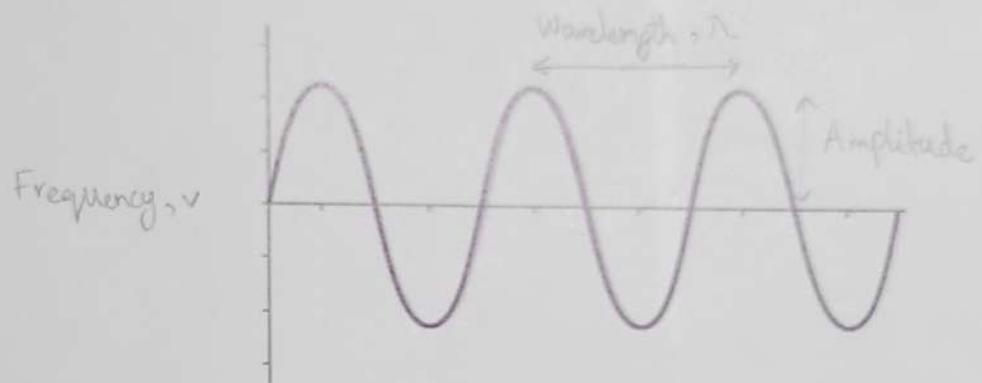


Electromagnetic Energy

Electromagnetic radiation can be imagined as a self-propagating transverse oscillating wave of electric and magnetic fields.

All electromagnetic radiation travels at the same velocity: the speed of light: $c = 299,792,458 \text{ m s}^{-1}$
 $\sim 3 \times 10^8 \text{ m s}^{-1}$



Waves have 3 properties:-

Amplitude is the height of the wave maximum from the centre.

Wavelength is the distance between successive wave peaks.

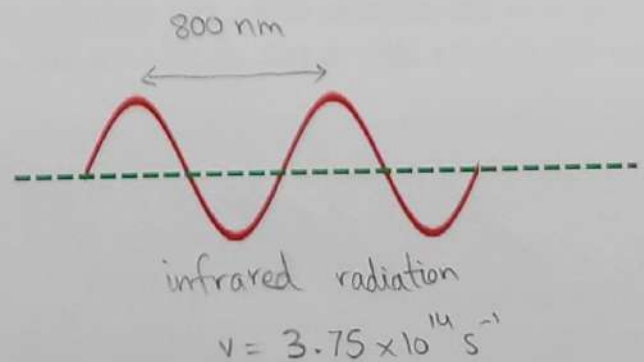
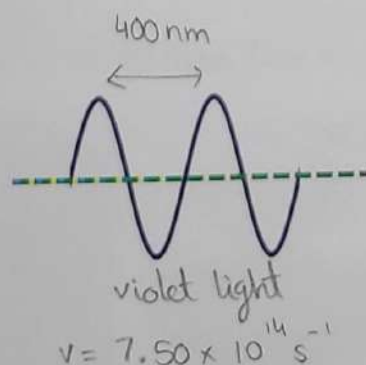
wavelength, λ (lambda) has units of distance, m.

The number of waves passing a given point per unit of time is the **frequency**

frequency, ν (nu) has units of Hertz, s^{-1}

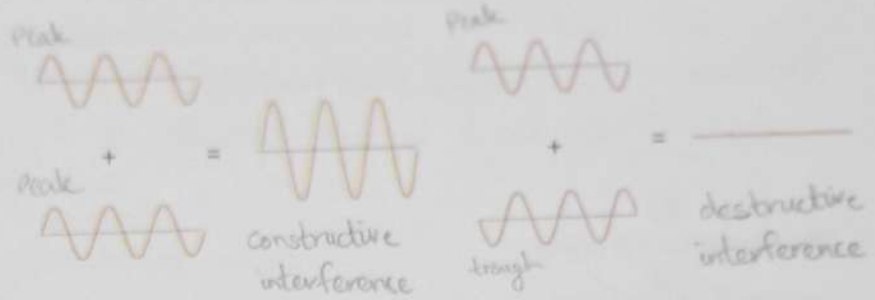
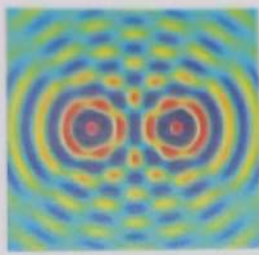
For waves traveling at the same velocity, the longer the wavelength, the smaller the frequency. The wavelength and frequency of light are therefore related in a straightforward way:

$$c = \lambda \nu$$

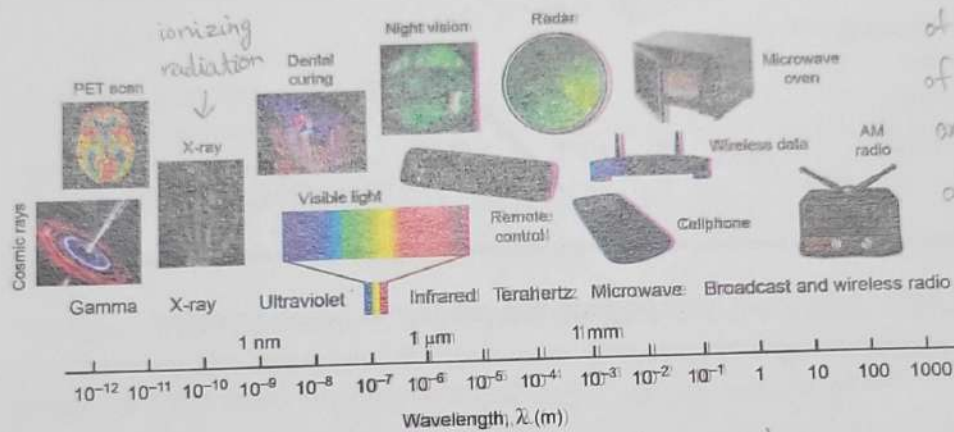


What we perceive as different kinds of electromagnetic energy are waves with different wavelengths and frequencies.

Wave nature of light successfully explains a range of different phenomena, e.g. interference:

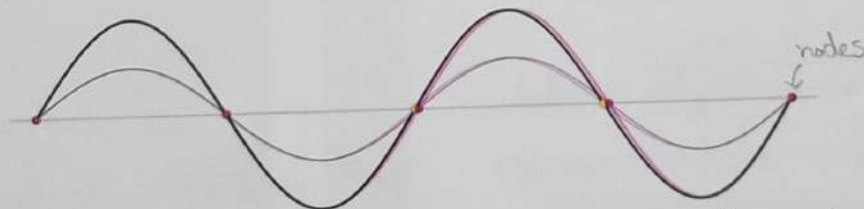


Much of our understanding of the electronic structure of atoms comes from analyzing light emitted or absorbed by substances



the electromagnetic spectrum

Not all waves are travelling waves. Standing waves are constrained within some region of space:



Energy increases with no. of nodes

A one-dimensional standing wave. Because the ends are fixed, only waves with an integer number of half-wavelengths can form

Wave theory could NOT explain some phenomena...

Blackbody radiation

Hot objects emit light, and the wavelength depends on the temperature of the substance.



A blacksmith's steel colour/temperature chart

classical theories could not predict this behaviour

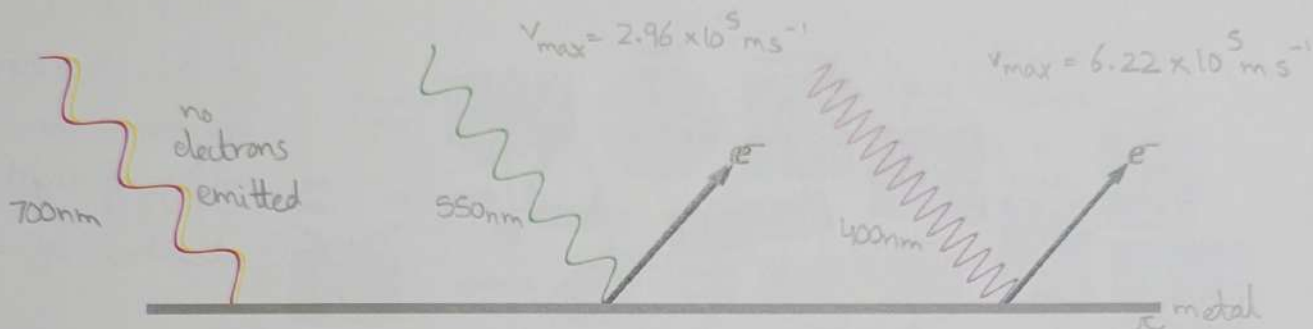
Max Planck proposed a theory that helped explain blackbody radiation: that energy can only be absorbed or released from atoms in certain amounts: called "quanta"

A quantum is the smallest amount of energy that can be emitted or absorbed as electromagnetic radiation.

The relationship between energy, E , and frequency is: $E = h\nu$ $\leftarrow (h\nu)$
 where h is the Planck constant = 6.626×10^{-34} joule-seconds (Js)

The photoelectric effect

Involves a metal surface absorbing light and emitting electrons:



Einstein proposed that light could have **particle-like properties**, which he called **photons**.

Energy of one photon = $E = h\nu = \frac{hc}{\lambda}$ $\leftarrow \text{from } c = \lambda\nu$

Line spectra

Radiation composed of only one wavelength is called *monochromatic*. eg laser

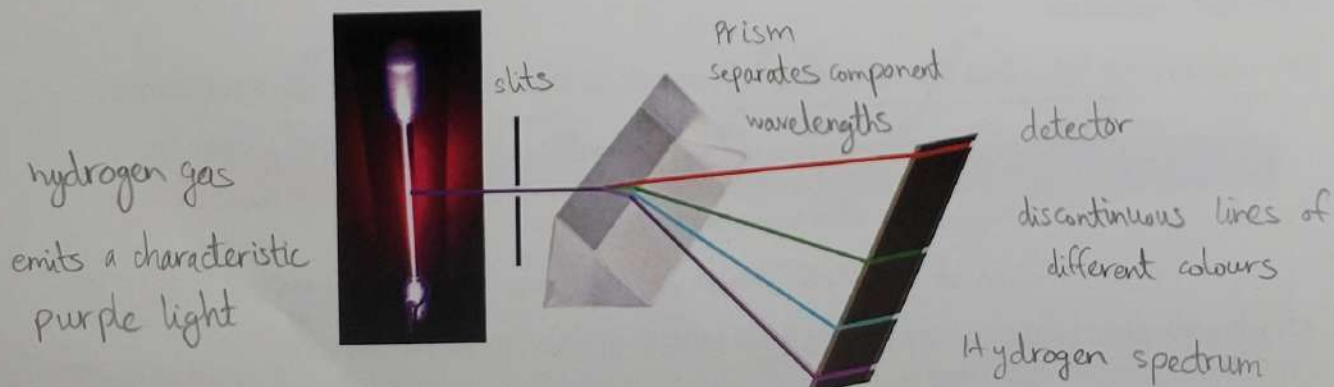
an array of different wavelengths is called continuous radiation.

When radiation from a light source, such as a light bulb, is separated into its different wavelength components, a **continuous spectrum** is produced:

Not true of light emitted from excited gaseous elements; instead, get a **line spectrum**, e.g. hydrogen:



Fireworks colours come from different excited elements



The Bohr model

Niels Bohr noted the line spectra of certain elements and assumed that electrons were confined to specific energy states.

These he called orbits

Bohr's model is based on three postulates:

1. Only orbits of specific radii are permitted for electrons in an atom

these correspond to certain definite energies

2. An electron in a permitted orbit has a specific energy

an "allowed" energy state

3. Energy is only emitted or absorbed by an electron as it moves from one allowed energy state to another

energy is gained or lost as a photon
i.e. in a quantum = $h\nu$



The ground state = the lowest energy state

An electron in a higher energy state is said to be in an excited state

That light is quantized helps us understand the structure of the atom, because energy levels in an atom are also quantized. Photoemission occurs as an electron relaxes from a higher energy state to a lower energy state.

Since the energy states are quantized, so is the light emitted from excited atoms

→ appear as line spectra

Quantized electron energy given by:

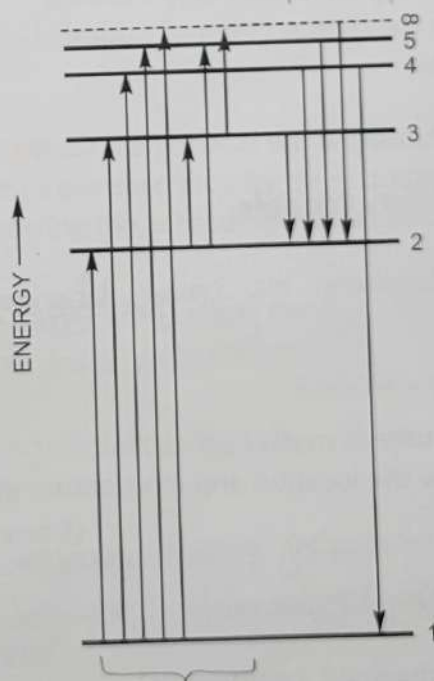
$$E_n = - (hcR) \left(\frac{1}{n^2} \right) \text{ J}$$

$$= - 2.18 \times 10^{-18} \left(\frac{1}{n^2} \right) \text{ J}$$

$$\Delta E = - 2.18 \times 10^{-18} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

↑
energy change
for absorption or
emission.

Electron moves to lower energy as light is emitted (exothermic)



Electron moves to higher energy as light is absorbed (endothermic)

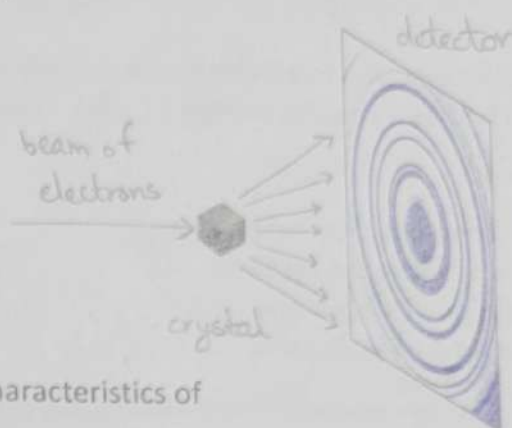
Development of Quantum Theory

Louis de Broglie suggested that if light can have material properties, matter should exhibit wave properties. He proposed that the characteristic wavelength of the electron or of any other particle depends on its mass, m , and on its velocity, v :

$$\lambda = h / mv$$

The momentum, mv , is a particle property, whereas λ is a wave property

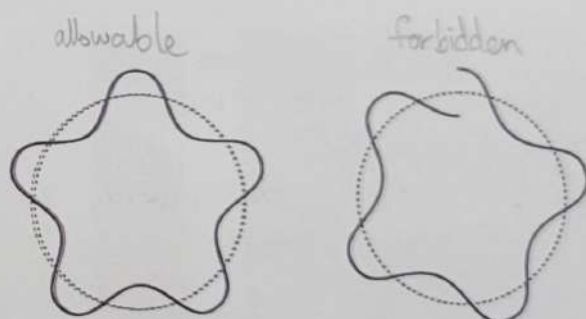
Soon after, experimental work demonstrated that electrons could be diffracted. Electron microscopes use electrons instead of a beam of light: they have higher resolution because they use shorter wavelengths.



Matter waves is the term used to describe wave characteristics of material particles.

Applicable to all matter but for objects of ordinary size, the calculated wavelength is unimaginably short and has no sensible interpretation.

de Broglie's work makes sense in the context of **quantization**: an electron can be thought of as a standing wave, and only standing waves with the right number of **nodes** are allowable:



The Uncertainty Principle

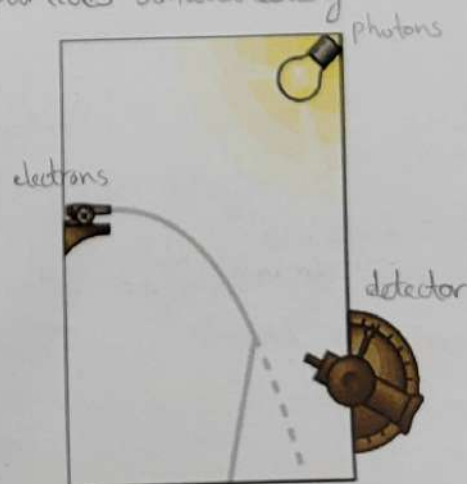
Werner **Heisenberg**: we cannot determine the exact position, direction of motion, and speed of subatomic particles simultaneously

wave-like AND particle-like

The **dual nature of matter** sets a limit on how precisely we can know the location and momentum of an object.

The measuring process interferes with what is being measured.

Heisenberg imagined a **gamma ray microscope** to explain his uncertainty principle.



Photons are used to illuminate an electron, and the position of the electron can be determined from the scattering of the photons

- BUT the photon scatters in a random direction and transfers a large and unknown amount of momentum to the electron.

Heisenberg related the uncertainty of the position, Δx , and the uncertainty in momentum $\Delta(mv)$ to a quantity involving Planck's constant:

$$\Delta x \cdot \Delta(mv) \geq \frac{h}{4\pi}$$

Erwin Schrödinger proposed an equation containing both wave and particle terms. The solution of the equation is known as a **wave function**, Ψ (psi). It describes the behavior of a quantum mechanical object, such as an electron.

Ψ^2 is the probability density

Ψ^2 gives the electron density for the atom

A region of high electron density = high probability of finding an electron

Schrödinger treated electrons in the hydrogen atom as standing waves.



Understanding Quantum Theory of Electrons in Atoms

If we solve the Schrödinger equation we get wave functions and corresponding energies.

These wave functions are called orbitals.

The probability density (or electron density) described by an **orbital** has a characteristic energy and shape. The energy and shape of orbitals are described by three quantum numbers. These arise from the mathematics of solving the Schrödinger equation.

the principal quantum number, n , describes the main energy level: specifies electron shell
must be a positive integer $n = 1, 2, 3, 4, \dots$

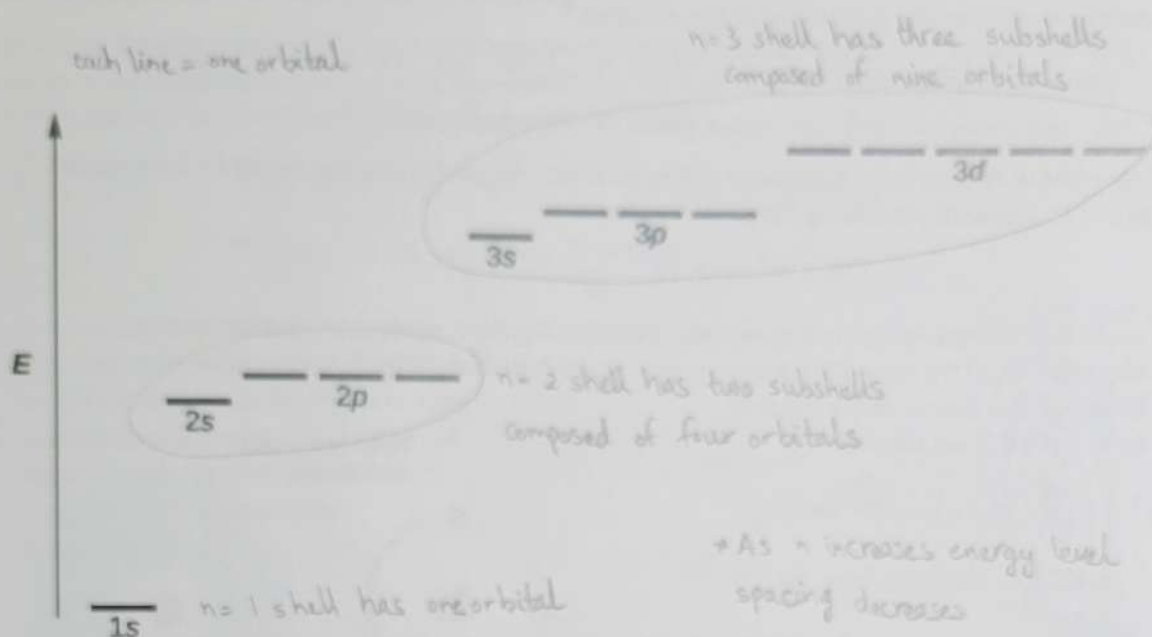
the angular momentum quantum number, ℓ , describes the shape: specifies subshell
maximum value is $(n-1)$, i.e. $\ell = 0, 1, 2, 3, \dots, (n-1)$
use letters for ℓ (s, p, d and f for $\ell = 0, 1, 2$, and 3).

the magnetic quantum number, m_ℓ , designates specific orbital: specifies orientation
maximum value depends on ℓ , can take integral values from $-\ell$ to $+\ell$

$$m_\ell = (-\ell), \dots, 0, \dots, (+\ell)$$

	ℓ	m_ℓ
s	0	0
p	1	-1, 0, 1
d	2	-2, -1, 0, 1, 2

Orbitals can be ranked in terms of energy.



Orbitals have different shapes, orientations, and number of nodes, depending on their quantum numbers.

The s-type orbitals are spherically symmetrical:

2d drawings



1s



2s



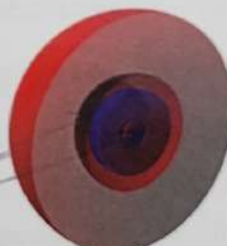
3s



1s

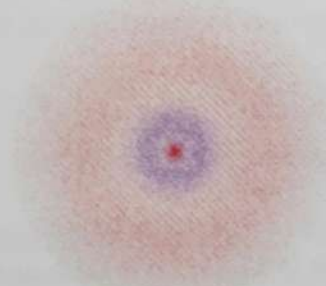
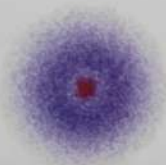


2s



3s

cutaway view



points view

node = probability of finding an electron is 0 (no node at nucleus for s orbitals)

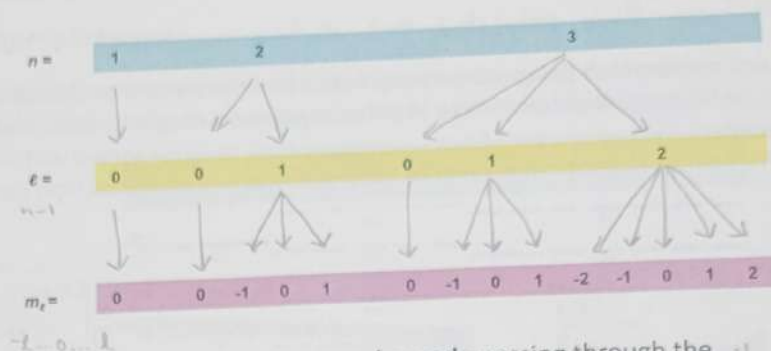
For ALL orbitals the number of nodes is given by $(n-1)$

s orbitals can only have radial nodes, no angular nodes



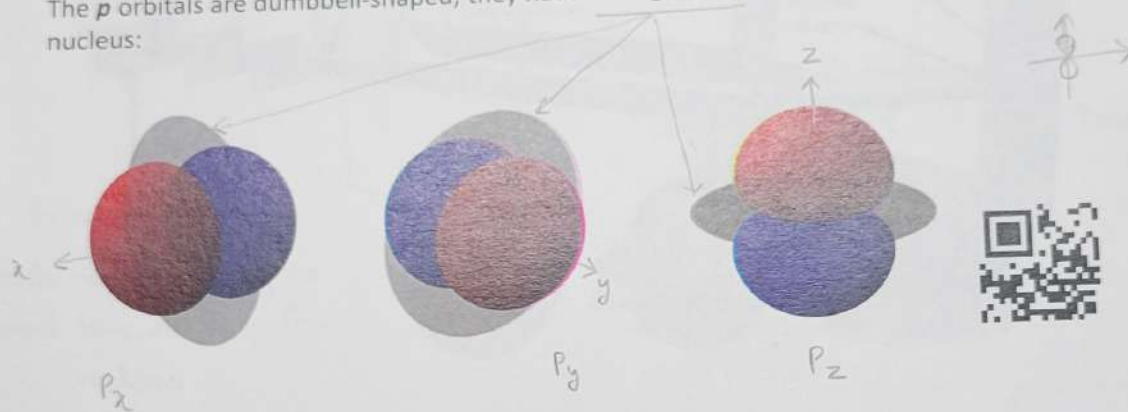
Each unique combination of n , ℓ , and m_ℓ produces one unique spatially quantised atomic orbital:

allowable combinations
of n, ℓ and m_ℓ for
 $n = 1, 2$ and 3
 $\ell = 0, 1, 2, 3$
corresponds to s, p, d, f



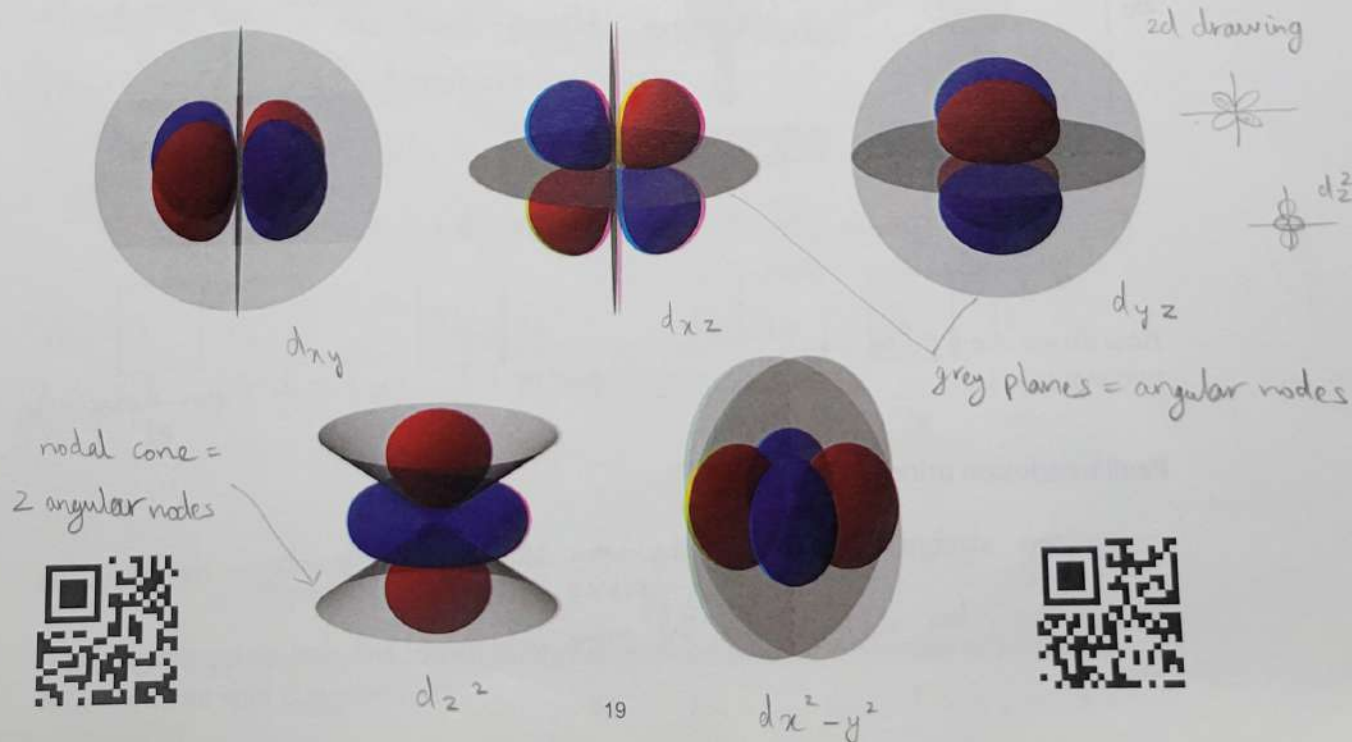
no. of possible
combinations
for $m_\ell = n^2$

The p orbitals are dumbbell-shaped; they have an angular node passing through the nucleus:



The number of angular nodes an atomic orbital has is equal to its ℓ value. So d orbitals have 2 angular nodes.

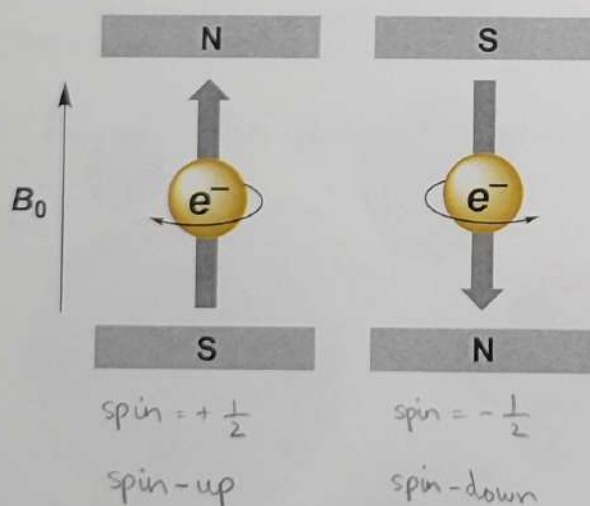
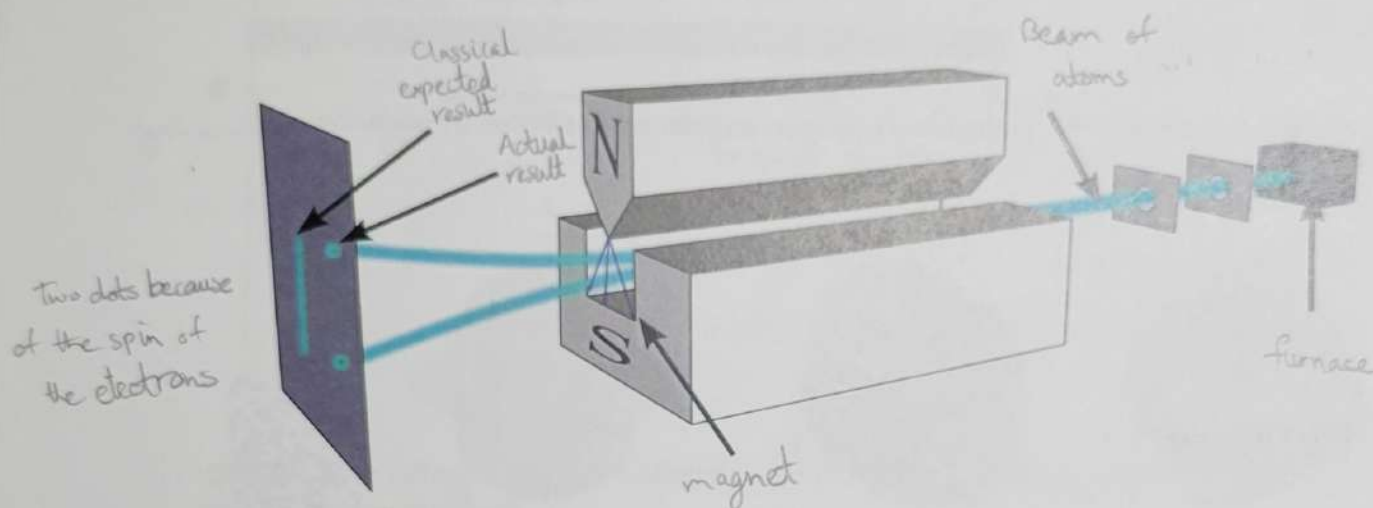
5 values of m_ℓ ($-2, -1, 0, 1, 2$) so 5 different orbitals with different orientations



Line spectra of many-electron atoms show each line as a closely spaced pair of lines.

Wolfgang Pauli postulated that electron must exist in two states

Stern and Gerlach designed an experiment to determine why. A beam of atoms was passed through a slit and into a non-homogeneous magnetic field and the atoms were detected. Two spots were found, corresponding to silver atoms with electrons in different states (note that silver atoms have one unpaired electron each).



We define a 4th quantum number
 m_s = spin magnetic quantum number
 $= \pm \frac{1}{2}$

How do we show these two states?

$$m_s = +\frac{1}{2} \text{ (spin-up)} \uparrow \quad m_s = -\frac{1}{2} \text{ (spin-down)} \downarrow$$

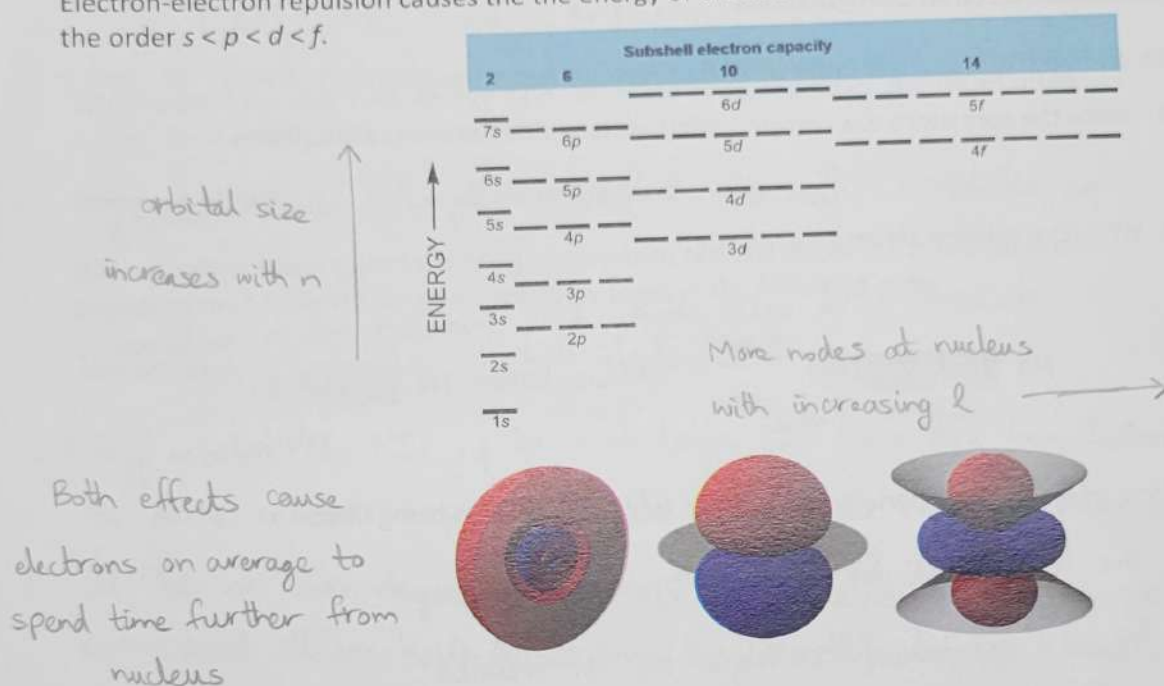
Pauli's exclusion principle states that:

- no two electrons can have the same set of four quantum numbers
- therefore, two electrons in the same orbital must have opposite spins
i.e. $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$

Electronic Structure of Atoms (Electron Configurations)

Orbital Energies and Atomic Structure

The energy of atomic orbitals increases as the principal quantum number, n , increases. Electron-electron repulsion causes the the energy of orbitals to increase within a shell in the order $s < p < d < f$.

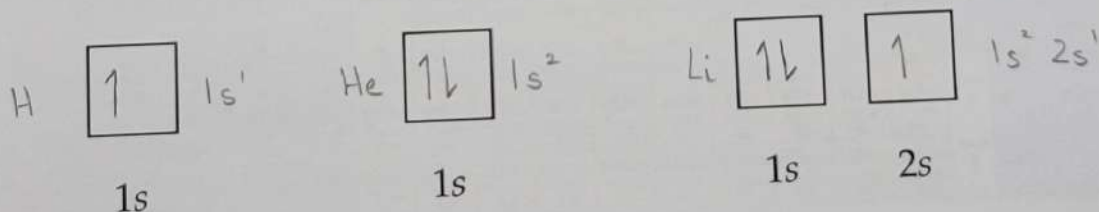


Electron configurations tell us how the electrons are distributed among the various orbitals (energy levels) of an atom.

The most stable configuration, or ground state, is that in which the electrons are in the lowest possible energy state

When writing ground-state electronic configurations:

- electrons fill orbitals in order of increasing energy
- no two electrons can fill one orbital with the same spin (Pauli)



Hund's Rule

degenerate = same energy

"For degenerate orbitals, the lowest energy is attained when the number of electrons with the same spin is maximized"

- electrons fill each orbital singly with their spins parallel before any orbital gets a second electron

- electron-electron repulsions are minimized

Condensed Electron Configurations

Electron configurations may be written using a shorthand notation:

1. Write the **core electrons** corresponding to the noble gas in square brackets

= electrons in the inner shells; generally not involved in bonding

2. Write the **valence electrons** explicitly

= electrons in the outer shell; those gained or lost in reactions

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

core valence

Abbreviation Na $[\text{Ne}] 3s^1$

core valence

Blocks of elements in periodic table relate to which orbital is being filled

- the 4s orbital fills before the 3d orbitals

- the 6s orbital fills before the 4f orbitals

The periodic table can be used as a guide for electron configurations.

the period number is the value of n for the s orbitals

		Group																		
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
Period	1	1H 1s ¹																	2He 1s ²	
	2	3Li 2s ¹	4Be 2s ²	<div>Number Symbol Valence electrons</div> <div>d-block transition metals</div>										5B 2s ² 2p ¹	6C 2s ² 2p ²	7N 2s ² 2p ³	8O 2s ² 2p ⁴	9F 2s ² 2p ⁵	10Ne 2s ² 2p ⁶	
	3	11Na 3s ¹	12Mg 3s ²											13Al 3s ² 3p ¹	14Si 3s ² 3p ²	15P 3s ² 3p ³	16S 3s ² 3p ⁴	17Cl 3s ² 3p ⁵	18Ar 3s ² 3p ⁶	
	4	19K 4s ¹	20Ca 4s ²	21Sc 4s ² 3d ¹	22Ti 4s ² 3d ²	23V 4s ² 3d ³	24Cr 4s ¹ 3d ⁵	25Mn 4s ² 3d ⁵	26Fe 4s ² 3d ⁶	27Co 4s ² 3d ⁷	28Ni 4s ² 3d ⁸	29Cu 4s ¹ 3d ¹⁰	30Zn 4s ² 3d ¹⁰	31Ga 4s ² 3d ¹⁰ 4p ¹	32Ge 4s ² 3d ¹⁰ 4p ²	33As 4s ² 3d ¹⁰ 4p ³	34Se 4s ² 3d ¹⁰ 4p ⁴	35Br 4s ² 3d ¹⁰ 4p ⁵	36Kr 4s ² 3d ¹⁰ 4p ⁶	
	5	37Rb 5s ¹	38Sr 5s ²	39Y 5s ² 4d ¹	40Zr 5s ² 4d ²	41Nb 5s ² 4d ³	42Mo 5s ¹ 4d ⁵	43Tc 5s ² 4d ⁵	44Ru 5s ² 4d ⁶	45Rh 5s ² 4d ⁷	46Pd 4d ¹⁰	47Ag 5s ¹ 4d ¹⁰	48Cd 5s ² 4d ¹⁰	49In 5s ² 4d ¹⁰ 5p ¹	50Sn 5s ² 4d ¹⁰ 5p ²	51Sb 5s ² 4d ¹⁰ 5p ³	52Te 5s ² 4d ¹⁰ 5p ⁴	53I 5s ² 4d ¹⁰ 5p ⁵	54Xe 5s ² 4d ¹⁰ 5p ⁶	
	6	55Cs 6s ¹	56Ba 6s ²	57-70 †	71Lu 6s ² 4f ¹⁴ 5d ¹	72Hf 6s ² 4f ¹⁴ 5d ²	73Ta 6s ² 4f ¹⁴ 5d ³	74W 6s ² 4f ¹⁴ 5d ⁴	75Re 6s ² 4f ¹⁴ 5d ⁵	76Os 6s ² 4f ¹⁴ 5d ⁶	77Ir 6s ² 4f ¹⁴ 5d ⁷	78Pt 6s ¹ 4f ¹⁴ 5d ⁹	79Au 6s ¹ 4f ¹⁴ 5d ¹⁰	80Hg 6s ² 4f ¹⁴ 5d ¹⁰	81Tl 6s ² 4f ¹⁴ 5d ¹⁰ 6p ¹	82Pb 6s ² 4f ¹⁴ 5d ¹⁰ 6p ²	83Bi 6s ² 4f ¹⁴ 5d ¹⁰ 6p ³	84Po 6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁴	85At 6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁵	86Rn 6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁶
	7	89Fr 7s ¹	88Ra 7s ²	89-102 †	103Lr 7s ² 5f ¹⁴ 6d ¹	104Rf 7s ² 5f ¹⁴ 6d ²	105Db 7s ² 5f ¹⁴ 6d ³	106Sg 7s ² 5f ¹⁴ 6d ⁴	107Bh 7s ² 5f ¹⁴ 6d ⁵	108Hs 7s ² 5f ¹⁴ 6d ⁶	109Mt 7s ² 5f ¹⁴ 6d ⁷	110Ds 7s ² 5f ¹⁴ 6d ⁸	111Rg 7s ² 5f ¹⁴ 6d ⁹	112Cn 7s ² 5f ¹⁴ 6d ¹⁰	113Nh 7s ² 5f ¹⁴ 6d ¹⁰ 7p ¹	114Fl 7s ² 5f ¹⁴ 6d ¹⁰ 7p ²	115Mc 7s ² 5f ¹⁴ 6d ¹⁰ 7p ³	116Lv 7s ² 5f ¹⁴ 6d ¹⁰ 7p ⁴	117Ts 7s ² 5f ¹⁴ 6d ¹⁰ 7p ⁵	118Og 7s ² 5f ¹⁴ 6d ¹⁰ 7p ⁶

†lanthanides

†actinides

s-block

alkali and
alkaline earth
metals

†lanthanides

†actinides

f-block lanthanoids and actinoids

p-block
main
group
elements

Anomalous Electron Configurations

There are elements that appear to violate the electron configuration guidelines:

e.g. Cr $[\text{Ar}] 3d^5 4s^1$ not $[\text{Ar}] 3d^4 4s^2$

Cu $[\text{Ar}] 3d^{10} 4s^1$ not $[\text{Ar}] 3d^9 4s^2$

- due to special stability of half-filled and filled shell configurations
When atomic number > 40 , energy differences are small and other anomalies often occur. These usually act to reduce electron repulsions.

Summary of rules

Aufbau - German for "building up"

We can collect these rules for adding electrons to orbitals under the useful umbrella known as the "Aufbau Principle". We apply them in the following order:

- 1- Lower energy orbitals fill with electrons first
- 2- Any orbital can hold up to 2 electrons. If there are two electrons in the same orbital, they have opposite spins (Pauli Exclusion Principle)
- 3- If two or more degenerate orbitals are available, one electron goes into each until all are half-filled, then they start pairing up (Hund's rule)
- 4- A particularly stable configuration is one in which a set of p or d orbitals is either filled or half-filled (e.g. Cr, Cu)

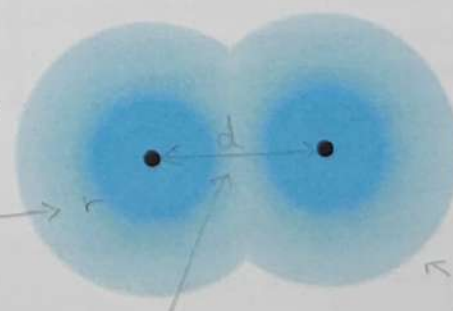
Periodic Variations in Element Properties

The elements in groups (vertical columns) of the periodic table exhibit similar chemical behavior. An understanding of the electronic structure of the elements allows us to examine some of the properties that govern their chemical behavior.

Variation in Covalent Radius

We can define atomic size in several ways, based on distances between nuclei in different situations.

non bonding radius =
half the closest distance
between nuclei during a collision



bonding radius =
half the distance between
nuclei in a compound = $\frac{1}{2}d$

electron
distribution in
molecule

Knowing atomic radii allows estimation of bond lengths in molecules

e.g. $\overset{\text{d}}{\text{C}}-\text{C}$ (diamond) = $\overset{\text{picometres}}{154 \text{ pm}}$

$\text{Cl}-\text{Cl}$ (Cl_2) = 199 pm

estimate C-Cl distance in CCl_4 as $0.5 \times (154 + 199) = 177 \text{ pm}$

Atomic size varies across and down the periodic table in a fairly consistent way:



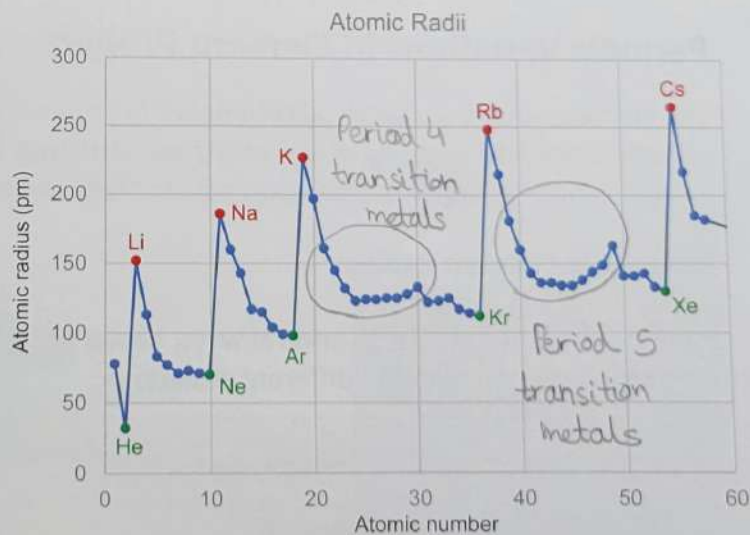
Effective nuclear charge (Z_{eff}) is the charge experienced by an electron on a many-electron atom.

\neq charge on the nucleus because of the effect of the inner electrons

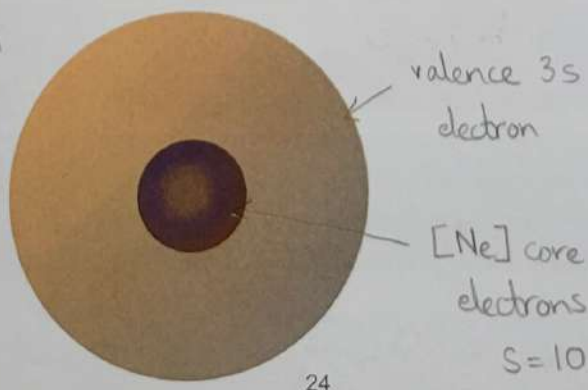
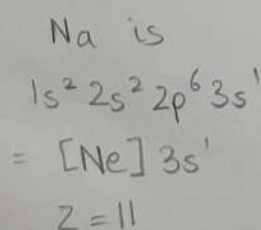
The electron is attracted to the nucleus, but repelled by electrons that shield or screen it from the full nuclear charge.

atomic number
↓
 $Z_{\text{eff}} = Z - S$

S is called the *screening constant* or *shielding constant*. It represents the portion of the nuclear charge that is screened from the valence electron by other electrons in the atom.



S is given by the number of core electrons in an atom e.g Na



$Z_{\text{eff}} = 11 - 10$
 $= 1$

Core electrons are effective at screening the outer electrons from the full charge of the nucleus.

- electrons in the same shell do not screen each other effectively.
- Z_{eff} experienced by valence electrons is larger as we move left to right
- Z_{eff} gets slightly larger down a group because the screening is not perfect
- Filled d and f orbitals should be treated as core electrons

Variation in Ionic Radius

Ionic radius is the measure used to describe the size of an ion.

Cations are smaller than their parent atoms

- electrons removed from largest orbital

- Z_{eff} has increased



Al 118 pm



Al^{3+} 68 pm



S 104 pm



S^{2-} 170 pm

Anions are larger than their parent atoms

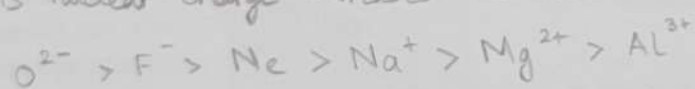
- electrons added to largest orbital

- total electron-electron repulsion has increased

- for ions with the same charge, ionic size increases down a group

All the members of an **isoelectronic series** have the same number of electrons

As nuclear charge increases the ions become smaller



Ionic size important in many applications: e.g. lithium ion batteries work because of the small size and low charge of the Li^+ ions allows them to migrate from cathode to anode.

Variation in ionization energy

The **ionization energy** is the minimum energy required to remove an electron from the ground state of the isolated gaseous atom or ion.

I_1 = energy required to remove an electron from a gaseous atom



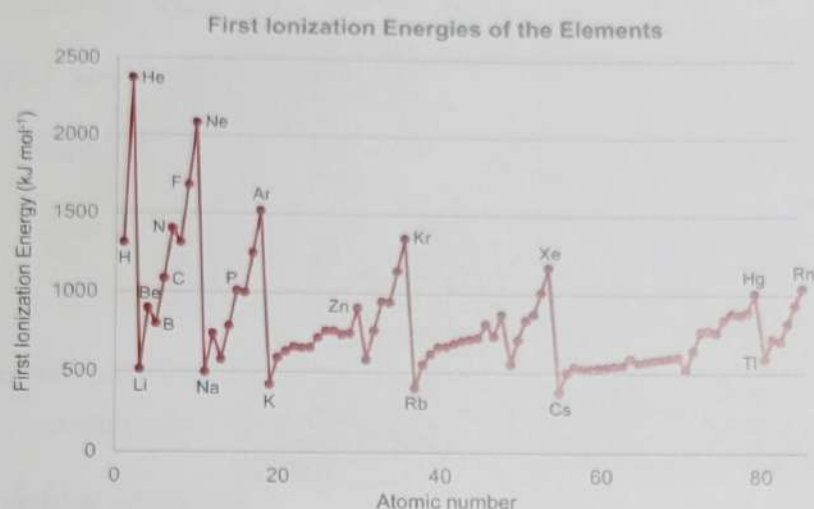
I_2 = energy required to remove an electron from a gaseous 1^+ ion, etc

The larger the ionization energy, the more difficult it is to remove the electron.

Positive values - energy is required to remove electrons

Ionization energy generally increases across a period.

Z_{eff} gets larger, making it more difficult to remove an electron

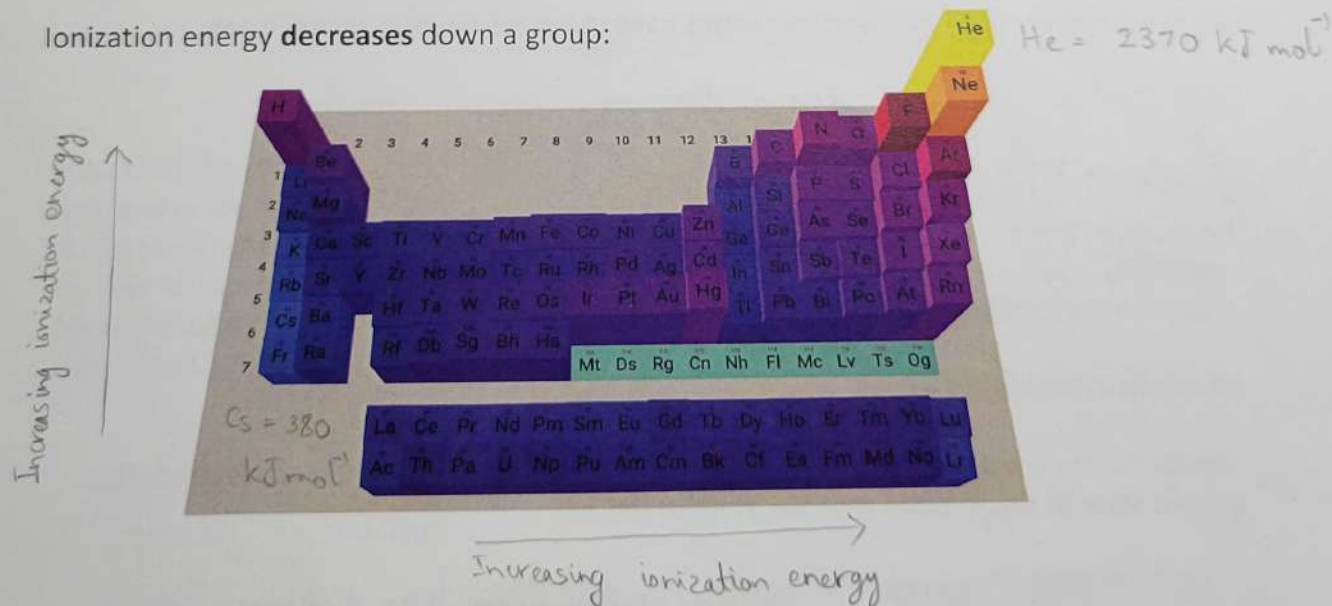


Two exceptions are removing the **first** p electron (e.g. B, Al) and removing the **fourth** p electron (e.g. O, S).

s electrons are more effective at shielding than p electrons

removal of 4th p electron easier than expected due to electron-electron repulsion

Ionization energy **decreases** down a group:



Small atoms have high IE: easier to remove an electron from the most spatially extended orbital.

Ionization energies for an element get larger as successive electrons are removed.

MUCH greater value of ionization energy when a core electron is removed

Element	1s	2s	2p	3s	3p	3d	4s
Na	496	4562					
Mg	738	1451	7733				
Al	578	1817	2745	11577			
Si	786	1577	3232	4356	16091		
P	1012	1907	2814	4964	6274	21267	
S	1000	2252	3357	4556	7004	8496	27107
Cl	1251	2298	3622	5158	6542	9362	11018
Ar	1521	2666	3831	5771	7238	8781	11995

kJ mol^{-1}

Electron configurations of ions are derived from the electron configurations of elements with the required number of electrons added or removed from the most accessible orbital.

$\text{Li}: [\text{He}] 2s^1$ becomes $\text{Li}^+: [\text{He}]$

$\text{F}: [\text{He}] 2s^2 2p^5$ becomes $\text{F}^-: [\text{He}] 2s^2 2p^6 = [\text{Ne}]$

Transition metals tend to lose the valence ns electrons first and then as many d electrons as are required to reach the charge on the ion.

Electrons are removed first from the orbital with largest principal quantum number n , e.g. $4s$ then $3d$

Variation in electron affinity

Electron affinity is the energy change when a gaseous atom gains an electron to form a gaseous ion. Electron affinity and ionization energy measure the energy changes of opposite processes:

Electron affinity: $\text{Cl}_{(g)} + e^- \rightarrow \text{Cl}_{(g)}^-$ $\Delta E = -349 \text{ kJ/mol}$ (exothermic)

Ionization energy: $\text{Cl}_{(g)} \rightarrow \text{Cl}_{(g)}^+ + e^-$ $\Delta E = 1251 \text{ kJ/mol}$ (endothermic)

Energy is *usually* released when an atom adds an electron. E_{ea} is **negative** for stable anions.

Electron affinities do not change much as we move down a group

Going down a group, the attraction of the added electron to the nucleus is less - but so is the electron-electron repulsion.

	1	2		13	14	15	16	17	18
1	1H -72								2He >0
2	3Li -60	4Be >0		5B -23	6C -123	7N >0	8O -141	9F -322	10Ne -30
3	11Na -53	12Mg >0		13Al -44	14Si -120	15P -74	16S -20	17Cl -348	18Ar >0
4	19K -48	20Ca >0		31Ga -29	32Ge -115	33As -7	34Se -195	35Br -324	36Kr >0
5	37Rb -46	38Sr >0		49In -29	50Sn -121	51Sb -101	52Te -190	53I -295	54Xe >0
6	55Cs -45	56Ba >0		81Tl -50	82Pb -101	83Bi -101	84Po -170	85At -270	86Rn >0

Electron affinity becomes more exothermic as we move left to right across a row.

Attraction of the electron to the nucleus goes up with increasing charge on the nucleus

Note discontinuities when entering a new subshell or when pairing electrons in p orbitals.

e.g. Be - electron into $2p$ instead of $2s$ e.g. Ne - electron into $3s$ instead of $2p$ e.g. N - electron into already occupied $2p$

The properties discussed in this section (size of atoms and ions, effective nuclear charge, ionization energies, and electron affinities) are central to understanding chemical reactivity.