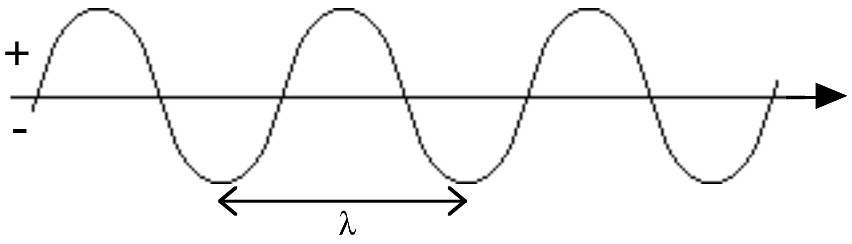
Electronic Structure and the Periodic Table

Electromagnetic radiation

Electromagnetic radiation (X rays, visible light, radio waves etc) is the manner by which energy travels through space. It consists of an electric field oscillating perpendicularly to the direction of travel.

(N.B. The oscillating electric field generates an oscillating magnetic field perpendicular to the electric field)

It travels with a velocity $c = 3 \times 10^8$ ms^{-1}



This wave is an oscillating dipole becoming alternately + and - as it passes one fixed point.

The wave length λ is the distance between two consecutive crests of the wave.

The number of waves passing a given point in one second is therefore c/λ (the frequency, υ) i.e.

frequency $\boxed{\upsilon = \frac{c}{\lambda}}$ waves per second (Hertz Hz)

The number of waves in unit length (usually 1 cm) is called the wave number,

wave-number $\boxed{\bar{\upsilon} = \frac{1}{\lambda}}$ waves per unit length

The higher the frequency the higher the energy of the radiation i.e.

$$E \propto \nu$$

Since

$$\nu \propto \frac{1}{\lambda}$$

the lower λ the higher the energy of the radiation.

Visible light, which is the part of the electromagnetic spectrum capable of exciting the nerve cells of the eye, consists of different radiations ranging from red light to violet light.

Colour	Wave length range nm (10^{-9} m)
red	760 - 620
orange	620 - 595
yellow	595 - 560
green	560 - 500
blue	500 - 460
indigo	460 - 430
violet	430 - 380

↓ Energy increasing

The full electromagnetic spectrum (below) extends from gamma rays with a wave length of a millionth of a millionth of a centimetre (10^{-14} m) to radio and TV waves some of which are over 10 kilometres long (10^4 m).

λ/m 10^{-14} --- 10^{-10} 10^{-9} 10^{-8} 10^{-7} 10^{-6} 10^{-5} 10^{-4} 10^{-3} 10^{-2} 10^{-1} --- 10^{3} 10^{4}

γ rays X rays UV VIS IR RADAR TV RADIO

Photons and their energy

In 1905 Einstein proposed that electromagnetic radiation could be considered not only as a wave-form but as a stream of particles called Photons each having an energy proportional to the frequency of the radiation i.e.

$$E_{\text{photon}} = h\upsilon$$

where h = Planck's constant = 6.625×10^{-34} Js

It now becomes possible to assign an energy to the individual photons of any particular electromagnetic radiation.

Problem

Find the energy of (i) one photon (ii) one mole of photons of IR radiation of wave number 1000 cm^{-1}.
(N.B. 1000 $\text{cm}^{-1} = 10^5\ \text{m}^{-1}$)

$$E_{\text{photon}} = h\upsilon$$

$$= \frac{hc}{\lambda}$$

$$= hc\overline{\upsilon}$$

$$= 6.625 \times 10^{-34} \times 3.0 \times 10^{8} \times 10^{5} \quad \{(\text{Js})(\text{ms-1})(\text{m-1})\}$$

$$= \underline{1.988 \times 10^{-20}\ \text{J}}$$

$$\text{Energy of one mole of photons} = Nhc\bar{\nu}$$

$$= 6.023 \times 10^{23} \times 1.988 \times 10^{-20}$$

$$= 11971\ \text{J} = \underline{11.971\ \text{kJ}}$$

Problem

Find the energy of (i) one photon (ii) one mole of photons of yellow light of wave length 589 nm.

$$E_{photon} = h\nu$$

$$= \frac{hc}{\lambda} = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^{8}}{589 \times 10^{-9}} \qquad \{(Js)(ms^{-1})(m^{-1})\}$$

$$= \underline{3.37 \times 10^{-19}\ \text{J}}$$

$$\text{Energy of one mole of photons} = Nhc/\lambda$$

$$= 6.023 \times 10^{23} \times 3.37 \times 10^{-19}$$

$$= 2.03 \times 10^{5}\ \text{J}$$

$$= \underline{203\ \text{kJ}}$$

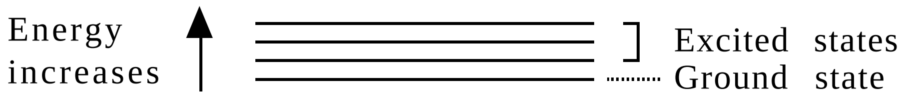
The Interaction of Electromagnetic Radiation with Matter

The energy within all matter is the sum of the

- translational energy due to the lateral movement of the molecules
- rotational energy due to the rotation of the molecules
- vibrational energy due to the vibration of the bonds within molecules
- electronic energy associated with electron movement relative to the nuclei.

With lateral movement, the particles are free to move in any direction and may have any energy dependent on the temperature only.

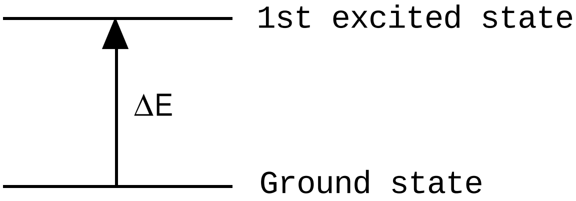
It is however a fundamental law of nature (The Quantum Theory) that particles moving within a very small volume (atomic dimensions) are allowed only certain values of energy i.e. their energies are quantised. This applies to a molecule's rotational, vibrational and electronic energies. Usually the molecule will exist in its lowest quantised level - the 'Ground State'. Higher energy levels are called 'Excited States'.



The more closely confined the oscillator the greater the restriction on the allowed energies and, consequently, the greater the spacing between the allowed energy levels.

Energy	Spacing between consecutive levels (J)
Rotational	7×10^{-22} ---- 7×10^{-25}
Vibrational	2×10^{-19} ---- 7×10^{-22}
Electronic	7×10^{-18} ---- 2×10^{-19}

A molecule in its ground state can change its energy to the next highest allowed energy level by absorbing a photon with that particular energy ΔE from electromagnetic radiation



Now $\Delta E = h\upsilon$

$$= \frac{hc}{\lambda}$$

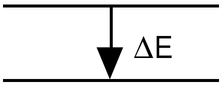
so the wavelength of the radiation required to supply photons of the right energy would be:

$$\lambda = \frac{hc}{\Delta E}$$

Energy	**Spacing ΔE (J)**	**$\lambda = \frac{hc}{\Delta E}$ (m)**	**Required radiation**
Rotational	7×10^{-22} -- 7×10^{-25}	3×10^{-4} -- 3×10^{-1}	Radar (Microwaves)
Vibrational	2×10^{-19} -- 7×10^{-22}	1×10^{-6} -- 3×10^{-4}	Infra Red
Electronic	7×10^{-18} -- 2×10^{-19}	3×10^{-8} -- 1×10^{-6}	UV and Visible

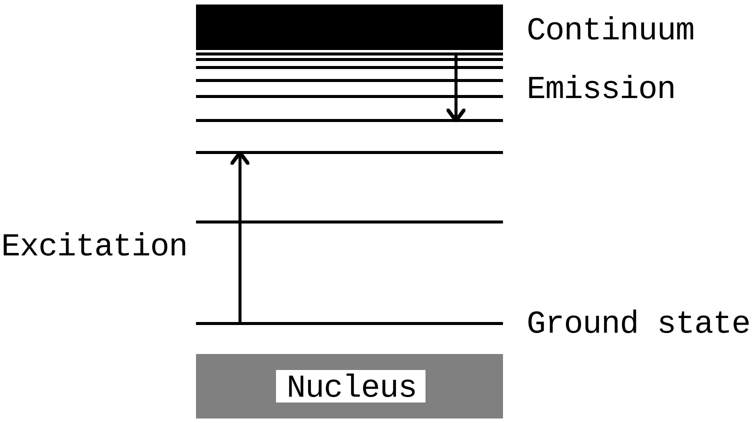
Electromagnetic radiation of the correct energy would therefore lose some of its energy on passing through the sample. This loss in intensity could be recorded : its magnitude would indicate the amount of absorbing material ; its energy would indicate the nature of the absorbing material.

Conversely a molecule in an excited state can change its energy to the next lowest allowed energy level by emitting a photon with energy ΔE :



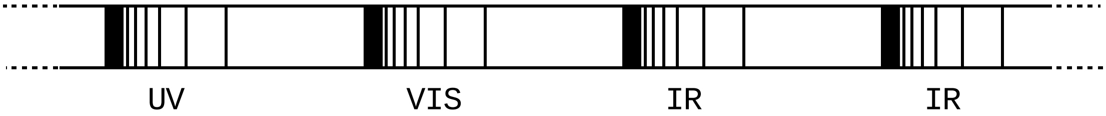
Energy Levels within the Atom

Being confined to a small space (the volume of the atom) the energy of the electrons in an atom is quantised. The higher the energy the further from the nucleus the electron and the more space available to the electron. As the space available becomes greater the energy levels come closer together until they reach a continuum. Then the electron would be free of the atom - in space.

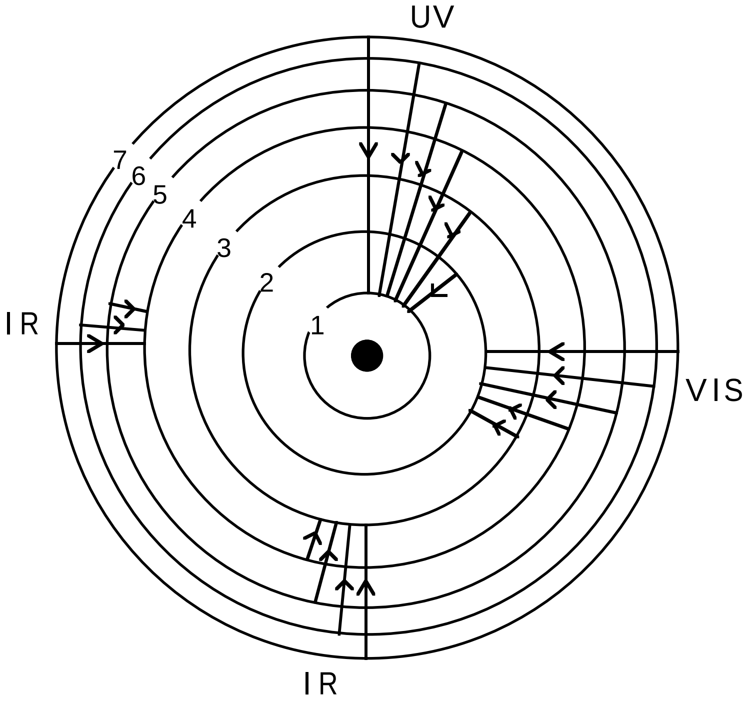


Subjected to an electric discharge or high temperature, collisions between high energy electrons provide enough energy to excite a ground state electron, by a series of jumps, into one of the excited levels.

An electron, returning from an excited state to a level below it, will give out a quantum of radiation whose frequency will depend on the size of the energy jump. Thus excited atoms emit energy which can be detected as a series of lines of specific frequency - a line spectrum e.g. Hydrogen :



In 1913 the Danish physicist Neils Bohr attempted to explain this spectrum by postulating the following picture of the Hydrogen atom :



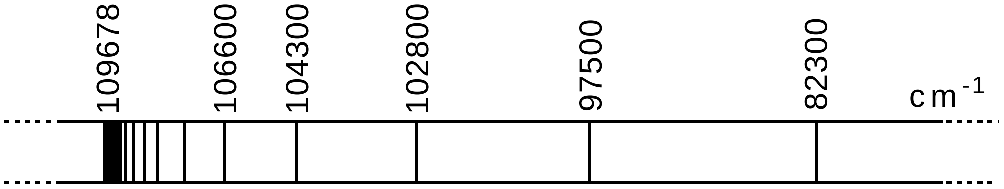
The electrons circled round the nucleus in circular, well defined orbits like the planets going round the sun.

Lines in the **UV** spectrum were due to transitions from higher energy levels down to the **first** quantum level.

Lines in the **Visible** spectrum were due to transitions from higher energy levels down to the **second** quantum level.

Lines in the **IR** spectrum were due to transitions from higher energy levels down to the **third**, **fourth**, **fifth** quantum levels etc.

Each set of lines converged to a continuous spectrum at the high energy end. This corresponded to the convergence of the quantum levels further from the nucleus e.g. UV spectrum :



It is interesting to note that $\bar{\nu}$ at the convergence limit of the UV spectrum is the wave number of the radiation emitted when an electron in the outer-most energy level of the atom (i.e. the surface of the atom) falls to the ground state. The energy of this radiation would be

$$E = hc\bar{\upsilon}$$

This would also be the energy required to promote a ground state electron to the outer surface of the atom i.e. remove it completely or ionise the atom.

So $E = hc\bar{\upsilon}$ = ionisation energy of one Hydrogen atom

$IE = Nhc\bar{\upsilon}$ = ionisation energy of one mole of Hydrogen atoms

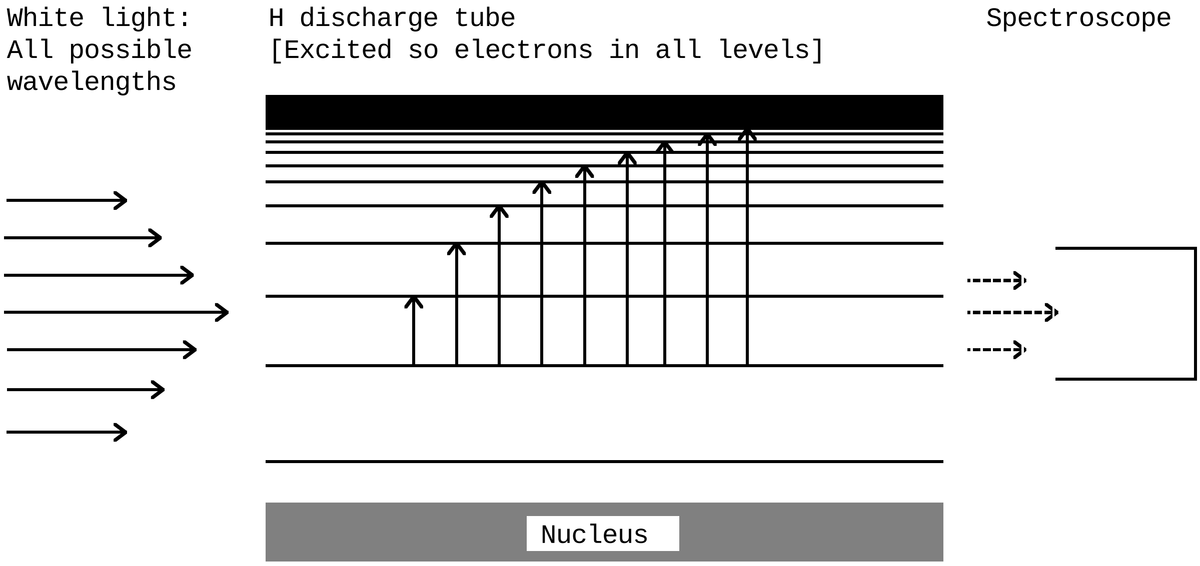
$$= 6.023 \times 10^{23} \times 6.625 \times 10^{-34} \times 3.0 \times 10^{8} \times 109678 \times 10^{2}$$

$$\{(\ )\ (\mathrm{Js})\ (\mathrm{ms^{-1}})\ (\mathrm{m^{-1}})\}$$

$$= 1.3129 \times 10^{5}\ \mathrm{J}$$

$$= \underline{1313\ \mathrm{kJ\ mol}}^{-1}$$

Absorption from white light can also be studied by placing the excited source between the white light source and the spectroscope.



The spectroscope records the visible spectrum (rainbow) showing dark lines where the photons were absorbed by the excited Hydrogen.

In emission and absorption spectra the intensity of the lines can be used to measure the amount of the element present.

Emission spectra can be obtained from other elements :

Element	Principal lines	Colour
Sodium	589 nm 616 nm	yellow orange
Lithium	671 nm	red
Barium	552 nm	green
Potassium	768 nm 405 nm	IR/red violet

The pattern of lines was complicated and could not be explained using Bohr's theory.

The Modern Theory of Electronic Structure

Bohr's simple model of the atom, for which he received the Nobel prize in 1922, could not explain the spectra of more complicated atoms.

A new model of the atom was developed in the 1920's by W.Heisenberg and Erwin Schrodinger.

Heisenberg began by showing that Bohr's atom was not valid since it could never be verified experimentally. In order to prove that electrons circled the nucleus in well-defined orbits their positions and velocity at any one instant would have to be found. Electromagnetic radiation is not scattered by objects smaller than its own wave length. To 'see' an electron would therefore require using electromagnetic radiation of wave length similar to the size of the electron. Such radiation (X rays) would necessarily consist of high energy photons which, on collision with the electrons, would cause a drastic change in their velocity.

There is therefore an uncertainty in finding the position and velocity of an electron since 'the act of observing destroys the scene being observed' (Heisenberg's Uncertainty Principle, 1927, Nobel Prize 1932).

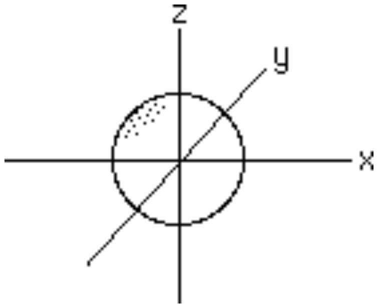
In the new approach, devised by Schrodinger, Bohr's energy levels were retained but it was recognised that they did not correspond to electron movement in circular orbits around the nucleus. Each electron was distinguished from another by assigning it a set of **four quantum numbers.** No two electrons in the atom have the same four quantum numbers.

The **Principal Quantum Number** ($n = 1,2,3$ etc) gives the energy level in which the electron is to be found. The number of electrons accommodated in each energy level is $2n^2$.

Each electron was assigned an **Orbital Quantum Number** (or 'azimuthal' Quantum Number) describing the region of space in which it had a 95% probability of being found. This region is called an Atomic Orbital.

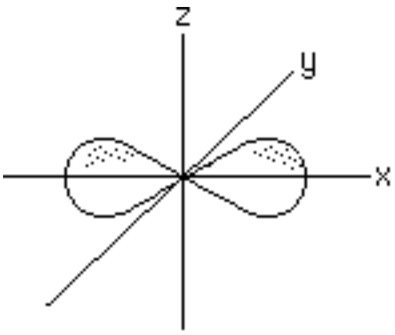
A further quantum number, called the **Orbital Direction Quantum Number** (or 'magnetic' quantum number) was required to specify the direction of the orbital in space (x,y,z, etc)

Orbital QN : S

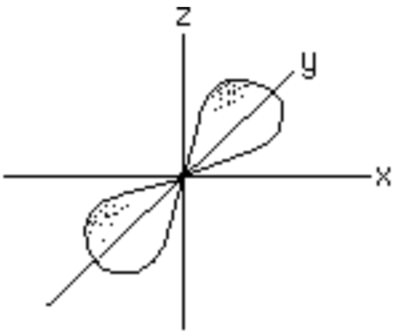


Only one S orbital since it is spherically symmetrical.

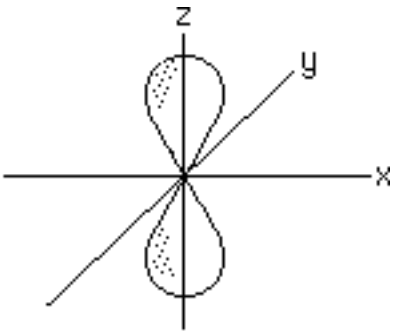
Orbital QN : P



P_x



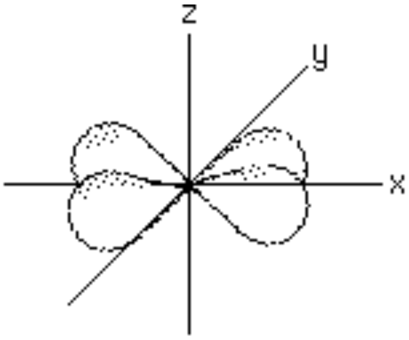
P_y



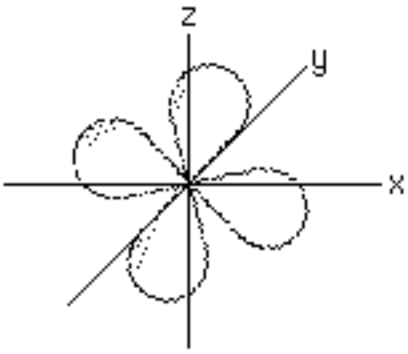
P_z

Three P orbitals are possible, distinguished from each other by their orbital direction quantum number.

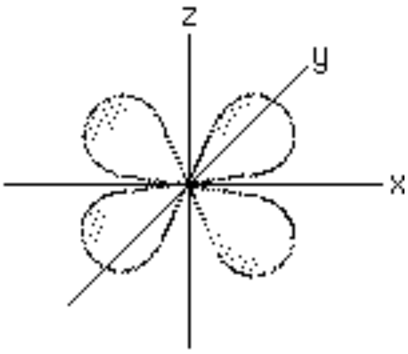
Orbital QN : d



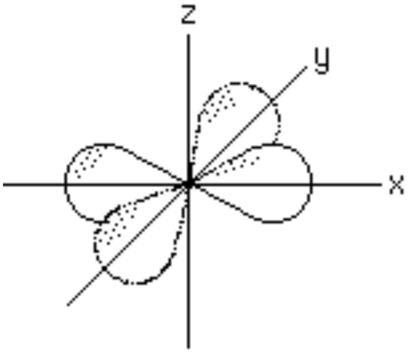
d_{xy}



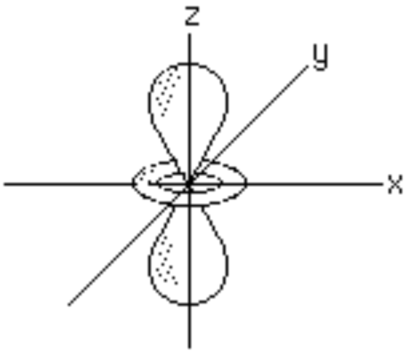
d_{yz}



d_{xz}



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



d_{z^2}

Five d orbitals are possible.

Orbital QN : f

Seven f orbitals are possible (too complicated to draw !)

In addition to the quantum numbers specifying its energy, space and direction each electron was assigned a **Spin Quantum Number** specifying its spin about its own axis (+1/2 or -1/2) clockwise or anti-clockwise.

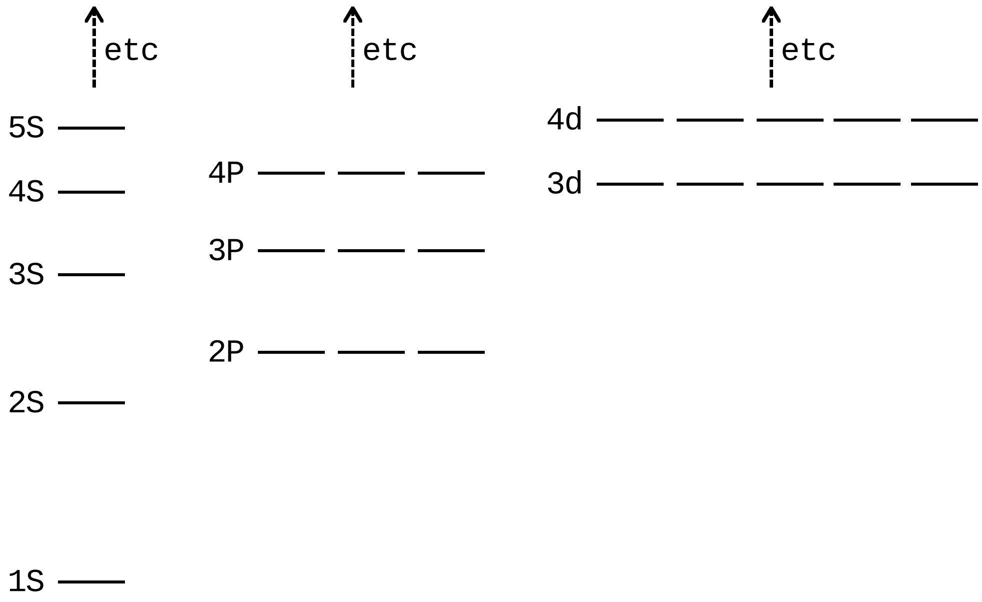
A spinning electron behaves like a small magnet whose polarity depends on the direction of spin : two opposed spins (+1/2 and -1/2) attract and two parallel spins (+1/2 and +1/2 OR -1/2 and -1/2) repel. In an atomic orbital the electrons are forced to occupy the same space. It is therefore essential that two electrons in the same orbital have opposed spins (**The Pauli Principle**) and that one orbital can only hold two electrons.

We can now draw up a diagram of the atom showing the energy levels and orbitals allocated to the electrons.

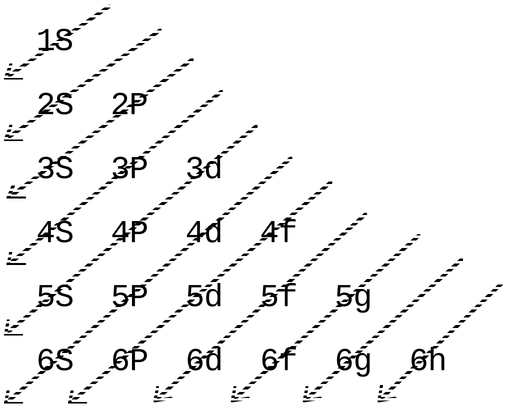
Since the number of electrons in each energy level is $2n^2$ and each orbital holds 2 electrons the number of orbitals in each energy level is n^2.

The orbitals have different energies : S < P < d < f etc

We will describe an orbital as $\mathbf{nO_D}$ meaning an orbital with orbital quantum number **O**, directional quantum number **D** in the **n** th energy level.

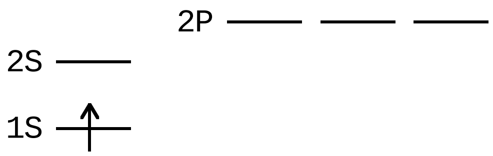


For values of n 3 the sub-levels from one energy level tend to overlap with those of other energy levels. The energy order can, however, be quickly found using the following memory aid :



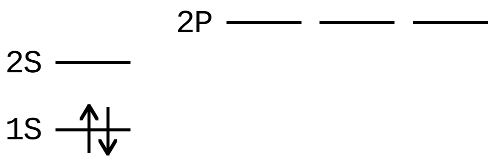
When filling these new energy levels we must keep the following rules in mind :

1. The electron goes into the first available orbital with the lowest energy (Aufbau principle) e.g. $_1H$



Denoted $1S^1$

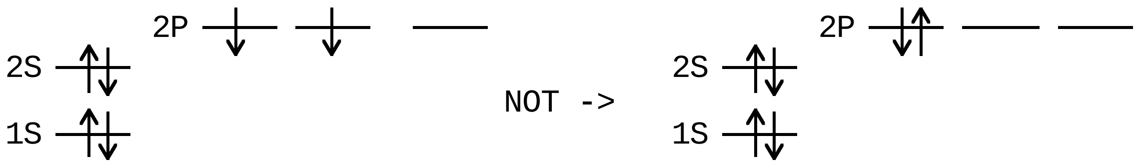
2. Two electrons in one orbital must have opposed spins (Pauli) e.g. $_2He$



Denoted $1S^2$

3. When a number of equal energy (degenerate) orbitals are available they will be occupied singly before any pairing results (Hund's Rule).

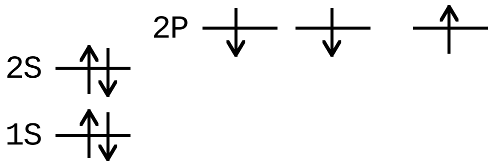
   This is a consequence of coulombic repulsion e.g. $_6C$



Denoted $1S^2$ $2S^2$ $2P^2$

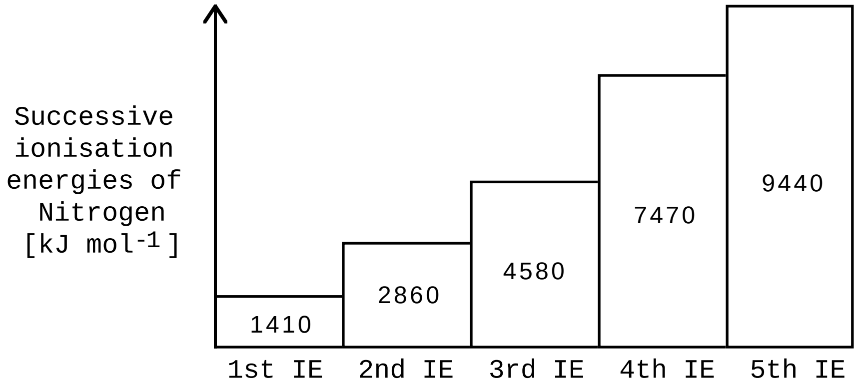
4. Half-filled and completely filled sub levels are particularly stable. The more degenerate electrons there are, the more chance they have of changing places with one another. This lowers the inter-electronic repulsions and stabilises the atom.

   Example 1 : $_7N$



Denoted $1S^2$ $2S^2$ $2P^3$

The first five ionisation energies of Nitrogen are shown below:



Once the first electron is removed there is a gradual increase in the energies required to remove subsequent electrons. This is due to the attraction afforded by the increasing positive charge on the ion.

Note also the larger increase between the 3rd and 4th IEs of Nitrogen. The fourth electron is taken from the 2S level, nearer the nucleus.

A consequence of the stability of the half filled 2P level is that the 1st ionisation energy is higher than normal.

Example 2 : $_{24}Cr$ $1S^2$ $2S^2$ $2P^6$ $3S^2$ $3P^6$ $4S^1$ $3d^5$

NOT -> $1S^2$ $2S^2$ $2P^6$ $3S^2$ $3P^6$ $4S^2$ $3d^4$

Example 3 : $_{29}Cu$ $1S^2$ $2S^2$ $2P^6$ $3S^2$ $3P^6$ $4S^1$ $3d^{10}$

NOT -> $1S^2$ $2S^2$ $2P^6$ $3S^2$ $3P^6$ $4S^2$ $3d^9$

Periodic Table

The periodic table can now be grouped into FOUR blocks of elements corresponding to the outer electron configurations of the elements within these blocks:

▨ S block

e.g. Sodium $1S^{2}\ 2S^{2}\ 2P^{6}\ 3S^{1}$

☐ P block

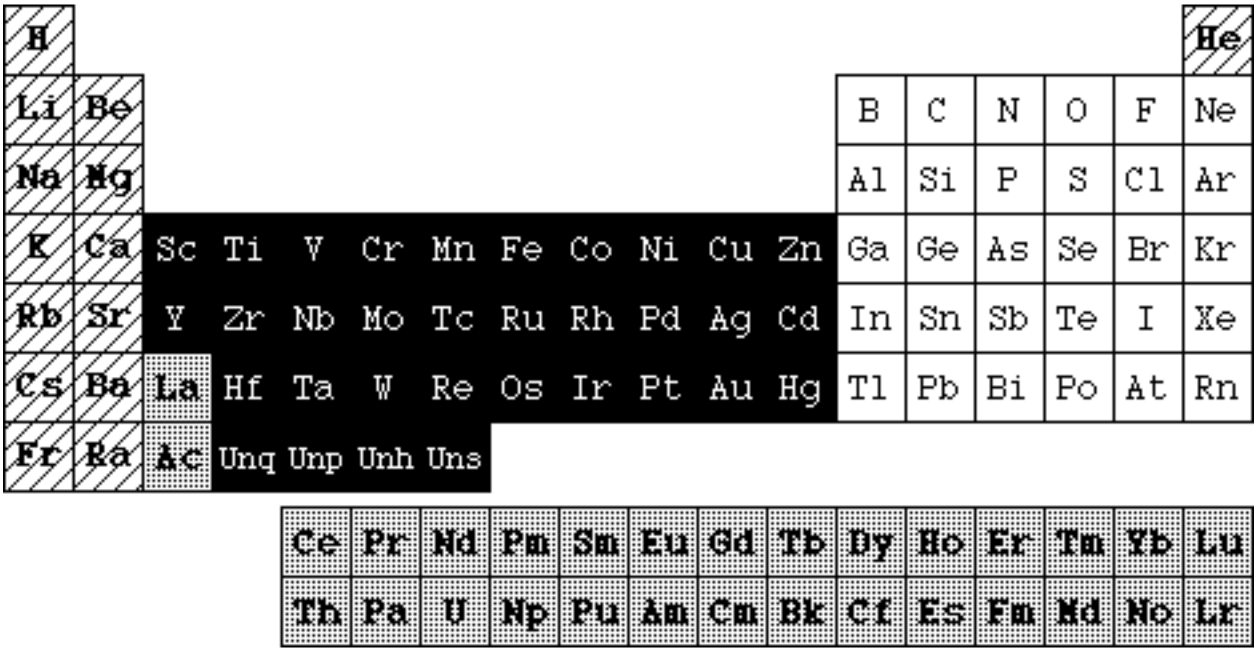
e.g. Phosphorus $1S^{2}\ 2S^{2}\ 2P^{6}\ 3S^{2}\ 3P^{3}$

■ d block

e.g. Iron $1S^{2}\ 2S^{2}\ 2P^{6}\ 3S^{2}\ 3P^{6}\ 4S^{2}\ 3d^{6}$

▒ f block

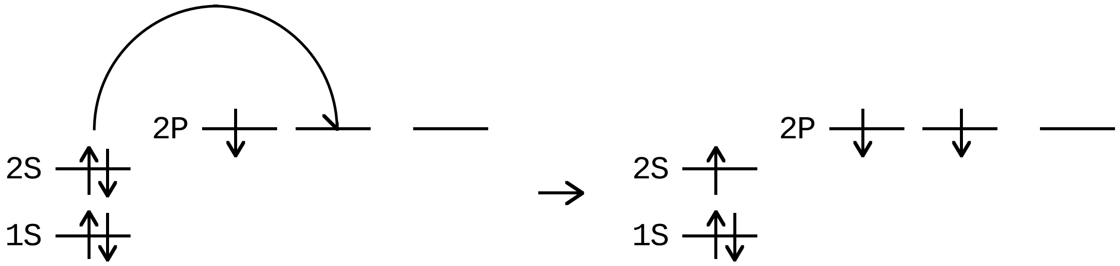
e.g. Europium $1S^{2}\ 2S^{2}\ 2P^{6}\ 3S^{2}\ 3P^{6}\ 4S^{2}\ 3d^{10}\ 4P^{6}\ 5S^{2}$
$4d^{10}\ 5P^{6}\ 6S^{2}\ 4f^{7}$



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Unq	Unp	Unh	Uns											
				Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
				Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Nd	No	Lr

We can see why the inert gases are unreactive : they have no unpaired electrons. Their valency is 0. We can see why group 1 metals are so reactive : only one electron from the S orbital needs to be lost.

The use of electronic structures for predicting valency (no. of unpaired electrons) must be treated with caution. The drive to form as many bonds as possible (so that as much energy is given out as possible) often causes unpairing of paired electrons to give more unpaired electrons than is suggested by the valency. This can only happen if extra orbitals are available within the same quantum level e.g. $_5B$ valency 3 (**not 1**)



i.e. all 3 valence electrons are used to form 3 bonds.

We must therefore never make the mistake of applying this theory to bonding electrons. The theory is only applicable to the isolated atom.

Its crowning achievement was in the explanation of atomic spectra. The multitude of lines in spectra of multi-electron atoms is due to transitions between sub levels

e.g. Sodium