

## **IB Chemistry DP**

# YOUR NOTES

## 2. Atomic Structure

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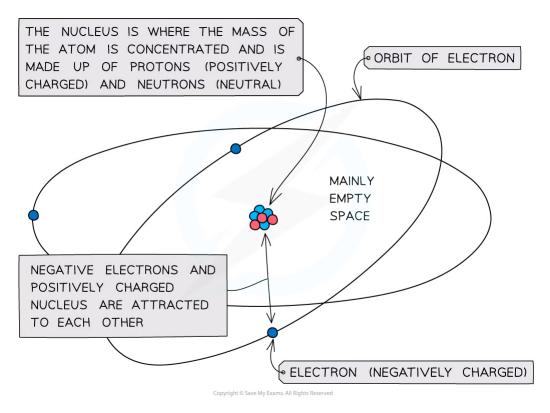
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#### 2.1 Atomic & Electronic Structure

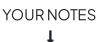
#### 2.1.1 The Nuclear Atom

## **Mass & Charge Distribution**

- The mass of an atom is **concentrated** in the nucleus, because the nucleus contains the heaviest subatomic particles (the neutrons and protons)
  - The mass of the electron is negligible
- The nucleus is also **positively charged** due to the protons
- Electrons orbit the nucleus of the atom, contributing very little to its overall mass, but creating a 'cloud' of negative charge
- The **electrostatic attraction** between the **positive nucleus** and **negatively charged electrons** orbiting around it is what holds an atom together



The mass of the atom is concentrated in the positively charged nucleus which is attracted to the negatively charged electrons orbiting around it





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## **Types of Subatomic Particles**

- The **protons**, **neutrons** and **electrons** that an atom is made up of are called **subatomic particles**
- These subatomic particles are so small that it is not practical to measure their masses and charges using **conventional units** (such as grams or coulombs)
- Instead, their masses and charges are compared to each other, and so are called **'relative** atomic masses' and **'relative atomic charges**'
- These are not actual charges and masses, but rather charges and masses of particles relative to each other
  - Protons and neutrons have a very similar mass, so each is assigned a relative mass of 1
  - Electrons are 1836 times smaller than a proton and neutron, and so their mass is often described as being negligible
- The relative mass and charge of the subatomic particles are:

#### Relative Mass & Charge of Subatomic Particles Table

Subatomic Particle	Relative Charge	Relative Mass	
Proton	+1	1	
Neutron	0	1	
Electron	-1	<u>1</u> 1836	

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## Exam Tip

You can see from the table how the **relative mass** of an electron is **almost negligible**The **charge** of a single **electron** is  $-1.602189 \times 10^{-19}$  coulombs, whereas the charge of a **proton** is  $+1.602189 \times 10^{-19}$  coulombs. However, relative to each other, their charges are -1 and +1 respectively. This information can also been found in the IB Data Booklet





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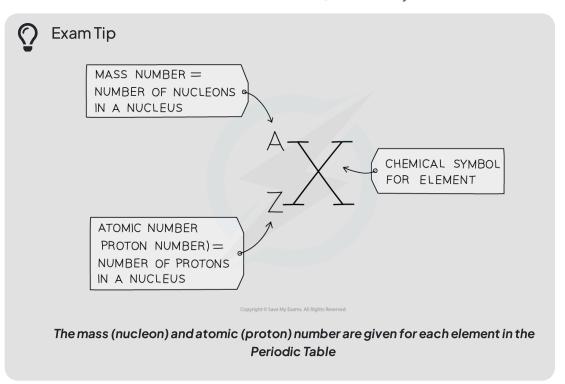
## 2.1.2 Deducing Subatomic Particles

## **Atoms: Key Terms**

- The **atomic number** (or **proton number**) is the number of protons in the nucleus of an atom and has the **symbol Z** 
  - The atomic number is also equal to the number of electrons that are present in a **neutral atom** of an element
  - E.g. the atomic number of lithium is 3, meaning that a neutral lithium atom has 3 protons and, therefore, also has 3 electrons
- The mass number (or nucleon number) is the total number of protons + neutrons in the nucleus of an atom, and has the symbol A
- The number of **neutrons** can be calculated by:

#### Number of neutrons = mass number - atomic number

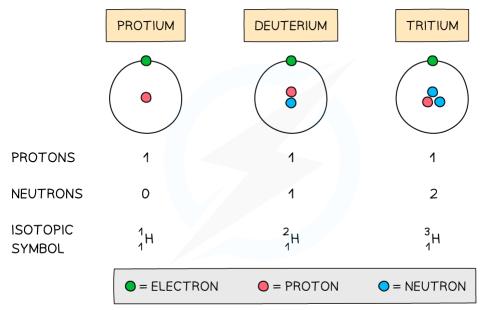
Protons and neutrons are also called nucleons, because they are found in the nucleus





## **Isotopes: Basics**

- Isotopes are atoms of the **same element** that contain the same number of **protons** and electrons but a different number of **neutrons**
- The way to represent an isotope is to write the **chemical symbol** (or the **word**) followed by a **dash** and then the **mass number** 
  - E.g. carbon-12 and carbon-14 are isotopes of carbon containing 6 and 8 neutrons respectively
  - These isotopes could also be written as <sup>12</sup>C or C-12, and <sup>14</sup>C or C-14 respectively



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The atomic structure and symbols of the three isotopes of hydrogen



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## **Determining the Subatomic Structure of Atoms & Ions**

- An atom is **neutral** and has no overall charge
- lons on the other hand have either gained or lost electrons causing them to become charged
- The number of **subatomic particles** in atoms and ions can be determined given their atomic (proton) number, mass (nucleon) number and charge

#### **Protons**

- The atomic number of an atom and ion determines which element it is
- Therefore, all atoms and ions of the **same element** have the same number of protons (atomic number) in the nucleus
  - E.g. lithium has an atomic number of 3 (three protons) whereas beryllium has atomic number of 4 (4 protons)
- The number of protons equals the atomic (proton) number
- The number of protons of an **unknown** element can be calculated by using its mass number and number of neutrons:

Mass number = number of protons + number of neutrons

Number of protons = mass number - number of neutrons



### Worked Example

Determine the number of protons of the following ions and atoms:

- 1. Mg<sup>2+</sup>ion
- 2. Carbon atom
- 3. An unknown atom of element X with mass number 63 and 34 neutrons

#### Answer:

**Answer 1:** The atomic number of a magnesium atom is 12 suggesting that the number of protons in the magnesium element is 12

 Therefore the number of protons in a Mg<sup>2+</sup> ion is also 12 - the number of protons does not change when an ion is formed

**Answer 2:** The atomic number of a carbon atom is 6 suggesting that a **carbon atom** has 6 protons in its nucleus

Answer 3: Use the formula to calculate the number of protons

Number of protons = mass number - number of neutrons

Number of protons = 63 - 34

Number of protons = 29

• Element X is therefore copper

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#### Electrons

- An atom is **neutral** and therefore has the **same** number of **protons** and **electrons**
- lons have a different number of electrons to the number of protons, depending on their charge
  - A positively charged ion has lost electrons and therefore has fewer electrons than protons
  - A negatively charged ion has gained electrons and therefore has more electrons than protons



## Worked Example

Determine the number of electrons of the following ions and atoms:

- $1.\,\mathrm{Mg}^{2+}\mathrm{ion}$
- 2. Carbon atom
- 3. An unknown atom of element X with mass number 63 and 34 neutrons

#### Answer:

**Answer 1:** The atomic number of a magnesium atom is 12 suggesting that the number of protons in the **neutral** magnesium **atom** is 12

- However, the 2+ charge in Mg<sup>2+</sup> ion suggests it has **lost** two electrons
- It only has 10 electrons left now

**Answer 2:** The atomic number of a carbon atom is 6 suggesting that the **neutral** carbon **atom** has 6 electrons orbiting around the nucleus

**Answer 3:** The number of protons of element **X** can be calculated by:

Number of protons = mass number - number of neutrons

Number of protons = 63 - 34

Number of protons = 29

• The **neutral atom** of element **X** therefore also has 29 electrons

#### **Neutrons**

• The mass and atomic numbers can be used to find the number of neutrons in ions and atoms:

Number of neutrons = mass number (A) - number of protons (Z)

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## Worked Example

Determine the number of neutrons of the following ions and atoms:

- 1. Mg<sup>2+</sup>ion
- 2. Carbon atom
- 3. An unknown atom of element X with mass number 63 and 29 protons

#### Answer:

Answer 1: The atomic number of a magnesium atom is 12 and its mass number is 24

Number of neutrons = mass number (A) - number of protons (Z)

Number of neutrons = 24 - 12

Number of neutrons = 12

• The Mg<sup>2+</sup> ion has 12 neutrons in its nucleus

Answer 2: The atomic number of a carbon atom is 6 and its mass number is 12

Number of neutrons = mass number (A) - number of protons (Z)

Number of neutrons = 12 - 6

Number of neutrons = 6

• The carbon atom has 6 neutrons in its nucleus

Answer 3: The atomic number of an element X atom is 29 and its mass number is 63

Number of neutrons = mass number (A) - number of protons (Z)

Number of neutrons = 63 - 29

Number of neutrons = 34

• The **neutral atom** of element **X** has 34 neutrons in its nucleus

#### 2.1.3 Relative Atomic Mass Calculations

#### Relative Atomic Mass Calculations

- **Isotopes** are different atoms of the **same element** that contain the **same number of protons** and electrons but a **different number of neutrons** 
  - These are atoms of the same **elements** but with different mass numbers
- Because of this, the mass of an element is given as **relative atomic mass**  $(A_r)$  by using the average mass of all of the isotopes
- The relative atomic mass of an element can be calculated by using the **percentage abundance** values
  - The percentage abundance of an isotope is either given or can be read off the mass spectrum
  - Firstly, find the mass of 100 atoms by multiplying the percentage abundance by the mass of each isotope
  - Secondly, divide by 100 to find the average atomic mass
  - For example, if you have two isotopes A and B:

total mass of 100 atoms = (% abundance<sub>A</sub> x mass<sub>A</sub>) + (% abundance<sub>B</sub> x mass<sub>B</sub>) mass of 1 atom =  $\frac{\text{total mass}}{100}$ 



## Worked Example

A sample of oxygen contains the following isotopes

Isotope	Percentage abundance		
<sup>16</sup> O	99.76		
<sup>17</sup> O	0.04		
<sup>18</sup> O	0.20		

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What is the relative atomic mass of oxygen to 2 dp?

**A** 16.00

**B** 17.18

C 16.09

**D** 17.00

#### Answer:

The correct answer is A

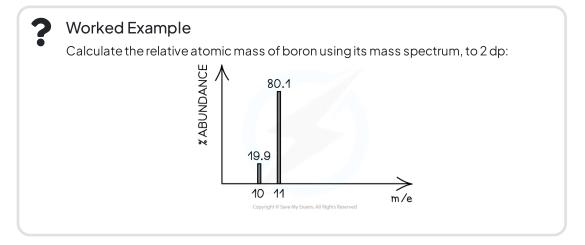
 $\circ$  Total mass of 100 atoms = (99.76 x 16) + (0.04 x 17) + (0.20 x 18) = 1600.44



• Mass of 1 atom =  $1600.44 \div 100 = 16.0044 = 16.00 (2 dp)$ 

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• Here is another example, but this time using a mass spectrum to obtain the information:



#### Answer:

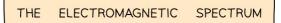
- Total mass of 100 atoms = (19.9 x 10) + (80.1 x 11) = 1080.1
- Mass of 1 atom = 1080.1 ÷ 100 = 10.801 = **10.80** (2 dp)

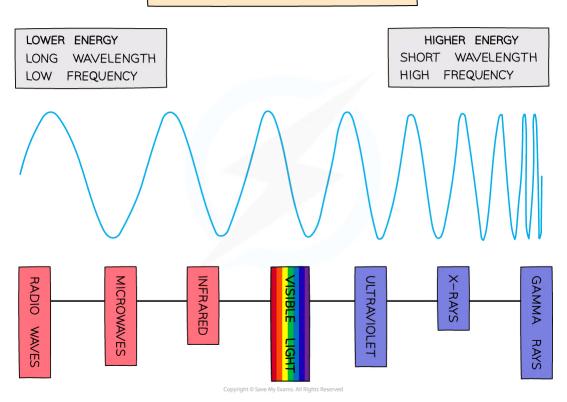


### 2.1.4 The Electromagnetic Spectrum

## The Electromagnetic Spectrum

- The **electromagnetic spectrum** is a range of **frequencies** that covers all electromagnetic radiation and their respective **wavelengths** and **energy**
- It is divided into bands or regions, and is very important in analytical chemistry
- The spectrum shows the relationship between frequency, wavelength and energy
- **Frequency** is how many waves pass per second, and **wavelength** is the distance between two consecutive peaks on the wave
- **Gamma rays**, **X-rays** and **UV** radiation are all dangerous you can see from that end of the spectrum that it is high frequency and high energy, which can be very damaging to your health





- All light waves travel at the same speed; what distinguishes them is their different frequencies
- The speed of light (symbol 'c') is constant and has a value of 3.00 x 10<sup>8</sup> ms<sup>-1</sup>
- As you can see from the spectrum, frequency (symbol 'v') is inversely proportional to wavelength (symbol 'λ')
  - o In other words, the higher the frequency, the shorter the wavelength
- The equation that links them is  $c = v\lambda$

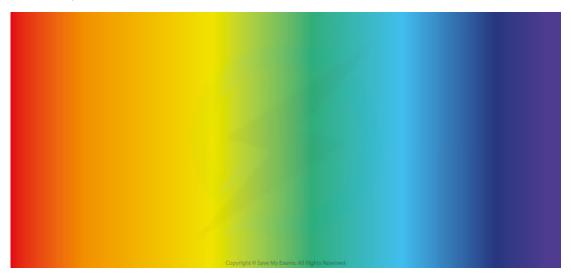




• Since  ${\bf c}$  is constant you can use the formula to calculate the frequency of radiation given the wavelength, and vice versa

## Continuous versus line spectrum

- A continuous spectrum in the visible region contains all the colours of the spectrum
- This is what you are seeing in a rainbow, which is formed by the refraction of white light through a prism or water droplets in rain



#### A continuous spectrum shows all frequencies of light

• However, a line spectrum only shows certain frequencies



#### The line spectrum of helium which shows only certain frequencies of light

- This tells us that the emitted light from atoms can only be certain fixed frequencies it is **quantised** (quanta means 'little packet')
- Electrons can only possess certain amounts of energy they cannot have any energy value



#### Exam Tip

The formula that relates frequency and wavelength is printed in Section 1 of the IB Chemistry Data Booklet so you don't need to learn it You will also find the speed of light and other useful constants in Section 2

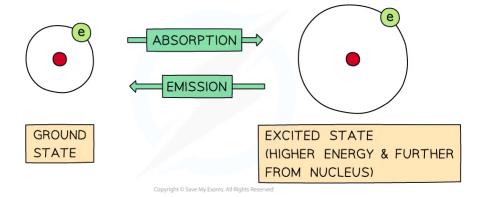


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#### 2.1.5 Emission Spectra

## **Emission Spectra**

- Electrons move rapidly around the nucleus in energy shells
- If their energy is increased, then they can jump to a higher energy level
- The process is reversible, so electrons can return to their original energy levels
  - When this happens, they emit energy
- The frequency of energy is exactly the same, it is just being emitted rather than absorbed:



## The difference between absorption and emission depends on whether electrons are jumping from lower to higher energy levels or the other way around

- The energy they emit is a mixture of different frequencies
- This is thought to correspond to the many possibilities of electron jumps between energy shells
- If the emitted energy is in the visible region, it can be analysed by passing it through a diffraction grating
- The result is a line emission spectrum

#### Line emission spectra



#### The line emission (visible) spectrum of hydrogen

- Each line is a specific energy value
  - This suggests that electrons can only possess a limited choice of allowed energies
- These packets of energy are called 'quanta' (plural quantum)
- What you should notice about this spectrum is that the lines get closer together towards the blue end of the spectrum
- This is called **convergence** and the set of lines is **converging** towards the higher energy end, so the electron is reaching a maximum amount of energy
- This maximum corresponds to the **ionisation energy** of the electron

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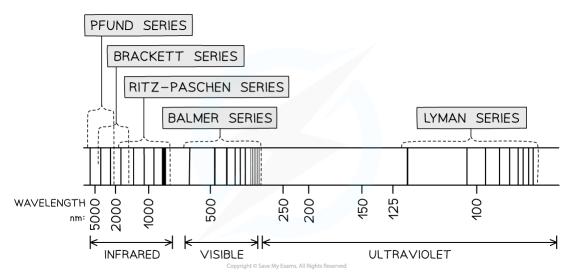


- These lines were first observed by the Swiss school teacher Johannes **Balmer**, and they are named after him
- We now know that these lines correspond to the electron jumping from higher levels down to the **second** or **n = 2** energy level



## The Hydrogen Spectrum

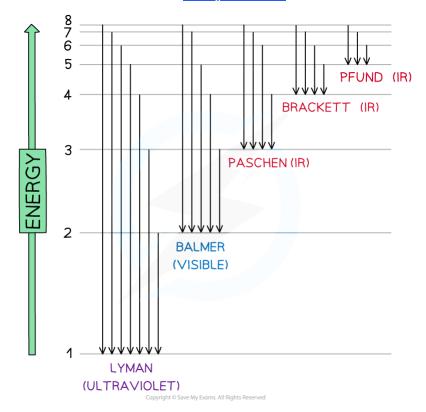
• A larger version of the hydrogen spectrum from the infrared to the ultraviolet region looks like this



#### The full hydrogen spectrum

- In the spectrum, we can see sets or families of lines
- Balmer could not explain why the lines were formed an explanation had to wait until the arrival of Planck's **Quantum Theory** in 1900
- Niels Bohr applied the **Quantum Theory** to electrons in 1913, and proposed that electrons could only exist in fixed energy levels
- The line emission spectrum of hydrogen provided evidence of these energy levels and it was deduced that the families of lines corresponded to electrons jumping from higher levels to lower levels





#### Electron jumps in the hydrogen spectrum

- The findings helped scientists to understand how electrons work and provided the backbone to our knowledge of energy levels, sublevels and orbitals
- The jumps can be summarised as follows:

#### **Electron Jumps & Energy Table**

Jumps	Region	Energy	
$n \sim \longrightarrow n_3$	Infrared	Low	
$n \sim \longrightarrow n_2$	Visible	$\rightarrow$	
$n \sim \longrightarrow n_1$	Ultraviolet	High	

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## Worked Example

Which electron transition in the hydrogen atom emits visible light?

 $\mathbf{A}$ . n = 1 to n = 2

 $\mathbf{B}$ . n = 2 to n = 3

**C**. n = 2 to n = 1

 $\mathbf{D}$ . n = 3 to n = 2

#### Answer:

Option **D** is correct

• Emission in the visible region occurs for an electron jumping from any higher energy level to **n = 2** 



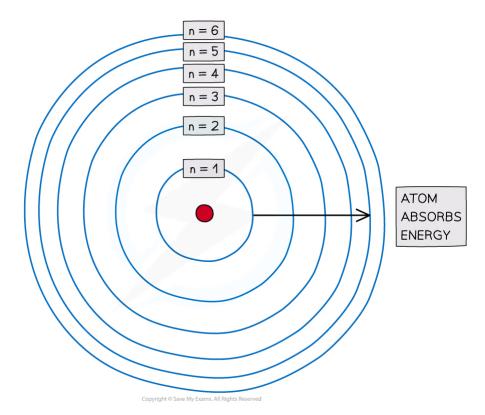
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#### 2.1.6 Energy Levels & Sublevels

## **Electron Energy Levels**

#### **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 lesser the energy of the shell
- Each principal quantum number has a fixed number of electrons it can hold
  - o n=1:upto2electrons
  - o n = 2: up to 8 electrons
  - $\circ$  n = 3: up to 18 electrons
  - $\circ$  n = 4:up to 32 electrons
- There is a pattern here the mathematical relationship between the number of electrons and the principal energy level is  $2n^2$ 
  - So for example, in the third shell n = 3 and the number of electrons is  $2x(3^2) = 18$

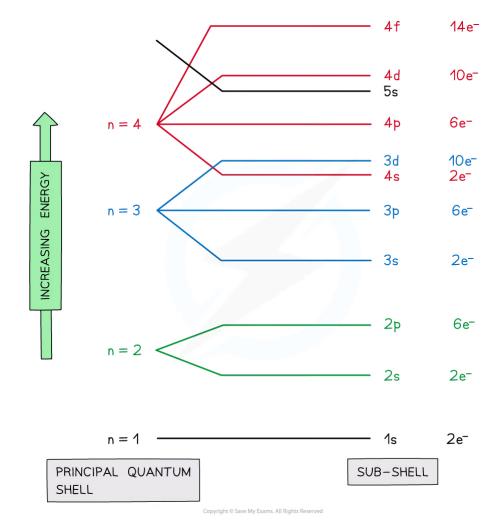


Electrons are arranged in principal quantum shells, which are numbered by principal quantum numbers

#### Subshells



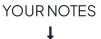
- The principal quantum shells are split into **subshells** which are given the letters **s**, **p** and **d** 
  - Elements with more than 57 electrons also have an **f** subshell
  - o The energy of the electrons in the subshells increases in the orders < p < d
- The order of subshells overlap for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



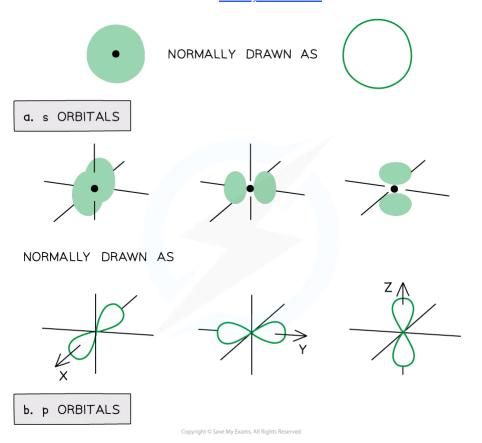
Electrons are arranged in principal quantum shells, which are numbered by principal quantum numbers

#### **Orbitals**

- The subshells 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
  - Each atomic orbital can be occupied by a maximum of two electrons
- The orbitals have specific 3D shapes



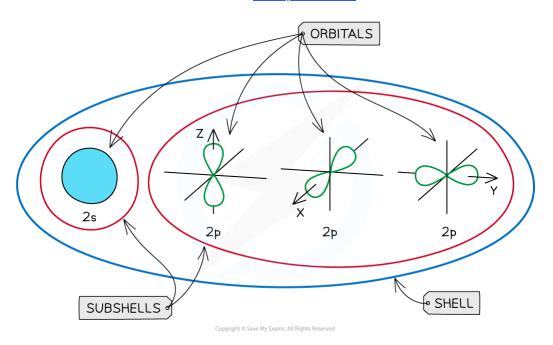




Representation of orbitals (the dot represents the nucleus of the atom) showing spherical s orbitals (a), p orbitals containing 'lobes' along the x, y and z axis

• Note that the shape of the d orbitals is **not** required for IB Chemistry

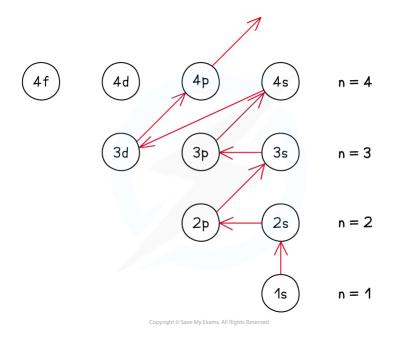




An overview of the shells, subshells and orbitals in an atom

#### 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 subshells of energy with the lowest energy first (1s) this is called the **Aufbau Principle**
- The order of the subshells in terms of increasing energy does **not** follow a regular pattern at n= 3 and higher



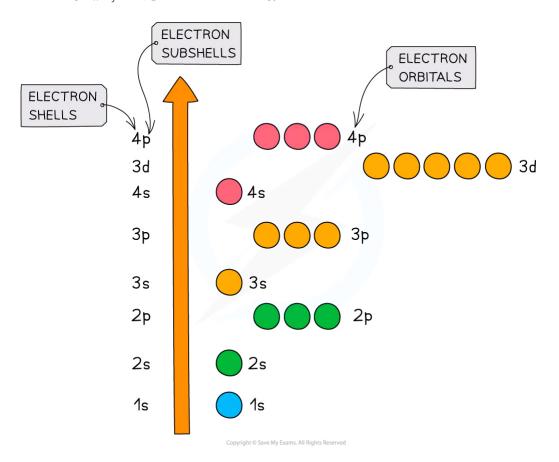
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The Aufbau Principle - following the arrows gives you the filling order

## Sublevels & Energy

- The **principal quantum shells** increase in energy with increasing **principal quantum number** 
  - $\circ$  Eg. n = 4 is higher in energy than n = 2
- The **subshells** 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, so the 4s orbital is filled before the 3d orbital
- All the orbitals in the **same** subshell have the same energy and are said to be **degenerate** 
  - $\circ$  Eg.  $p_x$ ,  $p_v$  and  $p_z$  are all equal in energy



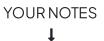
Relative energies of the shells and subshells



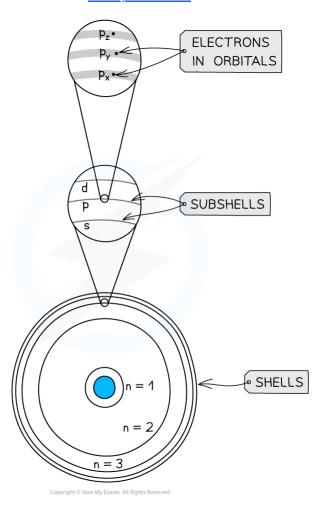
## 2.1.7 Sublevels & Orbitals

#### **Electron Orbitals**

- 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
  - $\circ$  p subshell: 3 orbitals labelled  $p_x$ ,  $p_y$  and  $p_z$
  - d subshell: 5 orbitalsf 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:
  - o s:1x2 = total of 2 electrons
  - $\circ$  p:3x2=total of 6 electrons
  - od:5x2=total of 10 electrons
  - o f:7x2=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<sub>x</sub> orbital is the same as a p<sub>y</sub> orbital







Shells are divided into subshells which are further divided into orbitals

Summary of the Arrangement of Electrons in Atoms Table





Principal quantum number, n (shell)	Subshells possible (s, p, d, f)	Orbitals per subshell	Orbitals per principal quantum number	Electrons per subshell	Electrons per shell
1	s	1	1	2	2
2	s	1	4	2	8
2	þ	3		6	δ
3	s	1	9	2	
	Þ	3		6	18
	d	5		10	
4	s	1		2	
	þ	3	16	6	32
	d	5		10	
	f	7		14	

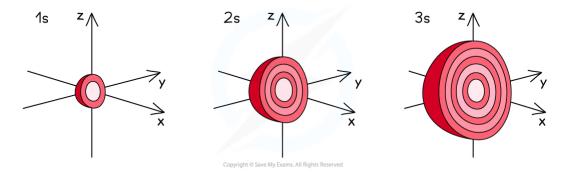
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## The s & p Orbitals

#### s orbitals

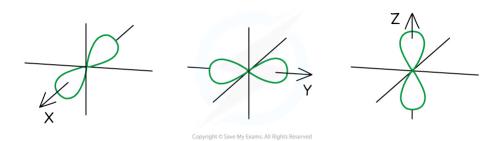
- The s orbitals are **spherical** in shape
- The **size** of the s orbitals increases with increasing shell number
  - E.g. the s orbital of the **third** quantum shell (n = 3) is bigger than the s orbital of the **first** quantum shell (n = 1)



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 axes 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



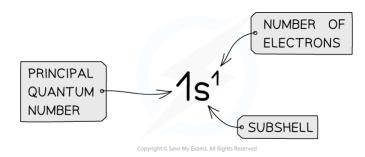
The p orbitals become larger and longer with increasing principal quantum number



## 2.1.8 Writing Electron Configurations

## **Electron Configurations: Basics**

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

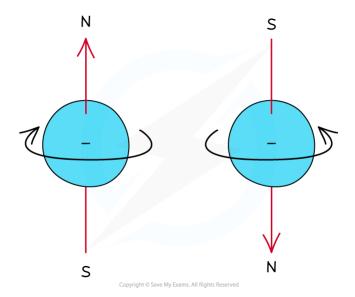


The electron configuration shows the number of electrons occupying a subshell in a specific shell



## **Electron Configurations: Explained**

- 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
  - The spin creates a tiny magnetic field with N-S pole pointing up or down



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

- Electrons with the same **spin** repel each other which is also called **spin-pair repulsion** 
  - Therefore, electrons will occupy separate orbitals in the same subshell first to minimise this repulsion and have their **spin** in the same direction
  - They will then pair up, with a second electron being added to the first p orbital, with its spin in the **opposite** direction
- This is known as Hund's Rule
  - $\circ$  E.g. if there are three electrons in a **p subshell**, one electron will go into each  $p_x$ ,  $p_y$  and  $p_z$  orbital



#### Electron configuration: three electrons in a p subshell

- The principal quantum number indicates the energy level of a particular shell but also indicates the energy of the electrons in that shell
  - $\circ$  A 2p electron is in the second shell and therefore has an energy corresponding to n = 2



- Even though there is repulsion between negatively charged electrons, they occupy the same region of space in orbitals
- An orbital can only hold two electrons and they must have opposite spin the is known as the **Pauli Exclusion Principle**
- This is because the energy required to jump to a higher empty orbital is **greater** than the inter-electron repulsion
- For this reason, they pair up and occupy the lower energy levels first

## **Orbital Diagrams**

- The electron configuration can also be represented using the orbital spin diagrams
- Each box represents an atomic orbital
- The boxes are arranged in order of **increasing** energy from lower to higher (i.e. starting from closest to the nucleus)
- The electrons are represented by opposite arrows to show the spin of the electrons
  - E.g. the box notation for titanium is shown below



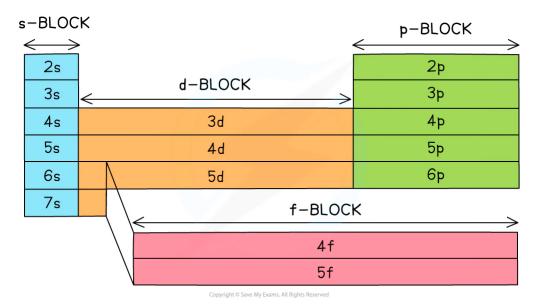
The electrons in titanium are arranged in their orbitals as shown. Electrons occupy the lowest energy levels first before filling those with higher energy



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## **Determining Electronic Configurations**

- Writing out the **electronic configuration** tells us how the electrons in an atom or ion are arranged in their shells, subshells and orbitals
- This can be done using the **full** electron configuration or the **shorthand** version
  - The **full** electron configuration describes the arrangement of all electrons from the ls subshell up
  - The **shorthand** electron configuration includes using the symbol of the nearest preceding **noble gas** to account for however many electrons are in that noble gas, followed by the rest of the electron configuration
- lons are formed when atoms lose or gain electrons
  - Negative ions are formed by **adding** electrons to the outer subshell
  - o Positive ions are formed by **removing** electrons from the outer subshell
  - The transition metals **fill** the 4s subshell before the 3d subshell, but they also **lose** electrons from the 4s first rather than from the 3d subshell
- The Periodic Table is split up into four main blocks depending on their electronic configuration:
  - s block elements (valence electron(s) in s orbital)
  - o p block elements (valence electron(s) in p orbital)
  - o d block elements (valence electron(s) in d orbital)
  - of block elements (valence electron(s) in forbital)



The elements can be divided into four blocks according to their outer shell electron configuration

## Exceptions to the Aufbau Principle

- Chromium and copper have the following electron configurations:
  - $\circ$  Cris [Ar] 3d<sup>5</sup> 4s<sup>1</sup> **not** [Ar] 3d<sup>4</sup> 4s<sup>2</sup>
  - Cu is [Ar] 3d<sup>10</sup> 4s<sup>1</sup> not [Ar] 3d<sup>9</sup> 4s<sup>2</sup>

**YOUR NOTES** 

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- This is because the [Ar] 3d<sup>5</sup> 4s<sup>1</sup> and [Ar] 3d<sup>10</sup> 4s<sup>1</sup> 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<sup>2+</sup>

#### Answer:

#### Answer 1:

• Potassium has 19 electrons so the **full electronic configuration** is:

- The 4s orbital is lower in energy than the 3d subshell and is therefore filled first
- The nearest preceding noble gas to potassium is **argon** which accounts for 18 electrons so the **shorthand electron configuration** is:

#### Answer 2:

o Calcium has 20 electrons so the full electronic configuration is:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$$

- o The 4s orbital is lower in energy than the 3d subshell and is therefore filled first
- The shorthand version is [Ar] 4s<sup>2</sup> since argon is the nearest preceding noble gas to calcium which accounts for 18 electrons

#### Answer 3:

o Gallium has 31 electrons so the **full electronic configuration** is:

$$[Ar] 3d^{10} 4s^2 4p^1$$

#### Answer 4:

 If you ionise calcium and remove two of its outer electrons, the electronic configuration of the Ca<sup>2+</sup> ion is identical to that of argon:

$$Ca^{2+}$$
 is  $1s^2 2s^2 2p^6 3s^2 3p^6$ 

**Ar** is also 
$$1s^2 2s^2 2p^6 3s^2 3p^6$$





## Exam Tip

Orbital spin diagrams can be drawn horizontally or vertically, going up or down the page - there is no hard and fast rule about this. The important thing is that you label the boxes and have the right number of electrons shown. The arrows you use for electrons can be full or half-headed arrows, but they must be in opposite directions in the same box.