1.2 Atomic Orbitals Electronic Configuration and the Periodic Table

Quantum Numbers

1. Principal Quantum Numbers (n)

- Each electron shell has a principal quantum number n

n = 1 is the 1st shell,
n = 2 is the 2nd shell,
n = 3 is the 3rd shell,
etc

2. Angular Momentum Quantum Number (l)

- Each shell has up to four subshells: s, p, d and f

Shell	Subshells
n=1	1s
n=2	2s, 2p
n=3	3s, 3p, 3d
n=4+	4s, 4p, 4d, 4f 5s, 5p, 5d, 5f 6s……….

Angular Momentum Quantum Number	Subshell	Location of Element with this Subshell Filling
l = 0	s block	Groups 1 – 2
l = 1	p block	Groups 3 – 0
l = 2	d block	Transition Metals
l = 3	f block	Lanthanides and Actinides

- Angular Momentum Quantum Number (l) has values from 0 up to n-1 where n is the principal quantum number

Value of n (Principal Quantum Number)	Values of l (Angular Momentum Quantum Number)	Energy Level Subshell
1	0	1s
2	0 1	2s 2p
3	0 1 2	3s 3p 3d
4	0 1 2 3	4s 4p 4d 4f

Heisenberg's Uncertainty Principal

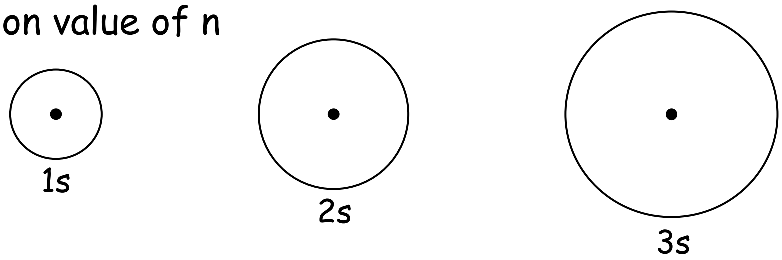
Wave-particle duality means that Electromagnetic Waves can behave like waves but also like particles. The converse is also true. Particles like electrons can also behave like waves. (The electron microscope uses this fact)

- Heisenberg's Uncertainty Principle states that it is not possible to define both the position and the momentum of an electron at the same instant
- Momentum is linked to the velocity of an electron and hence the (kinetic) energy of an electron
- As it is not possible to definitely locate an electron without affecting its momentum, electrons are allocated regions of space where there is a 90% probability of finding an electron. These are called atomic orbitals.
- Size of orbital is governed by the principal quantum number n
- Shape of the orbital is governed by the angular momentum quantum number l.

Shapes of Orbitals

a) l=0 (s orbitals) [you should be able to recognise and draw these orbitals]

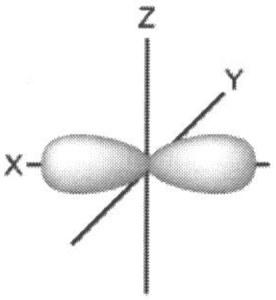
- all s-orbitals are spherical in shape
- size depends on value of n



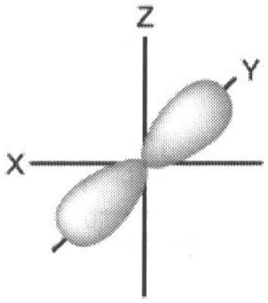
b) l=1 (p orbitals) [you should be able to recognise and draw these orbitals]

- orbitals are not spherical
- all 3 p-orbitals are degenerate (equal in energy)

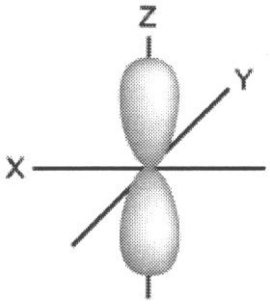
p_x orbital



p_y orbital

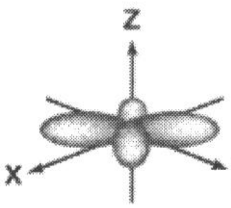


p_z orbital

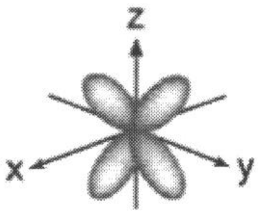


c) l=2 (d orbitals) [you should be able to recognise these orbitals]

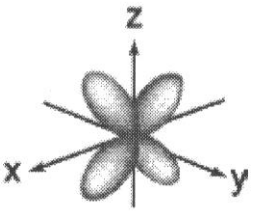
d_{xy} orbital



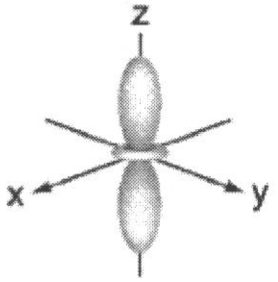
d_{yz} orbital



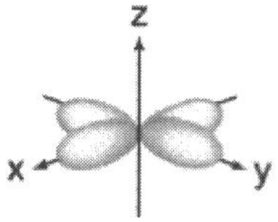
d_{xz} orbital



d_{z^2} orbital



$d_{x^2-y^2}$ orbital



- all 5 d-orbitals are normally degenerate (equal in energy). [This changes under certain circumstances as we will see later in Unit 1]

d) l=3 (f orbitals) [If you get this far in university chemistry to do this, well done]

3. Magnetic Quantum Number (m_l)

- magnetic quantum numbers distinguish between the different suborbitals within the s, p, d and f subshells
- magnetic quantum numbers have the values –l, …, 0, … +l

n Principal Quantum Number	l Angular Momentum Quantum Numbers	Type of subshell	m_l Magnetic Quantum Numbers
1	0	1s	0
2	0	2s	0
	1	2p	–1, 0, +1
3	0	3s	0
	1	3p	–1, 0, +1
	2	3d	–2, –1, 0, +1, +2
4	0	4s	0
	1	4p	–1, 0, +1
	2	4d	–2, –1, 0, +1, +2
	3	4f	–3, –2, –1, 0, +1, +2, +3

4. Spin Quantum Number (m_s)

- Electrons have a spin rotation in addition to orbital rotation around the nucleus.
- Spin can be described as $+\frac{1}{2}$ and $-\frac{1}{2}$ (clockwise and anticlockwise)
- No two electrons in the same atom can have the same 4 quantum numbers. This is the *Pauli Exclusion Principle.*
- The Pauli Exclusion principle also states that an orbital can only contain a maximum of two electrons

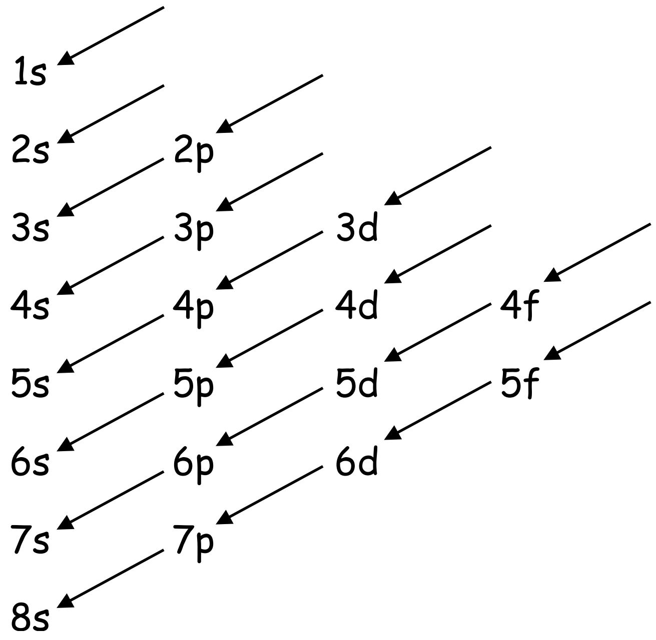
Electronic Configurations

a) Pauli Exclusion Principle

- No 2 electrons have the same 4 quantum numbers (n, l, m_l , m_s)
- An orbital can hold a maximum of 2 electrons

b) Aufbau Principle

- Orbitals of the lowest energy fill up first with electrons
- The lowest energy orbitals are not necessarily the closest to the nucleus
  e.g. 3d orbitals are closer to the nucleus but the 4s orbital fills up first
- The orbitals fill up in the order show in the diagram below



order orbitals fill up

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p, 8s

c) Hund's Rule of Maximum Multiplicity

- Where electrons occupy *degenerate* orbitals, each electron will take a separate orbital until all the degenerate orbitals in that subshell are half-filled.
- When all the degenerate suborbitals are half-filled, only then will the suborbitals start to fill with the 2nd electron
- Electrons spin in parallel in singly-filled suborbitals

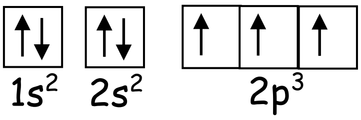
Writing Electron Configurations

a) Spectroscopic Notation

- Nitrogen atoms have 7 electrons
- Its electron configuration is $1s^2$, $2s^2$, $2p^3$

b) Orbital Box Notation

- Nitrogen atoms have 7 electrons
- Its electron configuration is



c) Shorthand Spectroscopic Notation

- Iron has an electron configuration of $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$
- Argon has an electron configuration of $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

- The electron configuration of iron can be shorted to [Ar] $4s^2\ 3d^6$

- As the inner electrons of any atom rarely take part in any chemistry of note, the inner electrons shells can be shortened to the appropriate Noble Gas. [Always a Noble Gas in square brackets]

Question

1. Using both spectroscopic and orbital box notations, write down the electronic configurations of

    a) Lithium
    b) Oxygen
    c) Sodium
    d) Aluminium
    e) Phosphorus
    f) Argon
    g) Calcium
    h) Li^+
    i) F^-
    j) Mg^{2+}
    k) S^{2-}
    l) K^+

Summary of Electron Configurations

Group 1	Group 2		Transition Metals	Group 3	Group 4	Group 5	Group 6	Group 7	Group 0
(s^1)	(s^2)			(p^1)	(p^2)	(p^3)	(p^4)	(p^5)	(p^6)
$1s^1$									$1s^2$
2s				2p					
3s				3p					
4s			3d	4p					
5s			4d	5p					
6s		4f	5d	6p					
7s		5f	6d	7p					

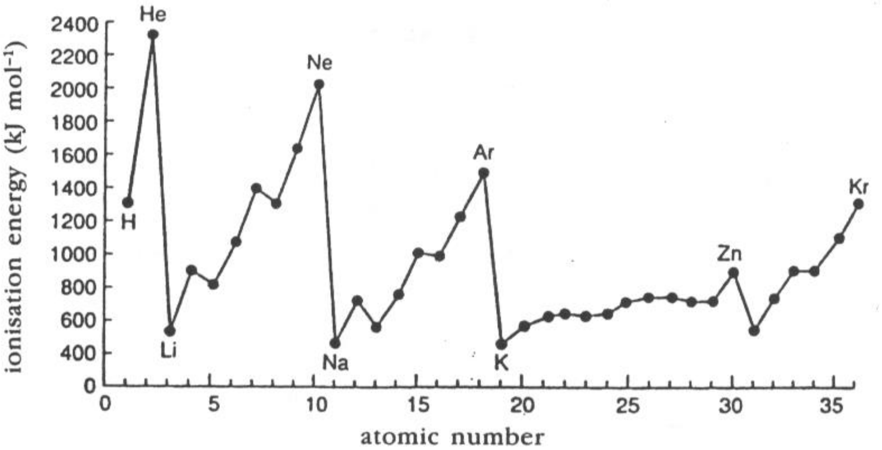
4f (Lanthanides)

5f (Actinides)

Ionisation Energy

Enthalpy of 1st Ionisation: $E_{(g)} \longrightarrow E^+_{(g)} + e^-$

- Peak points are all Noble Gases
- All the lowest points are Alkali Metals



Factors Affecting Ionisation Energy

a) Atomic Size

- The greater the atomic radius of the atom, the further the distance of the outermost electrons
- This lowers the ionisation energy as the electrons are less attracted to the nucleus the further away they are

b) Nuclear Charge

- The greater the number of protons, the greater the attraction to the outer electrons and harder it is to remove outer electrons
- Elements across a period have decreasing atomic size and therefore increasing 1st ionisation energy as the increasing positive charge holds onto the outer electrons

c) Screening Effect

- Inner electron shells shield the outer electron shell from the attractive forces from the nucleus
- The larger the atom, the more inner electron shells the atom has and the bigger the screening effect and the lower the ionisation energy.

Down A Group: 1st Ionisation Energy DECREASES
Across A Period: 1st Ionisation Energy INCREASES

However, the above graph shows some irregularities where these trends are generally followed but there is the occasional exception. We can now explain these irregularities using our new knowledge on electronic structure.

Why has Beryllium a higher 1st ionisation energy than the trend would suggest?

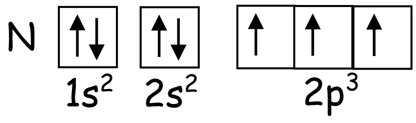
Element	Symbol	Electronic Configuration	1st Ionisation Energy
Lithium	Li	$1s^2\ 2s^1$	ΔH^{o}_{i} = +526 kJ mol^{-1}
Beryllium	Be	$1s^2\ 2s^2$	ΔH^{o}_{i} = +905 kJ mol^{-1}
Boron	B	$1s^2\ 2s^2\ 2p^1$	ΔH^{o}_{i} = +807 kJ mol^{-1}
Carbon	C	$1s^2\ 2s^2\ 2p^2$	ΔH^{o}_{i} = +1090 kJ mol^{-1}

- Removing an electron from Be breaks a full subshell (2s)
- Breaking full subshells requires more energy and this increases the 1st ionisation energy

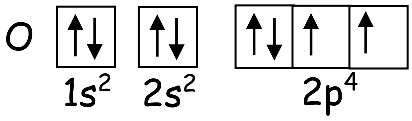
- Removing an electron from B empties the 2p subshell and makes the $2s^2$ the outer electron subshell.
- Creating a full outer subshell is favoured and this is why the 1st ionisation energy of B is lower than Be

Why has Nitrogen got a higher 1st ionisation energy than the trend would suggest?

Element	Symbol	Electronic Configuration	1st Ionisation Energy
Carbon	C	$1s^2\ 2s^2\ 2p^2$	ΔH^{o}_{i} = +1090 kJ mol^{-1}
Nitrogen	N	$1s^2\ 2s^2\ 2p^3$	ΔH^{o}_{i} = +1410kJ mol^{-1}
Oxygen	O	$1s^2\ 2s^2\ 2p^4$	ΔH^{o}_{i} = +1320 kJ mol^{-1}
Fluorine	F	$1s^2\ 2s^2\ 2p^5$	ΔH^{o}_{i} = +1690 kJ mol^{-1}



- Removing an electron from N breaks a relatively stable half-filled 2p subshell
- Breaking half-full subshells requires more energy and this increases the 1st ionisation energy



- Removing an electron from O creates a half-filled 2p subshell and this is more stable
- Creating a half-full subshell is favoured and this is why the 1st ionisation energy of O is lower than N