

Electromagnetic spectrum and associated calculations

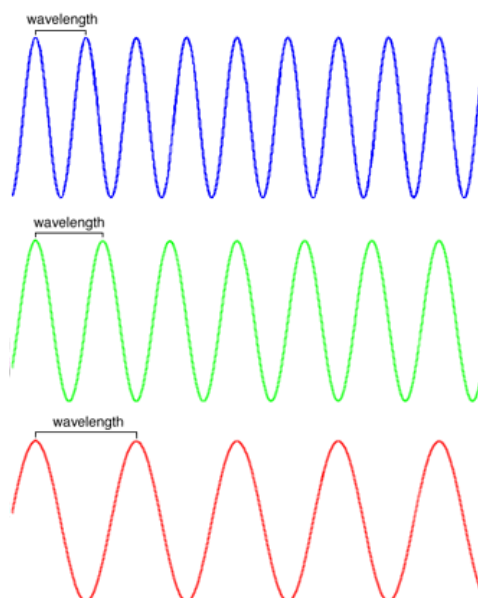
The work of Rutherford and others in the early part of the twentieth century resulted in the model of the atom in which negative electrons are arranged around a positive central nucleus.

It is the electrons, rather than the nucleus, which take part in chemical reactions and so it is necessary to understand the electronic structure of an atom to explain its chemical properties.

The key to understanding electronic structure and how electrons behave in an atom comes from the study of electromagnetic radiation.

In 1864 James Maxwell developed a theory describing all forms of radiation in terms of oscillating or wave-like electric and magnetic fields in space. Radiation such as light, microwaves, X-rays, television and radio signals is collectively called **electromagnetic radiation**.

Three simple waveforms are shown below:



Electromagnetic radiation can be described in terms of waves of varying length between 10^{-14} m and 10^4 m that travel in a vacuum at a constant velocity of approximately 3×10^8 m s⁻¹. This is one of the scientific constants – the speed of light and has the symbol c .

The **wavelength** of a wave is the distance between adjacent wavecrests or high points (or successive troughs or low points).

This distance is measured in metres (m) or an appropriate sub-multiple such as nanometres (nm). A nanometre is 10^{-9} metres. The symbol for wavelength is the Greek letter λ (lambda).

The top waveform has the most waves and the bottom one has the least. In moving from left to right, the top waveform has the greatest number of vertical “up and down” movements.

The number of these movements is called the **frequency** and is measured in **Hertz (Hz)**.

In chemistry, the symbol for frequency is the Greek letter ν (nu).

It can also be seen that the top waveform has the shortest wavelength.

The correct definition of frequency is *the number of waves passing a point in a given time*. The standard unit of time is the second and 1 Hertz is 1 wave passing a point each second.

There is a relationship between wavelength, frequency and velocity:

$$\text{Velocity (in ms}^{-1}\text{)} = \text{wavelength (in m)} \times \text{frequency (in Hz)}$$

since the velocity of all radiation is constant, the equation becomes

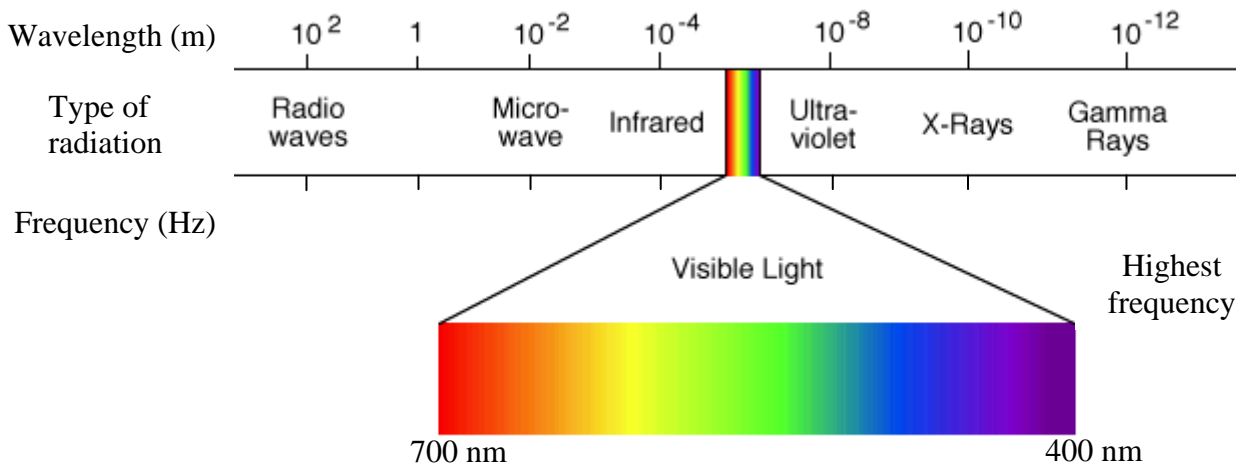
$$c = \lambda \nu$$

and can be rearranged to obtain λ or ν .

It also means that wavelength X frequency always equals 3×10^8 (the speed of light in a vacuum).

Chemists also use another number called the **wavenumber**. This is the number of waves in a given length (usually metre or centimetre) and is given the symbol $\bar{\nu}$ (nu bar). It is $1/\text{wavelength}$ with a unit of m^{-1} or cm^{-1} .

The complete range of em radiation is called the **electromagnetic spectrum** and can extend infinitely. We only need to concern ourselves with the frequencies (or wavelengths) shown in the diagram:



Human beings can only see a small portion of the spectrum. Our eyes can detect radiation with a wavelength between 400 nanometres (red) and 700 nanometres (violet). Commonly called the visible region of the spectrum.

Note the wavelength scale. It does *not* change in a linear way. On the scale above it changes by a factor of 100 each unit.

Such a scale is called a *logarithmic scale* and logarithmic scales have an important part to play in many areas of science.

Task: Work out the frequency of each wavelength shown and mark it on the diagram.

Energy associated with electromagnetic radiation

Energy can only be transferred in small bundles or packets, which are called **quanta**.

These quanta of energy are of a definite size and therefore the transfer of energy can only occur in definite amounts.

Each small bundle of energy is called a **photon**.

Studies of the energy associated with electromagnetic radiation has shown that the higher the frequency of radiation, the more energy each photon possesses.

This can be shown in a number of real-life cases:

- Photographers developing film will work in red light as the photons of red light do not possess enough energy to cause the light-sensitive chemicals on the film to change.
- House curtains will “fade in the sun” over time. This fading is caused by ultra-violet light which possesses enough energy to break the covalent bonds in the coloured dye molecules.

The energy of electromagnetic radiation can be calculated using the formula

Energy = a constant X the frequency of the radiation

The constant is **Planck’s constant**, symbol **h**

The formula becomes $E = hv$ h has the value of 6.67×10^{-34} Js

For visible light with a frequency of around 10^{14} Hz, the value of one photon comes out to around 10^{-20} joules. This is far too small to be meaningful, but if we have a *mole* of photons, it comes out to a meaningful number.

The formula now becomes $E = Lhv$ where L is 6.02×10^{23}

If radiation is expressed as a wavelength, the formula becomes

$$E = \frac{Lhc}{\lambda} \quad (\text{frequency} = c \div \text{wavelength})$$

The answer is in joules per mole and must be divided by 1000 to give the familiar kJ mol^{-1} .

If the radiation is expressed as a wavenumber, the wavenumber must first be converted to a wavelength and then this is used in the formula. (wavelength = $1 \div$ wavenumber)

If the wavenumber is given in cm^{-1} , it must be converted to m^{-1} by multiplying by 100.

Practice examples

Calculate the energy in kJ mol^{-1} corresponding to

- infra-red radiation with a wavenumber of 2000 cm^{-1} .
- visible light of wavelength 500 nm.

The energy of the Cl – Cl bond is 243 kJ mol^{-1} .

Prove by calculation that the wavelength of light required to break this bond falls within the visible region of the spectrum.

The evidence for electronic structure

In 1913, Danish physicist Neils Bohr predicted that electrons orbit atoms in fixed orbits, each of which possesses a certain amount of energy. These orbits are now known as energy levels. Electrons could move between energy levels if they acquired enough energy to do so but they could not move part of the way. They had to move the whole way or not at all.

How do we know this?

If white light from a tungsten filament bulb is passed through a prism, a continuous spectrum of colour is seen. Tungsten contains many electrons and when these move up and down within each atom, light of many different wavelengths is produced. Ordinary light bulbs also produce ultra-violet and infra-red light (a bulb gets very hot in use).

The spectrum of a tungsten filament bulb



If an electric current is passed through a gas such as neon at low pressure, an orange-red colour is seen. When this light is passed through a prism, the spectrum now seen is:



The spectrum contains a number of well-defined lines, mostly in the red, orange and yellow region of the visible spectrum.

This type of spectrum is called an **emission spectrum** as the light *emitted* from the sample under test is analysed.

An element commonly used in low-energy lighting is mercury.

The emission spectrum of mercury is:



perhaps explaining why low-energy and fluorescent lights have a slight bluish colour.

To understand the importance of a line spectrum and what it tells us about electronic structure, we have to examine the spectrum of the simplest element – hydrogen.



This is part of the hydrogen spectrum. There are precise lines at 656, 486, 434 and 409 nm.

These lines are produced when:

- Atoms absorb energy when excited by heat or electric discharge
- Electrons get promoted to higher energy levels
- They quickly fall back to lower energy levels, emitting precise quantities of energy
- This emitted energy is seen as a line in a spectrum.

This means that electrons are falling from one fixed energy level to another fixed one, so the energy levels themselves must be fixed.

Although a hydrogen atom has only one electron, the emission spectrum of hydrogen has different series of lines in different parts of the electromagnetic spectrum.

The differences in energy and hence the part of the electromagnetic spectrum in which the lines show up depend on the energy level to which the 'excited' electron falls back.

The full emission spectrum of hydrogen consists of one series of lines in the ultra-violet region, one series of lines in the visible region and several in the infra-red region.

These series of lines are named after the scientists who discovered them.

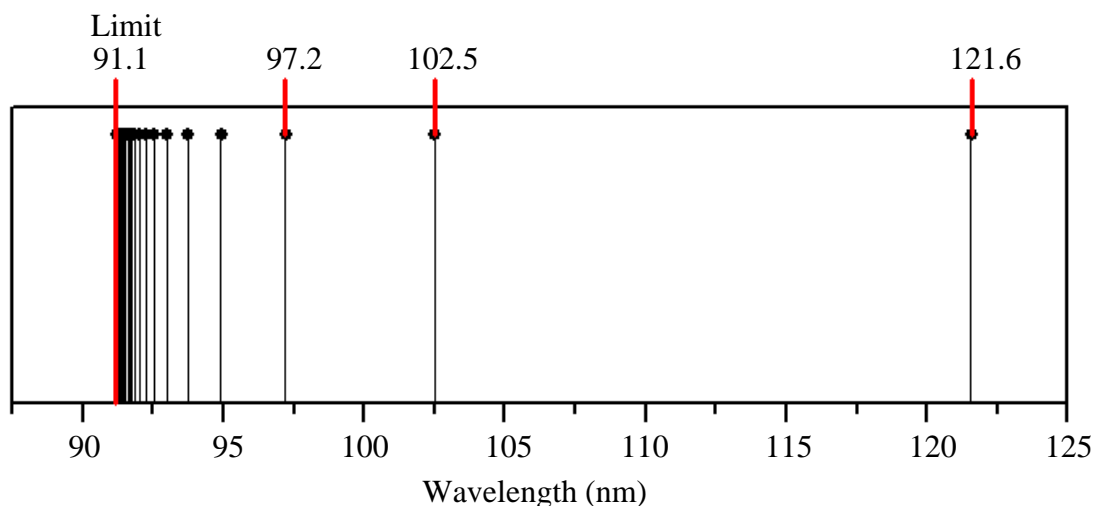
Name of series	Electron falling from a higher energy level to level	Region of the electromagnetic spectrum the series is in
Lyman	1	Ultra-violet
Balmer	2	Visible
Paschen	3	Infra-red
Brackett	4	Infra-red
Pfund	5	Infra-red

The Lyman series in the ultra-violet region is shown below.

The line with the longest wavelength is produced by electrons falling from energy level 2 to energy level 1.

The next line is produced by electrons falling from energy level 3 to energy level 1 and so on.

Notice that the lines are becoming closer together, which means that the energy levels are becoming closer together in energy terms. Eventually, the lines converge to a limit at 91.1 nm. This limit represents the energy associated with an electron falling from energy level infinity to energy level 1. If we reverse this process, it represents the energy required to move an electron from energy level 1 to energy level infinity. In other words, the ionisation energy.



The other series also converge to a limit.

Look at http://en.wikipedia.org/wiki/Hydrogen_spectrum for more information.

Task: Calculate the ionisation energy of hydrogen in kJ mol^{-1} if the lines converge at 91.1 nm.

Summary

Much of the work required to interpret and explain emission spectra was done by the Danish scientist Niels Bohr, who developed a model for the electronic structure of atoms. The equations derived from Bohr's model were used successfully to calculate values for the radius of the hydrogen atom and its energy levels, including its ionisation energy.

The main points of Bohr's theory can be summarised as follows;

- the electron in a hydrogen atom exists only in certain definite energy levels
- a photon of light is emitted or absorbed when the electron changes from one energy level to another
- the energy of the photon is equal to the difference between the two energy levels (ΔE), which is related to the frequency by the equation

$$\Delta E = h\nu$$

These definite quantities of energy possessed by electrons are known as **quanta**.

The limitation and next step

Bohr's theory could only be used for hydrogen atoms with one single electron.

To explain the behaviour of atoms with more than one electron a new science known as **quantum mechanics** was formulated. This treated electrons as waves as well as particles.

*The mathematics of waves is very complex. You do **not** require to know the mathematics, but you do require to know the results of the calculations.*

The results of the calculations are as follows:

- Electrons orbit an atom in a series of **shells**. (we already know these as energy levels)
- Each shell is described by a number called the **principal quantum number**, symbol n . n has the value 1, 2, 3 etc.
- The higher the value of n , the higher the potential energy associated with the shell and the further from the nucleus the electron is likely to be found.

The hydrogen atom has only one electron and its spectrum is fairly simple to interpret.

Other elements are more complex and close examination of their spectra under higher resolution shows that the lines are often not single lines but are actually two or three lines very close together. Lines like this are often described as doublets or triplets.

This suggests that the electron shells are further subdivided into **subshells**. These subshells are described by the letters **s, p, d and f**.

Calculations using quantum mechanics show that:

- the first shell has an s subshell.
- the second shell has an s and a p subshell.
- the third shell has s, p and d subshells.
- the fourth shell has s, p, d and f subshells.

Each type of subshell (s, p, d and f) contains one or more energy levels or **orbitals**.

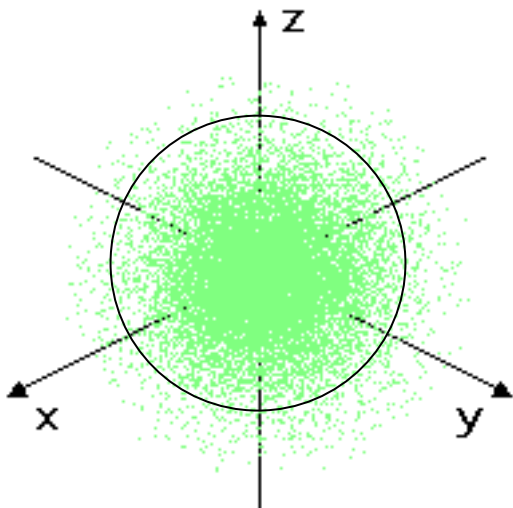
These are defined by another quantum number, the angular momentum quantum number ℓ .

This number is related to the **shape** of the orbital and has the values 0, 1, 2, ..., ($n - 1$).

The names and values of each shell and subshell is shown in the table

Value of n	Value of ℓ	Energy level
1	0	1s (holding 2 electrons)
2	0	2s (holding 2 electrons)
	1	2p (holding 6 electrons)
3	0	3s (holding 2 electrons)
	1	3p (holding 6 electrons)
	2	3d (holding 10 electrons)
4	0	4s (holding 2 electrons)
	1	4p (holding 6 electrons)
	2	4d (holding 10 electrons)
	3	4f (holding 14 electrons)

The calculations for an s orbital ($n = 1, 2, 3$ etc. and $\ell = 0$) produces a spherical shape.



The 1s orbital of a hydrogen atom.

This picture was produced by software which simulates the movement of an electron around the nucleus and takes a large number of “snapshots”.

The circle shows the volume of space in which the electron will spend 90% of its time in, and this is the accepted size a hydrogen atom.

This is the most accurate representation of an electron orbiting an atom – as a “cloud”.

Many representations of atoms and molecules make reference to **electron density**, and the diagram shows this.

The 2s and other s orbitals are also spherical, but larger.

When $\ell = 1$, we get the result for p orbitals.

At this point, another number enters the mathematics – the magnetic quantum number m .

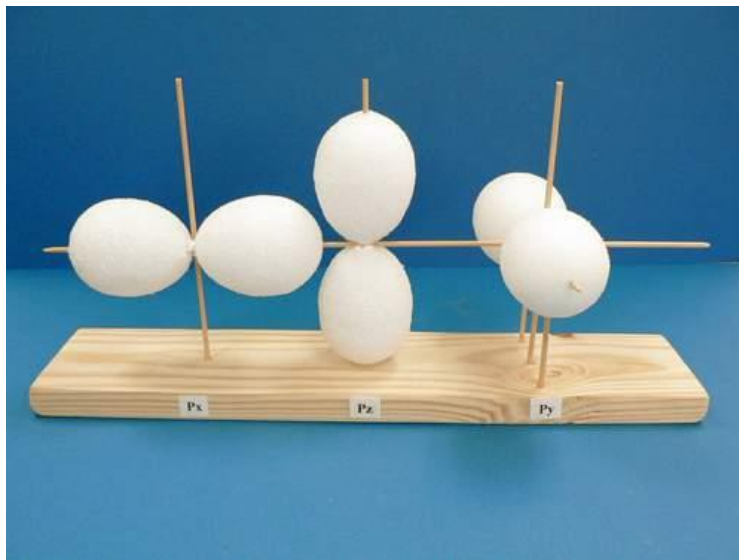
In the wave equation, m can have the value $-\ell$ to $+\ell$ (for the 1s orbital, $\ell = 0$, so $m = 0$)

Therefore there are three p orbitals, p_x , p_y and p_z .

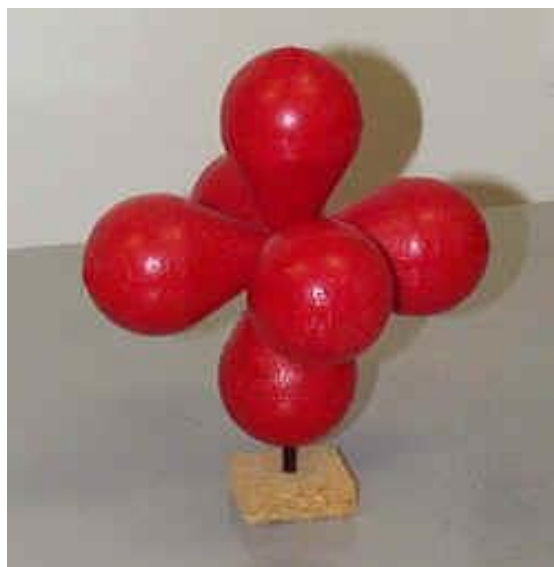
Results of the wave equation produces a “dumbbell” shape. i.e. each orbital has two lobes.

Each orbital points along an axis.

A model of the three 2p orbitals made from polystyrene is shown.



If all three orbitals are put together, the result is:



One question which you may be ask is – how do the electrons in an orbital move from one lobe to the other without colliding with the nucleus?

The answer is – you do not need to know this for Advanced Higher!!

Remember – these orbitals are volumes of space where there is a 95% probability of finding an electron, and their size and shape is the result of a mathematical wave equation.

The model shown above is what an atom of neon or argon may look like.

In the third energy level, l can have the value 0, giving 3s.
 It can have the value 1, so m can have the values -1, 0 or +1, giving 3p.
 And it can have the value 2, so m can have values of -2, -1, 0, +1 or +2.
 This produces five 3d orbitals, and their shapes and orientations are more complex.

The 3d orbitals are called d_{xy} , d_{xz} , d_{yz} , $d_{x^2-y^2}$, and d_{z^2} .
 They are given these names because of their orientation in space or because of the application of the wave equation to calculate them.

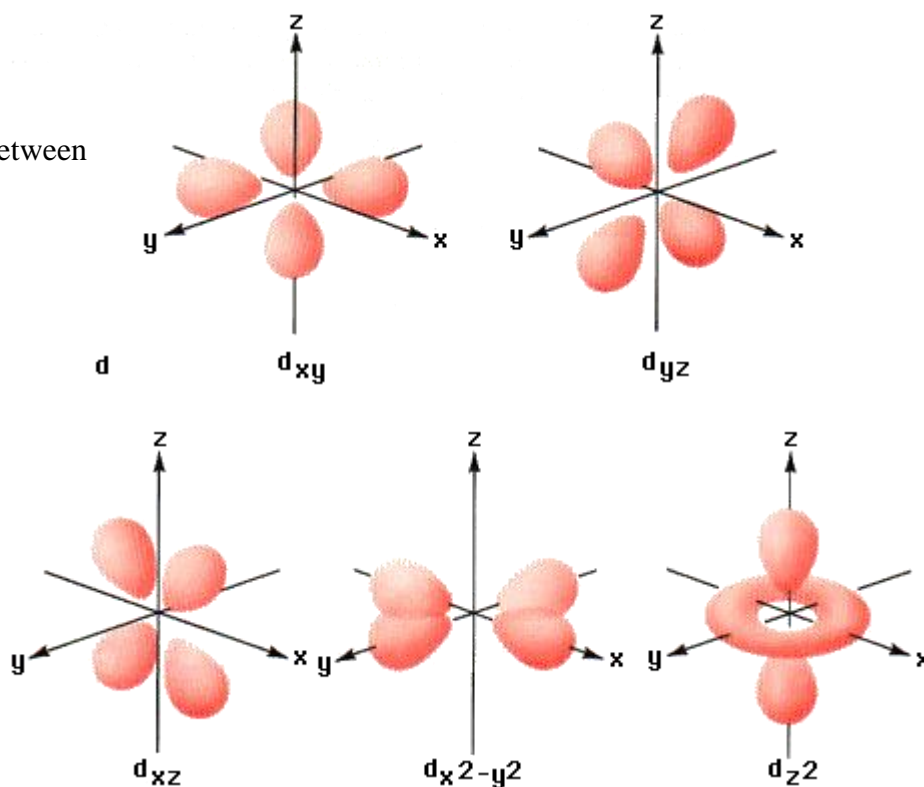
Their shapes and orientations

Important points to note

Three of the orbitals lie between the x, y and z axes.

Four of the orbitals have four distinct lobes.

The fifth has two lobes and a “doughnut” shape.



For advanced Higher, you are expected to be able to draw the shape of an s or a p orbital and you are expected to recognise a d orbital from a drawing.

As n increases, the number and shape of p, d and f orbitals becomes more complex.
 You are not expected to know any extended details about these.

If interested, download and run an application called orbital viewer. It can be programmed to show any orbital, even of atoms which do not exist.

Also of interest, in 2p orbitals, one lobe is where the result of the wave function has a positive value and the other is where it has a negative value. This has no bearing on the ability of the electron to occupy it. It can be likened in this respect to a sine wave, where from 0 to 180 degrees it has a positive value and from 180 to 360 it has a negative value.

Four of the 3d orbitals have four lobes, in two of the lobes, the wave function has a positive value and a negative value in the other two. In the fifth orbital, the lobes have a positive value and the doughnut has a negative value. You do not need to know this, but if you look up any information on them, particularly diagrams, you may well see lobes of different colours. This is the reason why.

The fourth quantum number

Around 1920, researchers into the behaviour of electrons realised that they had a spin. When quantum theory was being completed, electrons were allocated a spin quantum number. In the wave equation, the spin quantum number has the value $+\frac{1}{2}$ or $-\frac{1}{2}$.

It is now possible to define *any* electron in an atom by quantum numbers. In 1925, Wolfgang Pauli proposed that


in an atom, no two electrons can have exactly the same quantum numbers. This is known as the Pauli exclusion principle.


If two electrons occupy the same orbital, they will have different spins.

In an isolated atom, all orbitals of the same type have exactly the same energy. The word to describe this is **degenerate**. All 2p orbitals are degenerate for example.

Electrons in boxes

It is sometimes convenient to show electrons occupying orbitals by representing each orbital as a box. The electrons are shown as arrows, one pointing upwards and the other pointing downwards. This method of representing electrons is known as **orbital box notation**.

A hydrogen atom is represented as 

And a helium atom as  The arrows point in opposite directions to show opposing spins

There is another way of representing electrons called **spectroscopic notation**. Each orbital is written followed by a superscript number.

Hydrogen's electron arrangement is written as $1s^1$, and helium's is $1s^2$.

Before we can write the electronic configuration for multi-electron atoms, it is necessary to know the order in which the various orbitals are filled.

The aufbau principle states that the orbitals of the lowest energy levels are always filled first.

The word aufbau means "building up".

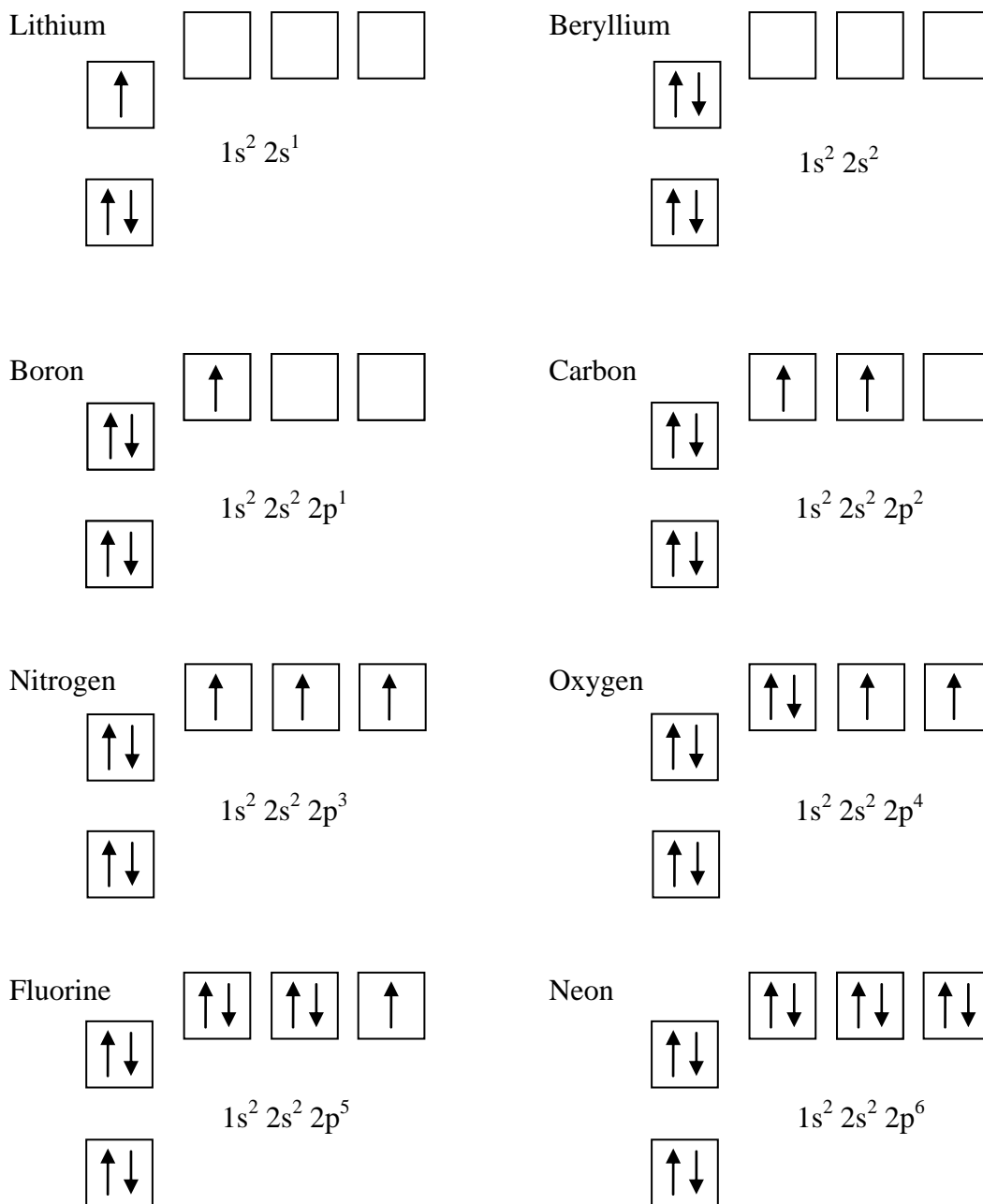
Thus, provided the relative energies of the orbitals are known, the electronic configuration can be deduced.

The order of **energy** of each orbital set is:

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

This is obviously very complicated, but for Advanced Higher we only require to know up as far as 4p but you *do* require to know that although the 4s orbital is further from the nucleus, it is actually lower in energy than 3d, and fills up before 3d. Look at the arrangements of calcium and scandium.

Orbital box notation of second period elements:



Looking at the arrangements of boron, carbon and nitrogen, you can see that electrons will occupy empty orbitals first, and their spins are all parallel.

This gives another rule about electronic structure:

Hund's rule of maximum multiplicity, which states that "electrons will occupy orbitals in order to maximise their parallel spins"

This is the last of four rules that you require to know about electronic structure.

It is acceptable to write a shortened form of spectroscopic notation where inner electrons can be represented as a noble gas in square brackets. Potassium would be represented as $[\text{Ar}] 4s^1$ using this method. Titanium would be $[\text{Ar}] 3d^2 4s^2$. Note that 3d is written before 4s.

The Periodic Table can be subdivided into four blocks (s, p, d and f) corresponding to the outer electronic configurations of the elements within these blocks.

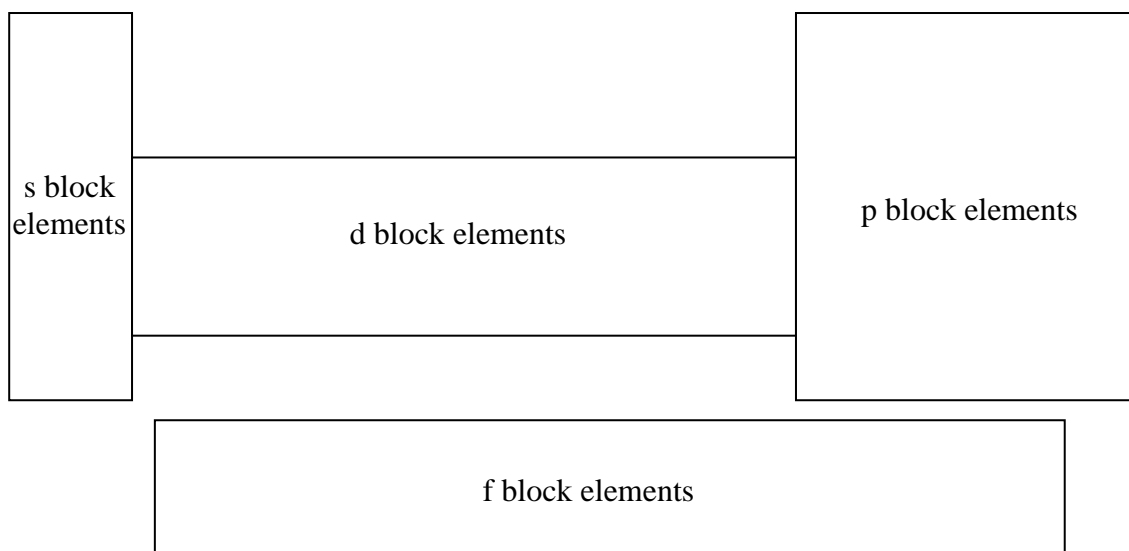
All the Group 1 and Group 2 elements have electronic configurations that end in s and are known as s-block elements.

The elements in Groups 3, 4, 5, 6, 7 and 0 are known as the p-block elements as their outermost electrons are in p subshells.

The elements where d orbitals are being filled (transition metals) are known as the d-block elements and those in which f orbitals are being filled are the f-block elements.

The f-block elements are known as the inner transition metals or the rare earth metals.

This is shown in the diagram



First ionisation enthalpy anomalies

Trends in ionisation enthalpy (knowledge from Higher Grade) are that in general, ionisation enthalpies increase going across a period (greater nuclear charge holds electrons tighter) and decrease going down a group (greater distance from nucleus and screening effect of inner electrons). Going across the second and third periods there are two anomalies in each: between beryllium and boron, between nitrogen and oxygen, between magnesium and aluminium and between phosphorus and sulphur.

Looking at the electron arrangements of these atoms, it can be seen why.

Beryllium's arrangement is $1s^2 2s^2$. Boron's is $1s^2 2s^2 2p^1$.

Removal of the 2p electron from boron requires less energy than one of the 2s electrons of beryllium.

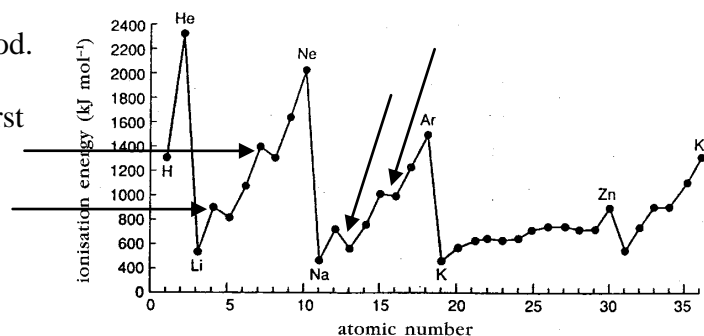
Nitrogen's arrangement is $1s^2 2s^2 2p^3$. Oxygen's is $1s^2 2s^2 2p^4$.

Nitrogen has 3 unpaired p electrons. Oxygen has 2 unpaired and 2 paired p electrons.

The repulsion effect of two electrons in one p orbital means that it is easier to remove one of them than it is to remove an unpaired p electron from a nitrogen atom.

The same principle applies in the third period.

The anomalies are shown in the graph of first ionisation enthalpy against atomic number.



Analysis for elements using spectroscopy

Just as specific lines in the emission spectra of elements give information about the electronic structure of these elements, the technique of **atomic emission spectroscopy** (AES) can be used to detect the presence of these elements.

Each individual element provides a characteristic spectrum that can be used to identify that particular element.

Both AES and atomic absorption spectroscopy (AAS) involve transitions between electronic energy levels in atoms.

Individual spectral lines correspond to definite electronic transitions.

In general the energy difference corresponds to the visible region of the electromagnetic spectrum (approximate wavelength 400-700 nm) but in some applications the ultra-violet region (approximate wavelength 200-400 nm) is used.

In AES a gaseous sample is excited with thermal or electrical energy, causing electrons to be promoted to higher energy levels. The wavelength of the radiation emitted as the electrons fall back to lower energy levels is recorded.

This technique can be used to detect metal elements in, for example, foodstuffs or effluent water since each element has a known characteristic spectrum. The element present can also be determined quantitatively by measuring the intensity of the emitted radiation. The greater the amount of that element present in the sample, the greater will be the intensity of its characteristic radiation.

AES detects both metallic and non-metallic elements. In fact, the element helium was discovered by the English scientist Sir Norman Lockyer, who pointed his telescope at the sun during the eclipse of 1868 and examined the light using a spectroscope. He observed bright emission lines but found it impossible to identify the source of the strong yellow light on earth. In 1870 Lockyer suggested that the spectrum was due to an unknown element which he thought was a metal and named helium after the Greek sun god, Helios. Lockyer was eventually knighted for his discovery but initially he was ridiculed. His critics were silenced when the Scottish chemist Sir William Ramsay managed to isolate helium from the uranium-containing mineral cleveite. Ramsay went on to discover the entire group of noble gases and was awarded the Nobel Prize for chemistry in 1904.

In AAS electromagnetic radiation is directed through a gaseous sample of the substance. Radiation corresponding to certain wavelengths is absorbed as electrons are promoted to higher energy levels. The wavelength of the absorbed radiation is measured and used to identify each element, as each element has a characteristic absorption spectrum.

The amount of the species present in the sample can also be determined by quantitative measurement of the amount of light absorbed by the atomised element. The measured absorbance is proportional to the concentration of the element in the sample.

An absorption spectrum is an emission spectrum in reverse. It has a coloured background with dark lines.



What an absorption spectrum might look like.

Both emission and absorption spectroscopy can detect elements in concentrations as low as a few parts per million (milligrams per litre) and is used extensively for this.

Many elements produce a very complex spectrum but will produce at least one line of high intensity. A spectrometer, if set to analyse for one particular element, will look for only one or two specific lines known to be produced by, and only by, the element being looked for.

A spectrometer has to be calibrated by analysing a sample of the element of known concentration, and then comparing the intensity of the line produced by the known sample to the intensity of the line produced by the unknown sample.

Shapes of molecules and polyatomic ions

[http://en.wikibooks.org/wiki/A-level_Chemistry/OCR_\(Salters\)/Molecular_geometry](http://en.wikibooks.org/wiki/A-level_Chemistry/OCR_(Salters)/Molecular_geometry) is a good site to show all molecular shapes you need to know.

The shapes of molecules or polyatomic ions (e.g. NH_4^+) can be predicted from the number of bonding electron pairs and the number of non-bonding electron pairs (lone pairs).

This is because the direction which covalent bonds take up in space is determined by the number of orbitals occupied by electron pairs and the repulsion between these orbitals.

The repulsive effect of a non-bonded pair or lone pair of electrons is greater than that of a bonded pair and so the trend in repulsive effect is:

bonded pair:bonded pair < bonded pair:lone pair < lone pair:lone pair

The shape adopted by the molecule or polyatomic ion is the one in which the electron pairs in the outer shell get as far apart as possible. In other words, the shape in which there is the minimum repulsion between the electron pairs.

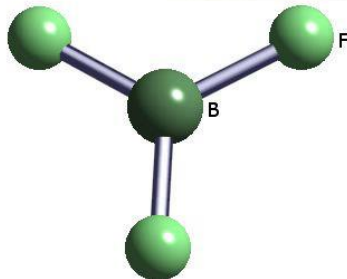
Consider some examples:

- (a) Two filled orbitals, both bonding pairs, e.g. beryllium chloride, $\text{BeCl}_2(\text{g})$

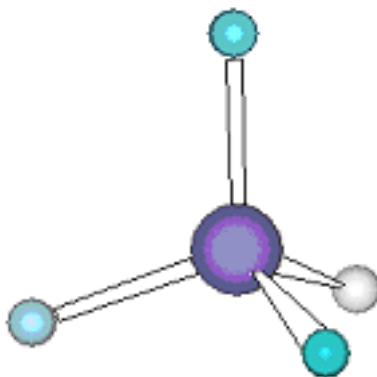
In the beryllium chloride molecule beryllium has two outer electrons and each chlorine atom contributes one electron and so there is a total of four electrons, i.e. two electron pairs, involved in bonding. These two bonding pairs will be as far apart as possible at 180° and so the beryllium chloride molecule is **linear**:



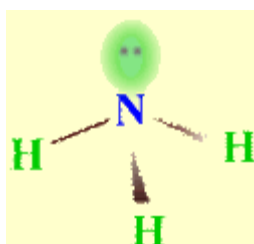
- (b) Three filled orbitals, all bonding pairs, e.g. boron trifluoride, BF_3 In the boron trifluoride molecule boron has three outer electrons and each fluorine atom contributes one electron to the structure. In total there are six electrons involved in bonding, resulting in three bonding pairs. Repulsions are minimised between these three bonding pairs when the molecule is flat and the bond angles are 120° . The name given to this shape of molecule is **trigonal planar** (or simply trigonal).



- (c) Four filled orbitals, all bonding pairs, e.g. methane, CH_4 In methane, the central carbon atom has four outer electrons and each hydrogen atom contributes one electron to the structure and so there is a total of eight electrons involved in bonding, resulting in four electron pairs. The methane molecule is tetrahedral because this is the shape in which there is minimum repulsion between these electron pairs. The exact bond angles in methane are found using X-ray diffraction to be 109.5° , which is the true tetrahedral value:

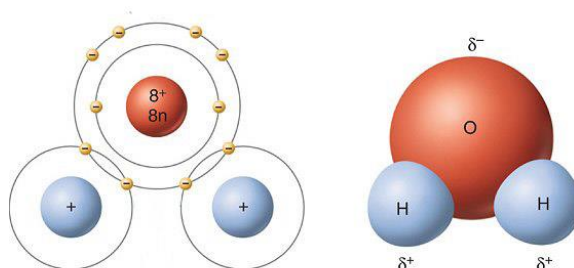


- (d) Four filled orbitals, three bonding pairs and one lone pair, e.g. ammonia, NH_3 In ammonia, the central nitrogen atom has five outer electrons and each hydrogen atom contributes one electron. There is a total of four electron pairs, but only three are bonding pairs, i.e. there are three N-H bonds while one pair of electrons is a non-bonding or lone pair. The arrangement of the electron pairs is tetrahedral but since there are only three bonds the shape is said to be **pyramidal**. There is greater repulsion between the lone pair and the three bonding pairs than there is between the three different bonding pairs with the result that the bonds are pushed closer together by the lone pair. Instead of a bond angle of 109.5° , the three bonds are angled at 107° to each other:

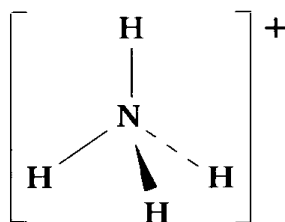


- (e) Four **filled orbitals, two bonding pairs and two lone pairs, e.g. water, H₂O**

In water, the central oxygen atom has six outer electrons and each hydrogen atom contributes one electron. There is a total of four electron pairs, but only two are bonding pairs. There are two O-H bonds and two non-bonding or lone pairs. The arrangement of the electron pairs is tetrahedral but since there is greater repulsion between the two lone pairs than between the lone pairs and the two bonding pairs the outcome is that the bonds are pushed even closer together in water than in ammonia. In water the bond angle is approximately 105° and the shape of the water molecule is **bent linear**:

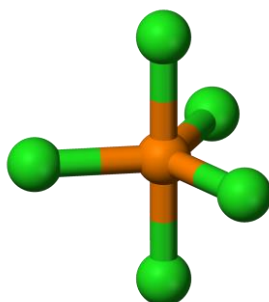


It is worth noting that if the lone pair on the nitrogen in ammonia were to form a dative covalent bond with a hydrogen ion to form the ammonium ion, there would be four equivalent bonding pairs and no non-bonding pairs. The shape of the ammonium ion would therefore be tetrahedral and all the bond angles would be 109.5°, as in methane:



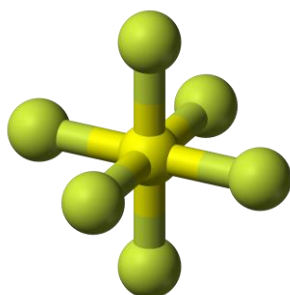
- (d) Five **filled orbitals, all bonding pairs, e.g. gaseous phosphorus(V) chloride, PCl₅(g)**

In gaseous phosphorus(V) chloride the central phosphorus atom has five outer electrons and each chlorine atom contributes one electron to make five electron pairs. There will be no lone pairs as there will be five P-Cl bonds. The shape of the molecule is **trigonal bipyramidal**:

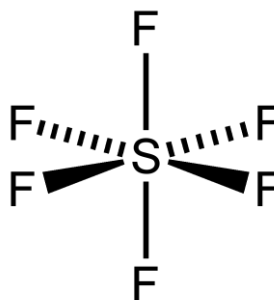


With no lone pairs on the central phosphorus atom, the bond angles between the three central chlorine atoms are 120°. The upper chlorine atom has bond angles of 90° to the three central chlorine atoms as does the lower chlorine atom. The bond angle between the upper and lower chlorine atom is 180°.

- (e) Six filled orbitals, all bonding pairs, e.g. sulphur hexafluoride, SF₆
 In sulphur hexafluoride, the central sulphur atom has six outer electrons and each fluorine atom contributes one electron, resulting in six electron pairs, all of which are bonding pairs.
 The shape of the molecule is octahedral, and all bond angles are 90°



or



Bearing in mind that the number of electron pairs decides the shape of molecules, the table below provides a useful summary of molecular shapes.

Number of bonded electron pairs	Number of Lone electron pairs	Molecular shape
2	0	Linear
3	0	Trigonal planar
4	0	Tetrahedral
5	0	Trigonal bipyramid
6	0	Octahedral
3	1	Pyramidal
2	2	Bent linear

Question

Draw molecules of the following species showing their shapes:

- | | | |
|-----------------------|----------------------------------|----------------------------------|
| (a) PCl ₃ | (b) BH ₄ ⁻ | (c) PF ₅ |
| (d) SnCl ₄ | (e) H ₂ S | (f) CH ₃ ⁺ |

