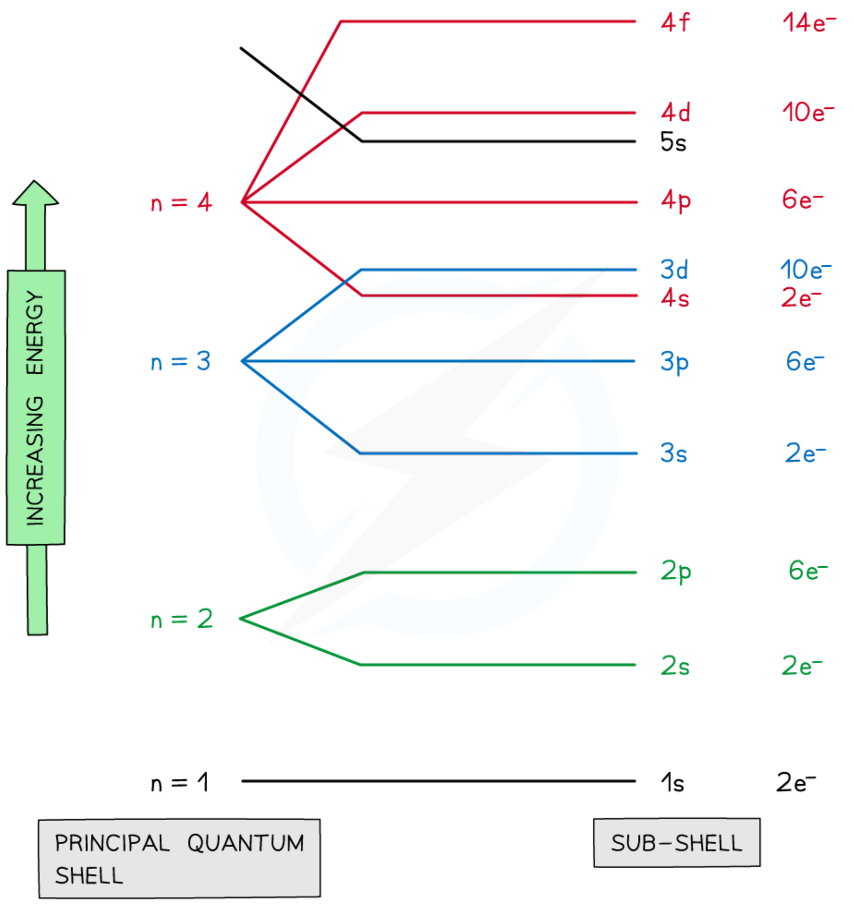
Sub-shells

- The principal quantum shells are split into **sub-shells** which are given the letters **s**, **p** and **d**
  - Elements with more than 57 electrons also have an **f** shell
  - The energy of the electrons in the sub-shells increases in the order s < p < d
- The order of sub-shells appear to overlap for the higher principal quantum shells as seen in the diagram below:

Energy levels of the quantum shells



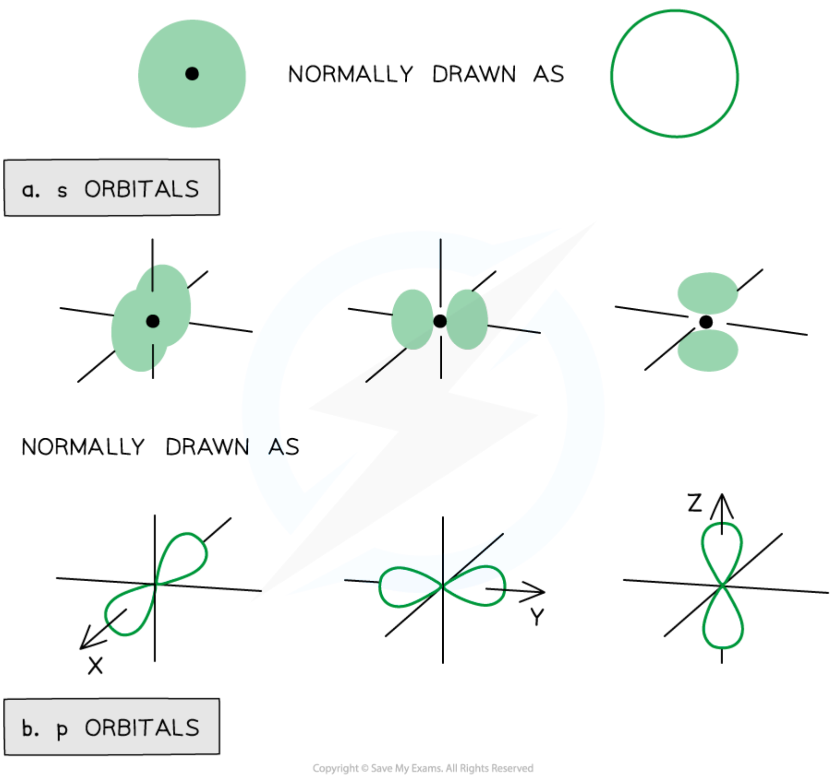
At principal quantum shell n = 3, the energy levels of the sub-shells start to overlap

Orbitals

- Sub-shells contain one or more **atomic orbitals**

- Orbitals exist at **specific** energy levels and electrons can only be found at these specific levels, **not** in between them
    - Each atomic orbital can be occupied by a maximum of two electrons
- This means that the number of orbitals in each sub-shell is as follows:
    - **s** : one orbital (1 x 2 = total of 2 electrons)
    - **p** : three orbitals (3 x 2 = total of 6 electrons)
    - **d** : five orbitals (5 x 2 = total of 10 electrons)
    - **f** : seven orbitals (7 x 2 = total of 14 electrons)
- The orbitals have specific 3-D shapes

Shapes of the electron orbitals



Representation of orbitals (the dot represents the nucleus of the atom) showing (a) spherical s orbitals and (b) p orbitals containing 'lobes' along the x, y and z axis

Examiner Tips and Tricks

Note that the shape of the d orbitals is **not** required at AS Level

An overview of the shells, sub-shells and orbitals in an atom

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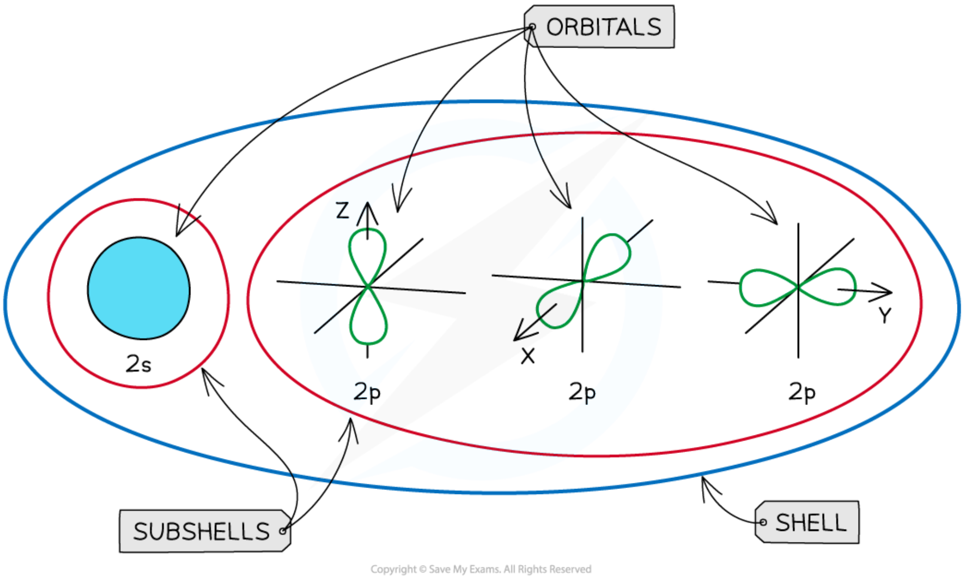
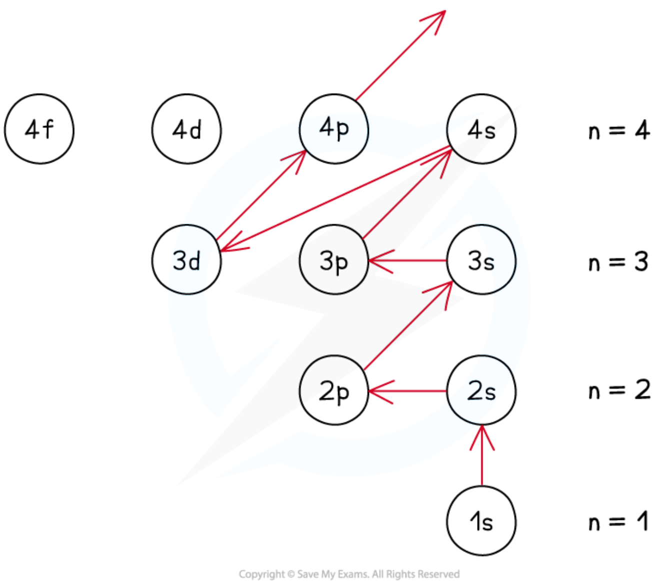


s and p orbitals have different shapes

Ground state

- The **ground state** is the **most stable electronic configuration** of an atom which has the **lowest amount of energy**
- This is achieved by filling the sub-shells with the lowest energy first (1s)
- The order of the sub-shells in terms of increasing energy does **not** follow a regular pattern at n = 3 and higher

Summary of filling sub-shells



The ground state of an atom is achieved by filling the lowest energy sub-shells first

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Electron Orbitals & Sub-shells

- Each shell can be divided further into **subshells, labelled s, p, d and f**
- Each subshell can hold a specific number of orbitals:
  - s subshell : 1 orbital
  - p subshell : 3 orbitals labelled p_x, p_y and p_z
  - d subshell : 5 orbitals
  - f subshell : 7 orbitals
- Each orbital can hold a maximum number of 2 electrons so the maximum number of electrons in each subshell are as follows:
  - s : 1 x 2 = total of 2 electrons
  - p : 3 x 2 = total of 6 electrons
  - d : 5 x 2 = total of 10 electrons
  - f : 7 x 2 = total of 14 electrons
- In the ground state, orbitals in the same subshell have the same energy and are said to be degenerate, so the energy of a p_x orbital is the same as a p_y orbital

Detailed summary of electron shells

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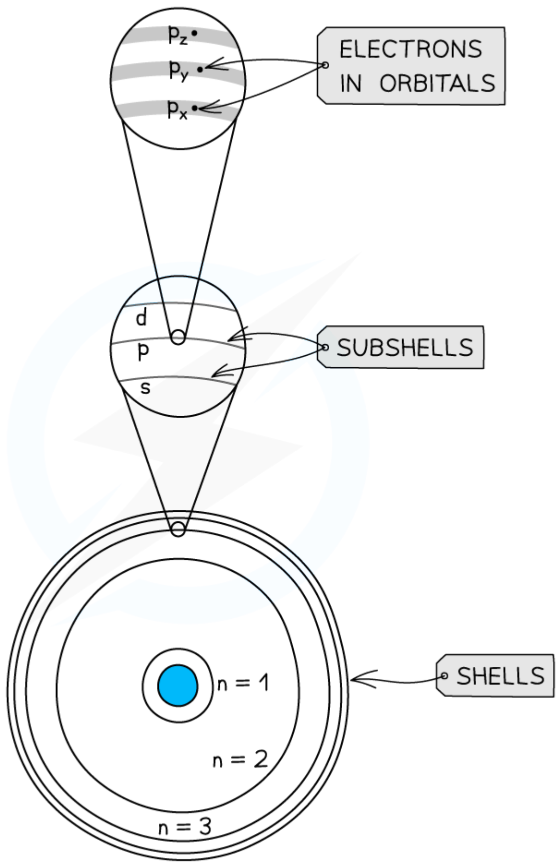

Shells are divided into subshells which are further divided into orbitals

Summary of the arrangement of electrons in atoms

Principal quantum number, n (shell)	Sub-shells possible (s, p, d, f)	Orbitals per sub-shell	Orbitals per principal quantum number	Electrons per sub-shells	Electrons per shell
1	s	1	1	2	2
2	s	1	4	2	8
	p	3		6	
3	s	1	9	2	18
	p	3		6	
	d	5		10	

4	s	1	16	2	32
	p	3		6	
	d	5		10	
	f	7		14	

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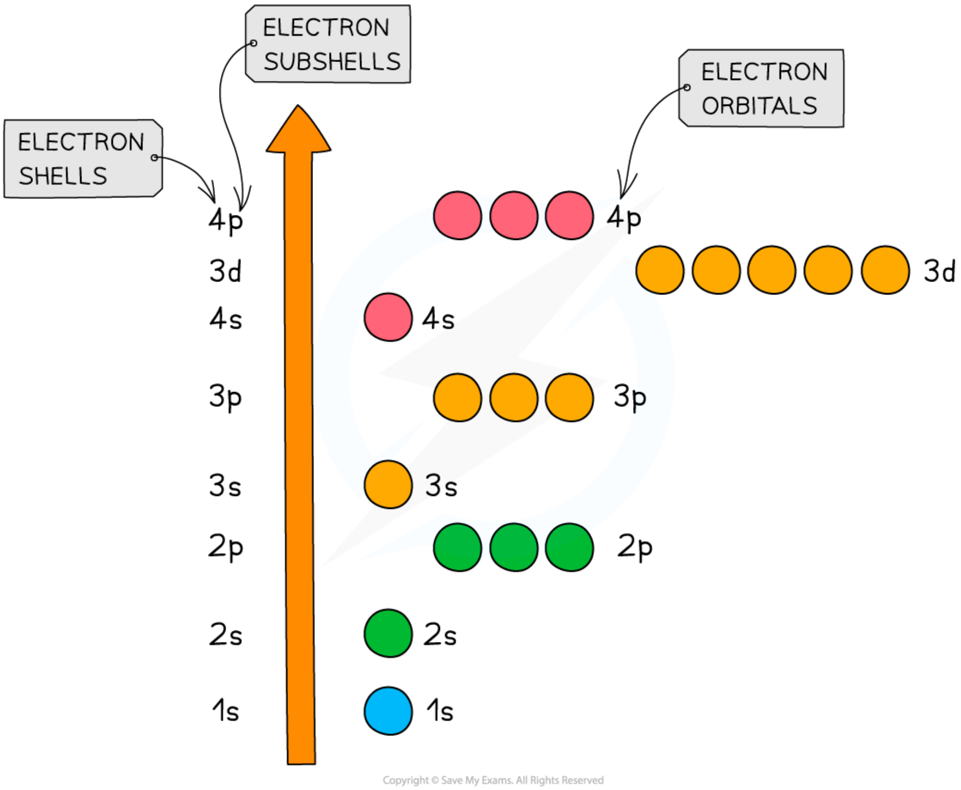
Energy of the Sub-shells

- The **principal quantum shells** increase in energy with increasing **principal quantum number**
  - E.g. *n* = 4 is higher in energy than *n* = 2
- The **sub-shells** increase in energy as follows: s < p < d < f
  - The only exception to these rules is the 3d orbital which has slightly higher energy than the 4s orbital
  - Because of this, the 4s orbital is filled before the 3d orbital
- All the orbitals in the **same** sub-shell have the same energy and are said to be **degenerate**
  - E.g. p_x, p_y and p_z are all equal in energy

Relative energies of the shells and sub-shells



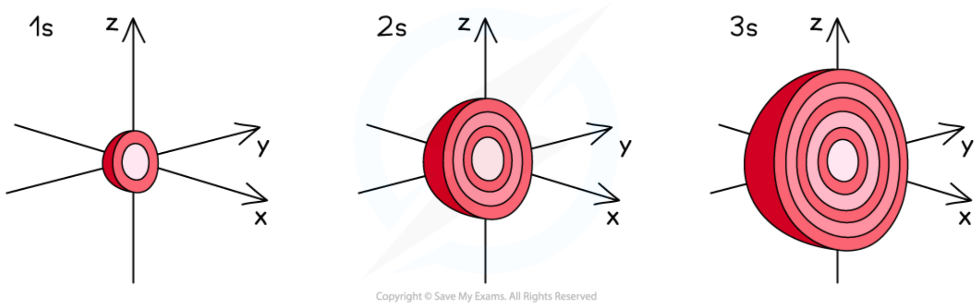
The 4s orbital is lower in energy than the 3d orbital

Shape of s & p Orbitals

s orbitals

- The s orbitals are **spherical** in shape
- The **size** of the s orbitals increases with increasing shell number
  - E.g. the s orbital of the **third** quantum shell (n = 3) is bigger than the s orbital of the **first** quantum shell (n = 1)

s orbital diagram

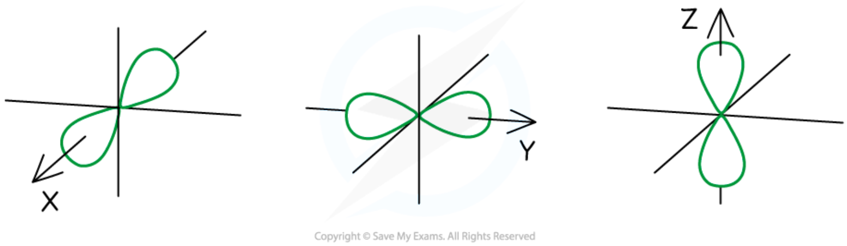


The s orbitals become larger with increasing principal quantum number

p orbitals

- The p orbitals are **dumbbell-shaped**
- Every shell has three p orbitals except for the first one (*n* = 1)
- The p orbitals occupy the x, y and z-axis and point at right angles to each other so are oriented **perpendicular** to one another
- The lobes of the p orbitals become **larger** and **longer** with increasing shell number

p orbital diagram

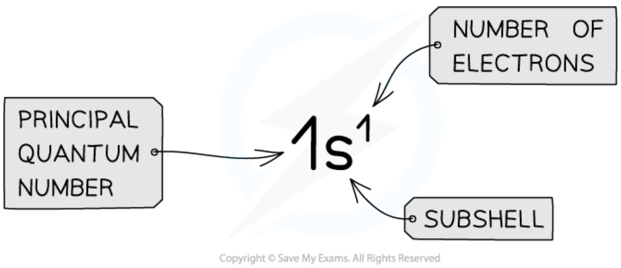


The p orbitals become larger and longer with increasing principal quantum number

Describing Electronic Configurations

- The **electron configuration** gives information about the number of electrons in each **shell, sub-shell** and **orbital** of an atom
- The sub-shells are filled in order of increasing energy

Representing electronic configurations

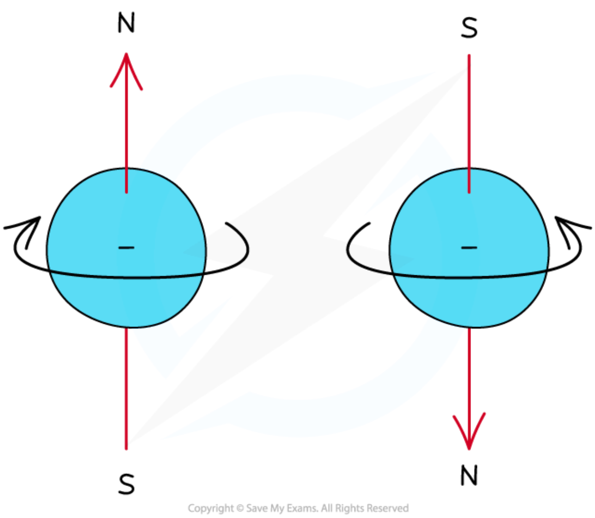


he electron configuration shows the number of electrons occupying a sub-shell in a specific shell

Explaining Electronic Configurations

- Electrons can be imagined as small **spinning charges** which rotate around their own axis in either a **clockwise** or **anticlockwise direction**
  - The spin of the electron is represented by its direction

Electron spin diagram



Electrons can spin either in a clockwise or anticlockwise direction around their own axis

- When two electrons occupy the same orbital, they must have opposite spins and experience a form of repulsion known as **spin-pair repulsion**
- Electrons will therefore occupy separate orbitals in the same sub-shell first, and with the same spin, to minimise repulsion

Electron configuration: three electrons in a p sub-shell

When there are three electrons in a p sub-shell, one electron will go into each px, py and pz orbital

- Electrons only pair when there are no more empty orbitals available within a sub-shell
  - When this happens, they adopt **opposite** spins to reduce repulsion

Electron configuration: four electrons in a p subshell

The fourth electron in a p sub-shell pairs up with one of the electrons in a px, py or pz orbital

- The principal quantum number indicates:
  - The energy level of a particular shell
  - The energy of the electrons in that shell
- For example:
  - A 2p electron is in the second shell
  - Therefore, it has an energy corresponding to $n = 2$
- Even though there is repulsion between negatively charged electrons (**inter-electrons repulsion**), they occupy the same region of space in orbitals
- This is because the energy required to jump to **successive** empty orbital is **greater** than the inter-electron repulsion
- For this reason, electrons pair up and occupy the lower energy levels first

Electron Box Notation

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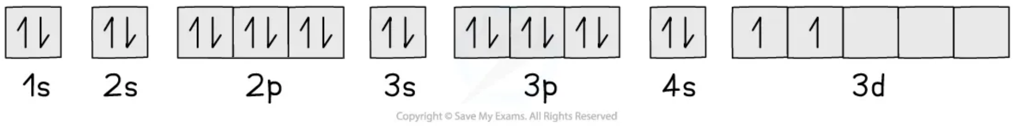
- The **electron configuration** can also be represented using the **electrons in boxes** notation
- Each box represents an **atomic orbital**
- The boxes are arranged in order of **increasing** energy from lowest to highest
- The electrons are represented by opposite arrows to show the **spin** of the electrons
  - E.g. the box notation for titanium is shown below
  - Note that since the 3d sub-shell cannot be either full or half full, the second 4s electron is not promoted to the 3d level and stays in the 4s orbital

Arrangement of electrons in titanium

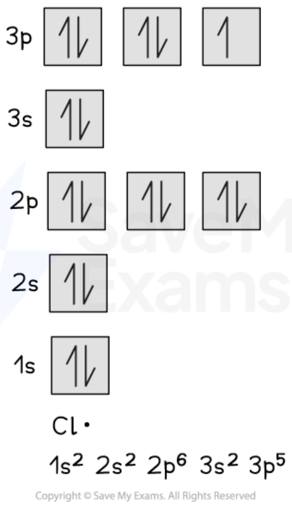


The electrons in titanium occupy the lowest energy levels first before filling those with higher energy

Free radicals

- A **free radical** is a species with one or more **unpaired electron**
- The unpaired electron in the free radical is shown as a **dot**
  - E.g. a chlorine free radical has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^5$
  - Two of the three p orbitals have paired electrons whereas one of them has an unpaired electron

Arrangement of electrons in a chlorine radical



One of the p orbitals has unpaired electrons in a chlorine radical

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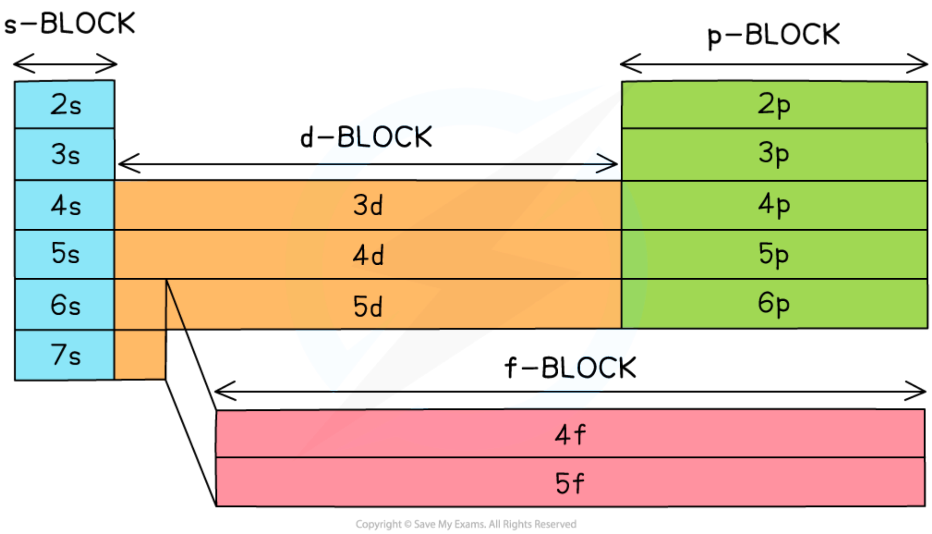
Examiner Tips and Tricks

Free radicals are formed when a molecule undergoes **homolytic fission** where the two electrons of a covalent bond are split evenly between the two atoms.

Determining Electronic Configurations

- Electron configuration shows how electrons are arranged in shells, subshells, and orbitals.
- There are two formats:
  - **Full configuration**; lists all electrons from 1s onward
  - **Shorthand configuration**; uses the symbol of the **nearest noble gas** in brackets to represent inner electrons (e.g. [Ar])
- **Ions** form when atoms **gain** or **lose** electrons:
  - **Anions** (negative) form by **adding** electrons to the outer shell
  - **Cations** (positive) form by **removing** electrons from the outer shell
- **Transition metals**:
  - Fill the **4s** before **3d** when neutral
  - **Lose electrons from 4s first**, not 3d, when forming ions
- In the Periodic Table the elements are grouped into blocks based on their **valence subshell**:
  - **s-block**: valence electrons in an s orbital
  - **p-block**: valence electrons in a p orbital
  - **d-block**: valence electrons in a d orbital
  - **f-block**: valence electrons in an f orbital

The blocks of the Periodic Table



The elements can be divided into the s, p, d or f block, according to their outer shell electron configuration

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Examples

- Electronic configuration of Fe
  - Atomic number = 26 so there are **26 electrons**
  - Full configuration: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$
  - Shorthand: $[Ar]\ 4s^2\ 3d^6$
- Electronic configuration of Fe^{2+}
  - Atomic number = 26 so there are 26 electrons, but the Fe^{2+} ion only has **24 electrons**
  - Electrons are removed from the **4s** orbital **before** the 3d
  - Full configuration: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$
  - Shorthand: $[Ar]\ 3d^6$

Exceptions to the Aufbau principle

- **Chromium** and **copper** have the following electron configurations:
  - Cr is $[Ar]\ 3d^5\ 4s^1$ **not** $[Ar]\ 3d^4\ 4s^2$
  - Cu is $[Ar]\ 3d^{10}\ 4s^1$ **not** $[Ar]\ 3d^9\ 4s^2$
- This is because the $[Ar]\ 3d^5\ 4s^1$ and $[Ar]\ 3d^{10}\ 4s^1$ configurations are **energetically favourable**
- By promoting an electron from 4s to 3d, these atoms achieve a half full or full d-subshell, respectively

Worked Example

- Write down the full and shorthand electron configuration of the following elements:

  1. Potassium
  2. Calcium
  3. Gallium
  4. Ca^{2+}

  Answer:

  - Potassium
    - Electrons: 19
    - Full configuration: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$
    - Shorthand: $[Ar]\ 4s^1$

- Note: Argon (Ar) has 18 electrons and is the previous noble gas
- Calcium
  - Electrons: 20
  - Full configuration: $1s^2\ 2s^2\ 2p^6 3s^2\ 3p^6\ 4s^2$
  - Shorthand: $[Ar]\ 4s^2$
  - Note: 4s is filled before 3d because it is lower in energy
- Gallium
  - Electrons: 31
  - Full configuration: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^1$
  - Shorthand: $[Ar]\ 3d^{10}\ 4s^2\ 4p^1$
  - Note: Includes filled 3d subshell after argon
- Calcium 2+ ion
  - Electrons: 18 (after losing two 4s electrons)
  - Full configuration: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
  - Shorthand: [Ar]
  - Note: Ca^{2+} has the same configuration as argon

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