

## Diffraction

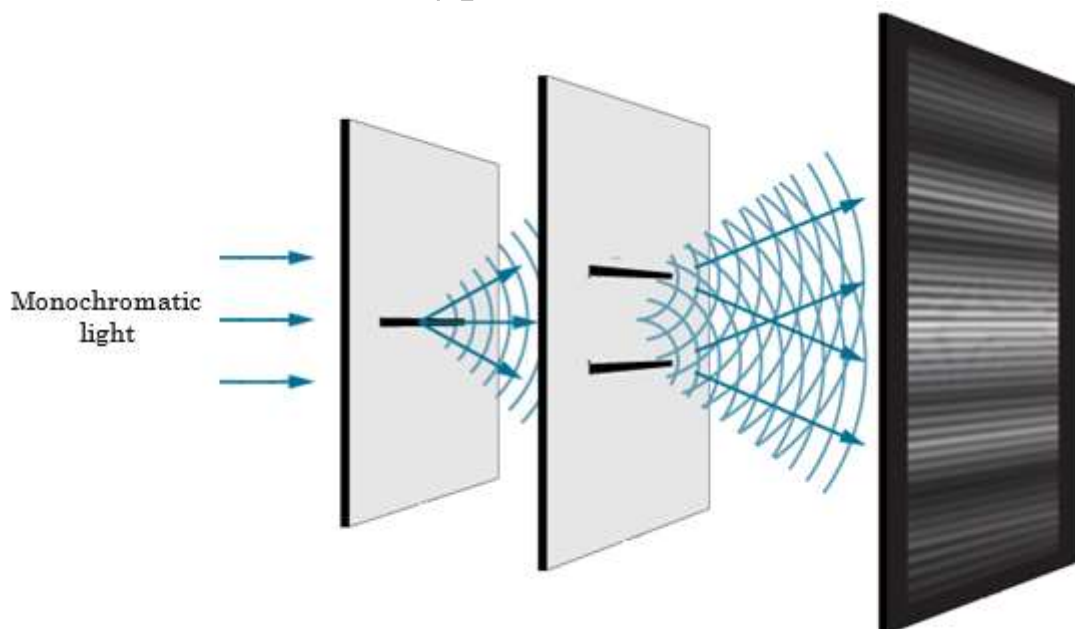
Until the very beginning of the 20<sup>th</sup> century, physicists considered their discipline to comprise the study of physical objects and of fields.

Essentially all physics can be described as the study of pushes or pulls i.e. *forces* effective physically, by contact, or at a distance, through *fields*. Isaac Newton originally believed that light consisted of particles which he termed '*corpuscles*'. From his own, Newtonian, mechanistic approach that could not be proven and the theory was discarded for a simple reason. If one constructs a barrier with two slits and throws balls at the barrier then the number of balls getting through the barrier and those bouncing off remain the same as the number of balls originally thrown.

In contrast, if a beam of light is shown at the barrier and passes through both slits, two bright spots of light appear on the other side of the barrier but, in addition, the light rays interfere with each other and produce an image of lighter spots and completely dark regions. Thomas Young (pictured right) performed this experiment in 1800 and demonstrated that the light rays must interfere.



If they *interfere constructively*, then they combine, reinforce each other and produce the bright lines (brighter than the impinging light) whilst with *destructive interference* they combine and cancel each other out creating the dark lines. This could not occur if the irradiating light was completely comprised of particles, however small.



There is no way to explain this if light is comprised of particles and the observation was analogous to the effect of two ripples in water which reinforce in places, creating higher waves, and, in other places, cancel each other out creating regions of completely still and flat water.



Huge advances were made over the next two centuries in the theory of waves, leading eventually to the explanation by James Clerk Maxwell (pictured left) that light is formed by the propagation of orthogonal electric and magnetic fields, that is fields at right angles,  $90^\circ$ , to each other. Numerous experiments confirmed this theory and led to, perhaps, the most dramatic demonstration of the transmission of energy by waves: radio.

This all appeared to demonstrate conclusively that light has the properties of waves and not particles.

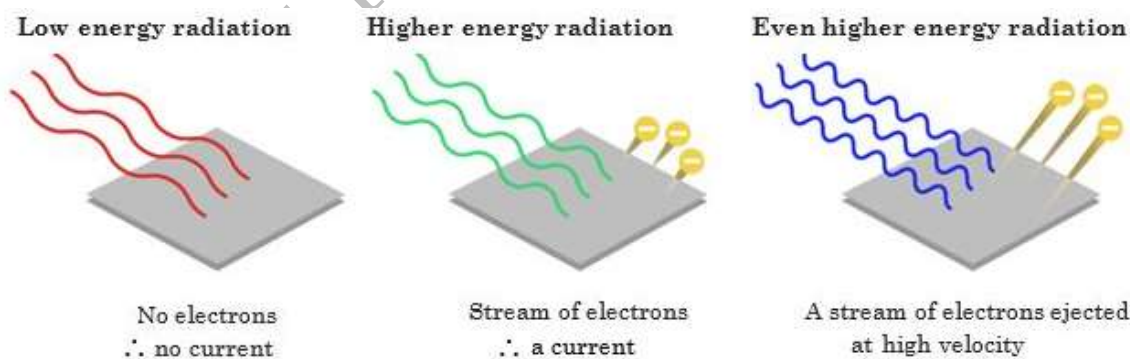
Perhaps not.

In 1900, Max Planck proposed the quantisation of energy, using the idea simply as a mathematical trick to explain atomic emission spectra. In essence, he concluded that if the spectra were not continuous i.e. comprised of every single possible wavelength then energy must exist as packets, discrete quantities.

### The Photoelectric Effect

In 1905, Albert Einstein used the theory of the quantisation of energy and the concept of light as particles to explain the *photoelectric effect*. It was for this work, and not for his special or general theories of relativity, that Einstein was awarded the Nobel Prize for Physics in 1921.

The photoelectric effect had mystified physicists for years. Essentially, if a beam of visible light irradiates a metal target then very little happens. If, however, the frequency (energy) of the light is increased then there comes a point at which an electric current is generated as illustrated below. If the energy (frequency) of light increases further then the electrons are ejected with greater velocity.



The photoelectric effect was discovered in 1887 by Heinrich Hertz (pictured right) during his research on radio waves. Hertz established that when uv light irradiates a pair of metal plates, the voltage at which a spark occurs varies with the frequency of light. In 1902, Philipp Lenard (left), demonstrated that electrons, then still known as cathode rays, were liberated from the surface of



a metal when irradiated with ultraviolet light.

Visible light had no effect on the metal and the frequency at which a current was detected varied with the metal targeted. This could not be explained but further complications arose when the kinetic energy of the ejected electrons was measured. Once liberated, the velocity i.e. the kinetic energy of the ejected electrons varied with the *frequency* of the light and not with its *intensity* (brightness). Increasing the intensity increased the current generated meaning that an increase in intensity resulted in more electrons being ejected.

Electromagnetic radiation can be best described as the means of transferring energy from one location to another without any physical contact between the two locations. This is in contrast to the means by which one particle can transfer energy to another and that can only be through physical contact e.g. collisions. If light was a wave then increasing the intensity (brightness) of even low frequency radiation should allow sufficient energy to be built up by the electron so that, eventually, it could escape from the surface of the metal whatever the frequency. The lower the frequency of light the greater the time that this would take to achieve and even at low frequencies electrons should be ejected, just with a greater time lag but this does **not** occur.

To summarise,

- Once the minimum frequency necessary had been achieved there was no time lag between irradiation and ejection;
- Increasing the frequency did not increase the current i.e. the number of electrons which escaped but did increase their kinetic energy;
- Increasing the intensity whilst maintaining the frequency increased the number of electrons which escaped but only once a minimum frequency of light was employed.



Albert Einstein (pictured right) reasoned that since a certain quantity of energy was required to release the electron this was possible if the irradiating radiation consisted of *particles* not waves. And continued:-

- The kinetic energy of the light particles could be transferred to the electrons. If the energy of the light particles was low then the metal would absorb the radiation as heat. However, once a particular energy was reached this energy would be sufficient to eject the electron from the metal and the electron would be ejected and travel at a low velocity.

**This explained the minimum frequency required.**

- Increasing the energy of the radiation above this minimum required to allow the electron to escape meant that there was surplus energy. This surplus energy of the light particles could be transferred to the electrons and so the electrons would leave at greater velocity i.e. with greater kinetic energy.

**This explained why the velocity of the ejected electrons was proportional to the frequency of the irradiating light, beyond the minimum required.**

- Increasing the frequency did *not* increase the current (the number of ejected electrons) but increasing the intensity did achieve precisely that. If the radiation was particulate in nature then the intensity was a measure of the number of particles. Increasing the intensity increases the number of light particles impinging on the metal and increases the number of electrons ejected.

**This explained why, at any particular frequency above the minimum required for ejection, increasing the intensity increased the number of ejected electrons i.e. the measured current.**

Einstein's theory also explained:-

- **The absence of a time lag:** Provided the impinging radiation had sufficient energy then the electrons would be ejected almost immediately as there would be no need to build up the quantity of energy necessary to eject the electron.
- **The energy needed to eject the electron varies with the nature of the metal:** Different metals held electrons within the structure to varying degrees and so required different energies (frequencies) of electromagnetic radiation. Einstein termed the energy required to eject the electron the metal's *work function* ( $\Phi$ ) and quantified his theory with the deceptively simple formula:

**Energy of light = Energy required to eject the electron + kinetic energy of the electron**

and, mathematically:

$$hf = \Phi + \frac{1}{2} mv^2$$

where: **h** is Planck's constant, **f** is the frequency of the light sufficient to ionise the atom,  **$\Phi$**  is the work function of the metal, **m** is the mass of the electron and **v** is the velocity of the ejected electrons.

In contrast to the wave nature of electromagnetic radiation which explained none of the observations of the photoelectric effect, Einstein's theory explained everything and it was for this that he was awarded the 1905 Nobel Prize in Physics.

Einstein's work was entirely theoretical as he was not an experimental physicist. It remained for others to determine the validity of his theory notably Robert Millikan. Millikan, famous for his elegant, experimental determination of the charge of an electron in 1909, verified the, deceptively simple, equation and demonstrated that Einstein's constant, **h**, was exactly the same as the constant that Planck had produced when he equated energy of light with frequency e.g.  $E = hf = c/\lambda$

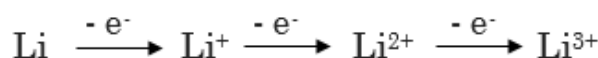
where **E** is the energy of the light, **c** is the velocity of light in a vacuum and  **$\lambda$**  is the wavelength of the radiation.

Einstein's theoretical explanation of the photoelectric effect became of even more profound significance when it was discovered that as the frequency of the light was increased but not much happened after the first current was detected until, suddenly, a second electric current was detected and then a third and then a fourth etc; These equated to successive ionisations of the original atom and equalled the atomic number, and hence the number of electrons of the target atom.

For example, hydrogen only showed one ionisation (only one electron to be removed) but helium exhibited two ionisations relating to:



whilst lithium displayed three currents:



and so on. No atom demonstrated more sudden peaks in the electric current than there were protons in the nucleus and hence the number of peaks also equated to the number of electrons in the original, target, neutral atom.

## The Wave - Particle Duality of Matter

The word *profound* has been used a number of times in this volume but the verification of Einstein's explanation of the photoelectric effect was even more than that.

Einstein had explained many matters by suggesting that light was not just a wave but could also be construed as a stream of particles.

This led Louis de Broglie (pictured right) and others to question if the opposite was true:

***If a wave can behave like a particle then can a particle behave like a wave?***

de Broglie won the Nobel Prize for Physics in 1929 for his answer to this question.

He is probably the only Nobel Laureate to win the accolade based on a doctoral thesis which was also extraordinarily for its brevity, amounting a mere handful of pages.

de Broglie proposed that the momentum of an electron (**p**) was related to its energy by the following relationship:

$$\lambda = \frac{h}{p}$$

where  $\lambda$  is the wavelength and **h** is Planck's constant.

Subsequently he wrote that *'The fundamental idea of the thesis was the following:*

*The fact that, following Einstein's introduction of photons in light waves, one knew that light contains particles which are concentrations of energy incorporated into the wave, suggests that all particles, like the electron, must be transported by a wave into which it is incorporated.*

*My essential idea was to extend to all particles the coexistence of waves and particles discovered by Einstein in 1905 in the case of light and photons.*

*With every particle of matter with mass  $m$  and velocity  $v$  a real wave must be 'associated', related to the momentum by the equation:*

$$\lambda = \frac{h}{p} = \frac{h}{mv} \sqrt{1 - \frac{v^2}{c^2}}$$

where  $\lambda$  is the wavelength, **p** is the momentum, **m** and **v** are, respectively, the mass and velocity of the particle whilst **c** is the velocity of light in a vacuum. The equation de Broglie quoted is the so called relativistic version which took account of Einstein's discoveries.

The next problem was to determine whether or not de Broglie's proposal had any validity.

It did.

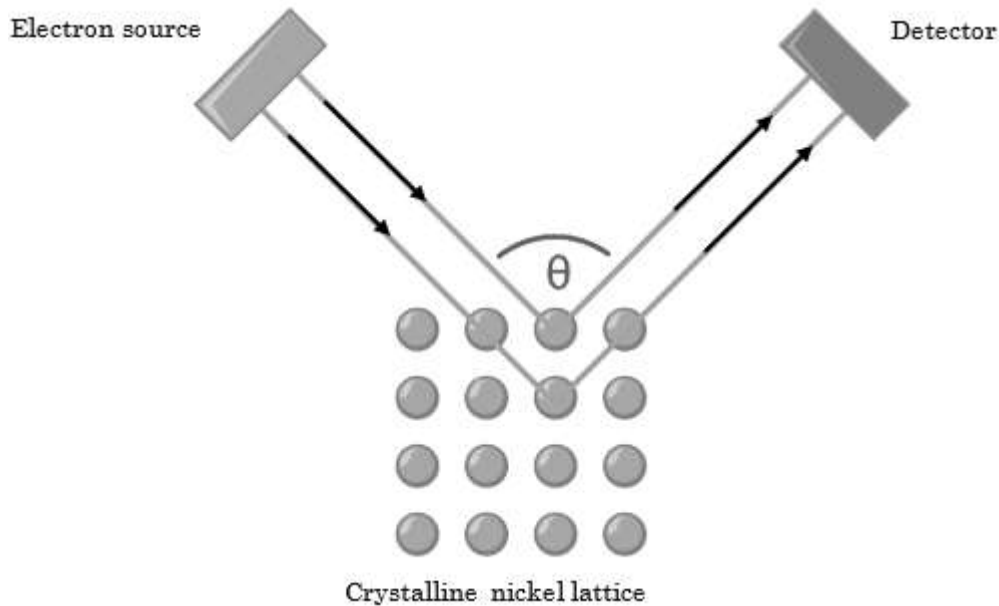




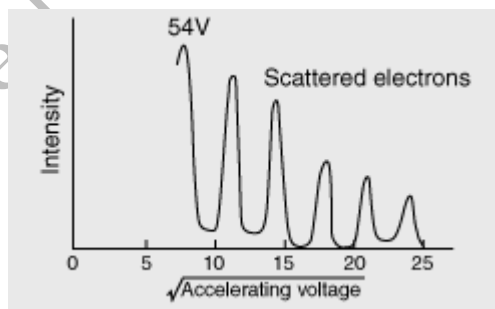
The validity of de Broglie's hypothesis was demonstrated at the Western Electric (later Bell) Labs in 1927 by Clinton Davisson (pictured left) and Lester Germer (right) who managed to achieve firing slow moving electrons at a nickel target and obtained a diffraction pattern that would have been expected of a wave. Ironically they were not looking for evidence of the wave nature of the electron but were attempting to study the structure of nickel as



demonstrated below.



The detector could be moved to measure the electrons at different angles and to their great surprise they discovered that rather than there being a consistent intensity of electrons, there were regular peaks observed at different voltages as shown below:



Davisson and Germer resolved this by relating the Bragg angle of diffraction to the de Broglie relationship

$$\frac{1}{\lambda} = \frac{n}{2d \sin \theta} = \frac{p}{h} = \frac{\sqrt{2mE}}{h} = \frac{\sqrt{2meV}}{h}$$

where  $\lambda$  is the wavelength,  $n$  is an integer,  $p$  is the momentum of the electron,  $m$  is the mass of the electron,  $V$  is the applied voltage,  $\theta$  is the angle of measurement,  $h$  is Planck's Constant and  $d$  is the distance between the atoms in the, crystalline, nickel lattice and  $E$  is energy.



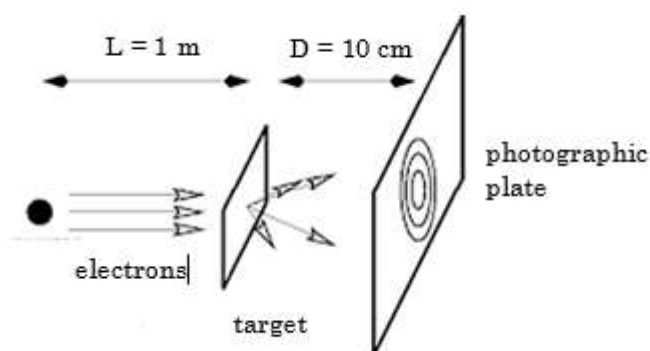
Nearly simultaneously, the same effect was demonstrated by Sir George Paget 'G.P.' Thomson FRS (below left), the son of Sir J. J. Thomson who had discovered electrons, initially termed cathode rays.



G.P. Thomson was the first person to deliberately search and to find evidence for the wave nature of electrons and in 1927, he discovered revealed the first experimental evidence by studying the diffraction of electrons by a celluloid film and continued to study the phenomena with thin foils of gold and of aluminium and of platinum.

He placed the electron source 1 metre from the target and placed a photographic plate 10 cm behind the target which was 1  $\mu\text{m}$  thick and generated a series of circles.

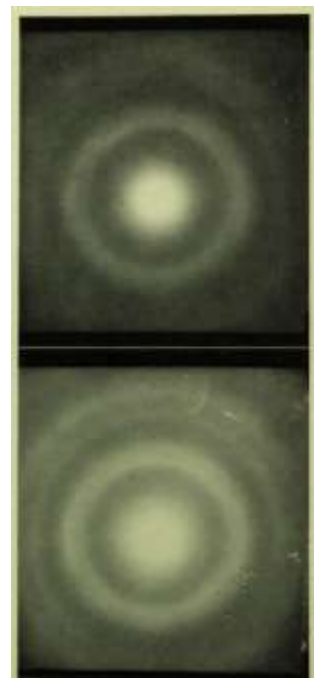
The experimental set up is shown below:



In all cases Thomson discovered and recorded the existence of rings caused by the diffracted electrons whose measurements concurred in full with the de Broglie equation.

The early diffraction patterns recorded in Thomson's first report of his experiment are shown on the right and they are so similar to the diffraction patterns produced by analogous x-ray diffraction experiments on targets of the same material that Thomson's experiment demonstrated beyond doubt that electrons possess wavelike properties.

It is noteworthy that J.J. Thomson received the 1906 Nobel Prize in Physics for his discovery of the electron which he regarded as a particle whilst his son, G. P. Thomson, received the 1937 Nobel Prize in Physics for discovering its wavelike properties which he shared with Davisson.



## Taking stock of these discoveries:

The period, 1885 – 1932, enveloped numerous discoveries which shook the world of classical physics to its core.

From the modest assumption of Victorian physicists that some questions were unanswerable and that the atom was a discrete solid and indivisible ball about which nothing could be determined, it had been established that:-

- Atoms contain negatively charged species, originally termed cathode rays but now called electrons.
- Atoms contain positively charged species (protons) and the same atoms contain an equal number of protons and negatively charged electrons but the electrons are of far less mass.
- The vast bulk of the density of the atom is contained within the central positively charged nucleus.
- Most of an atom is empty, so called *free space*, essentially a perfect vacuum.
- The electrons exist in a number of orbits circling the nucleus.
- The newly discovered particles, *electrons*, behave as particles and waves depending on the circumstances. Generally, however, and for simplicity, chemists visualise electrons as particles whilst always conscious of their wavelike properties as well.

It was a stunning change and is demonstrated, most extraordinarily, that if one raises an arm, then however solid it feels, one is mainly raising empty space through air which is itself mainly empty. Within that arm there are positively and negatively charged species which interact but the overall effect is still one of a neutral charge.

As ever, discoveries raised more questions than it answered:

1. Overall, the atom is neutral but is comprised of equal numbers of charged particles but the mass of the atom could not be accounted for by the masses of the constituent protons and electrons. This meant that there had to be another, as yet undiscovered, particle of no charge and of unknown mass. This has already been discussed in Chadwick's discovery of the neutron (p.23) which is important for the path we are taking through the discoveries (as it explained the existence of the isotopes) but, chronologically, Chadwick's discovery was made after Thomson's demonstration of the existence of the electron's wave-like properties.
2. If an electron can behave as both a wave and a particle then can other particles, such as protons and atoms, behave also as waves? The answer would appear to be Yes if only because if not then why not?

But the major question still arose and had not been answered:

3. Classically, a positively charged particle orbited by a negatively charged particle should attract the negative charge and the collision would result in the emission of radiation. That clearly does not occur since, if it did then we not be here to even ask the question, so why does it not occur? Why are electrons content to exist around the nucleus, held by it, but not pulled in to it?

Erwin Schrödinger had provided the answers to questions 2 and 3.



# Schrödinger's Wave Equation and the Atom's Electronic Distribution

By the mid 1920s, physicists knew that light which had been regarded as wavelike in nature also behaved as particles, which became known as *photons*, and that electrons, which had been believed to be particles, could behave as waves.

Everybody finds the concept of wave-particle duality difficult at first exposure and how a particle can behave like a wave, and vice versa, has been the subject of much discussion. It is not absolute but a general rule of thumb is that if something is smaller than the lower wavelength of visible light i.e. invisible to us then it behaves more like a wave than a particle. Conversely, if it is visible to the human eye then it behaves as a particle. When one property becomes dominant it is important to note that the other property is not lost but is just insignificant to the circumstance. It does not lose its other property but that other property becomes much less important. Mathematical descriptions of the wavelike natures of particles are known as *wave functions*, describe the state of a system at a particular time and predict the future state of the system.

The next question was:

**Since waves can behave like particles and particles can behave as waves does an atom also possess a wave nature?**

The answer was provided by Erwin Schrödinger who provided a wave equation to describe the atom. It is not necessary to have either the mathematical or physics knowledge to understand the consequences of the equation which are pertinent to chemistry.

Essentially, the Schrödinger equation predicts that if certain properties of a system are measured, only certain, discrete, values can be solutions to the equation. From a chemical point of view the importance of the equation is that it describes how electrons can be arranged in an atom. The mathematics is well outside of the scope of this volume, and unnecessary for chemists, but the conclusions can be summarised as follows:-

- Electrons *do* exist in regions remote from the nucleus which resonates with the Bohr model of orbits.
- There are a number of such regions which exist progressively further from the nucleus and these are now known as *energy levels*, since from the stepladder analogy, the electrons further from the nucleus **must** have more potential energy than those closer to the centre of the atom.
- Each energy level can hold a maximum number of electrons as shown below for the first four energy levels:

Energy Level	Maximum number of electrons
1	2
2	8
3	18
4	32

- When the atom is not being irradiated, it exists in its own lowest energy state, known as the *ground state*. In other words, the electrons exist in the lowest possible energy level and as the atomic number increases energy levels 1, 2, 3, 4, etc; become filled in that order. These are known as the ground states of the electrons.

- This means that the electron(s) of  ${}^1\text{H}$  and  ${}^2\text{He}$  exist in the first energy level and the electrons of atoms of atomic number 3 – 10 exist in the first two energy levels etc;
- The electrons do not circle the nucleus in one orbit, as envisaged by Rutherford nor do they *circle* the nucleus in the rings proposed by Bohr and neither do they exist in the Saturnian model proposed by Nagoako however Bohr's conception of energy levels was consistent with the Schrödinger wave equation and the solutions to the Schrödinger equation essentially detailed how the electrons are arranged within the energy levels.
- It is not possible to state exactly where the electrons exist within their energy levels but we can assign a probability to their locations. The specific regions of space which electrons can occupy are known as **orbitals**. The arrangement of the electron in the energy levels and, within the energy level, within the orbitals is known both as the *electron distribution* and as the *electronic configuration*. These two terms essentially have the same meaning.
- The orbitals are labelled using the letters **s**, **p**, **d** and **f**. There is no mystery about this as they simply relate to the appearance of different regions of absorption and emission spectra and the naming is as follows: **s**: *sharp* **p**: *principal* **d**: *diffuse* **f**: *fundamental*

Again, the *shape* of the orbitals indicates where the electron is most *likely* to be found. It is not exact and is a *probability*. Orbitals have no physical structure and they are best thought of as contour maps of the atom outlining where the electrons are most likely to be found.

We will now discuss the s – orbitals, p – orbitals and, briefly, the d – orbitals in order.

# The Arrangements and Distribution of Electrons within Orbitals

## S - Orbitals

- **S - orbitals** are ring-doughnut shaped. Topologically they are called toroids and, although conventionally drawn as a circle, there must be zero electron density in the centre as that is the nucleus.



Incidentally, this is the case with all orbitals:

they must have zero distribution at the centre of the atom as that is always occupied by the nucleus.

Every energy level contains an **s - orbital** and regardless of the number of energy levels it is the first orbital (region) to be filled. This means that the first two electrons fit into the 1s orbital and are described as 1s electrons and this accounts for hydrogen and helium:  ${}^1\text{H}: 1s^1$        ${}^2\text{He}: 1s^2$

The numeral describes the energy level, the letter denotes the orbital and the superscript records the number of electrons in that orbital and hence in that energy level. Since the first energy level can only have one orbital and that orbital can only hold a maximum of two electrons, that energy level is then filled.

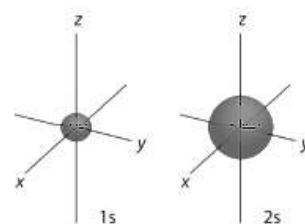
This is highly significant and explains the reactivity of hydrogen atoms and the complete inertness of helium and the rest of the Noble Gas atoms. It also begins to explain the reactivity of the Group I and II elements and the relative reactivity of the Group I and II elements, all of which is discussed later.

This leads us on to Period 2 of the Periodic Table and we can start with lithium.

Lithium has the atomic number 3 and so the atom has three electrons surrounding the nucleus.

- The first two electrons fit in to the 1s shell (energy level).
- The third electron must go into the second energy level (shell)

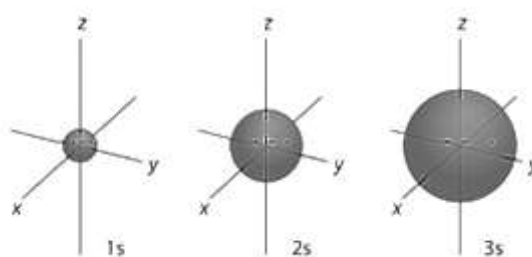
The third electron goes into the second energy level and fits into another s orbital, hence 2s, which is larger than the 1s orbital and envelopes it:



The electronic distribution of lithium ( ${}^3\text{Li}$ ) is thus:  $1s^2 2s^1$ .

Since each orbital can hold up to two electrons this also leads to the conclusion that beryllium has the electron configuration:  ${}^4\text{Be}: 1s^2 2s^2$ .

The principle that electrons fit into the orbital of lowest energy sequentially is known as the **Aufbau** ('building up') **Principle** and applies to all orbitals in all energy levels. All s - orbitals are symmetrically and spherically identical but as the atom gets bigger then the s - orbitals increase in volume so for the first three periods the s - orbitals 1s, 2s, 3s can be visualised as shown on the right.



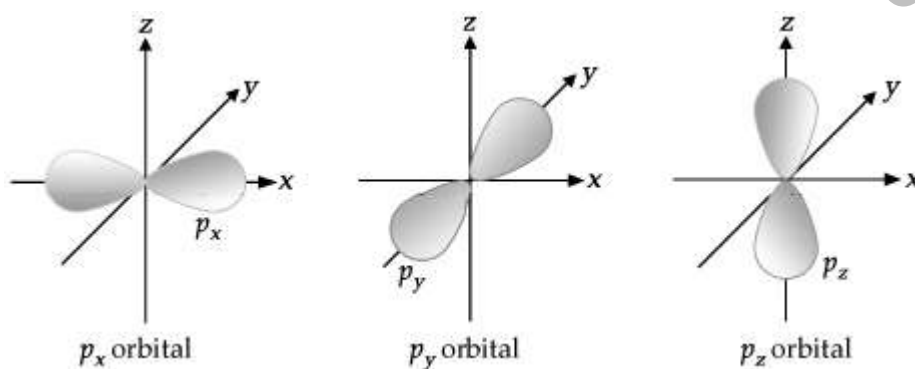
## P Orbitals

As we move across the Periodic Table and encounter atoms of atomic number greater than four we can confidently state that the first four electrons have the configuration  $1s^2 2s^2$ .

The question then is where do the other electrons exist?

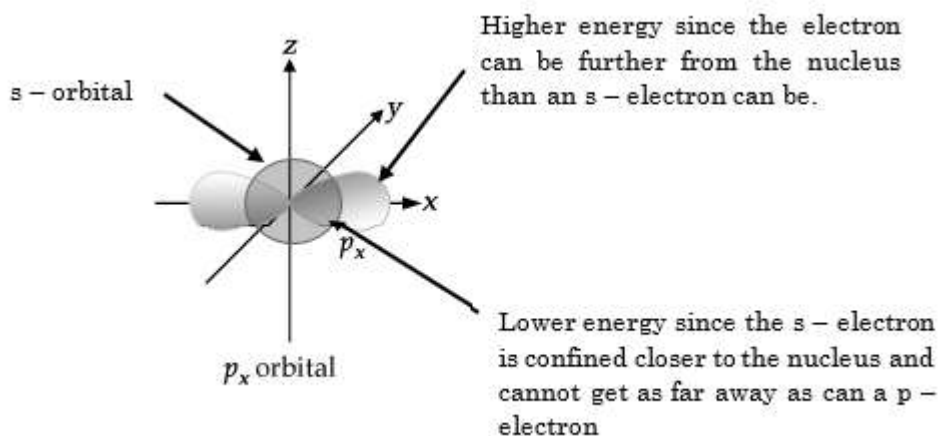
The answer is in a beautifully symmetrical set of three orbitals, each which can hold a maximum of two electrons. They are often described as dumb-bell shaped but it is better to consider them to resemble a figure of eight.

There are three of them, orthogonal to each other as shown:

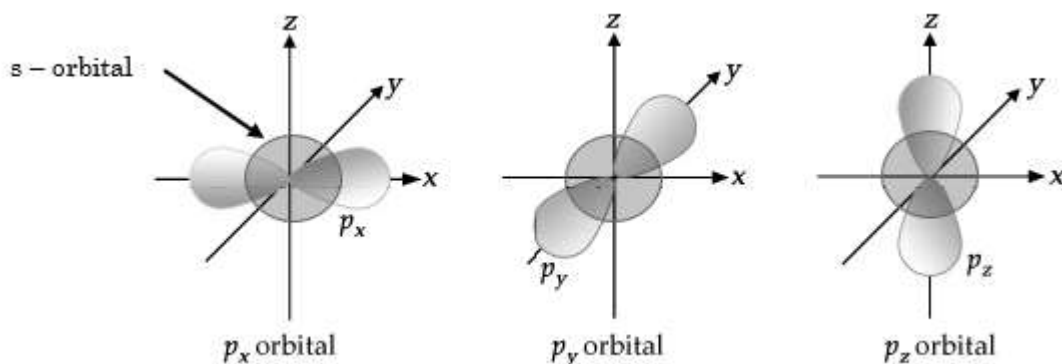


The easiest way to envisage the x, y and z axes is to stand up, extend one hand to the front and one to the right (or left). These are the x and y – axes and your body is the z – axis. There are several important principles to absorb and remember:-

- Although the 2s and 2p orbitals exist within the same energy level, the p-orbitals (all of equal energy to each other, *mutually degenerate*) are of higher energy than the 2s orbital. This must be the case since the p-orbitals extend further from the nucleus than the 2s orbital and there is a direct correlation between distance from the nucleus and energy as shown below:



This principle applies to all three 2p orbitals as shown below:



Moving right from beryllium, the next six elements have their extra electrons placed in the p – orbitals.

To understand this it is essential to remember that there are three p – orbitals, which are of the same energy i.e. *mutually degenerate*, and which are denoted, arbitrarily,  $p_x$ ,  $p_y$  and  $p_z$ .

Since electrons repel each other the first three electrons will exist in the three p – orbitals before they are then paired up so we can represent the electronic distribution of boron, atomic number 5, as:  $1s^2 2s^2 2p_x^1$ .

This indicates that the:-

- First two electrons in each energy level exist in the s – orbital;
- The fifth electron exists in one of the p – orbitals, arbitrarily denoted  $2p_x$  above.

Therefore, for:-

- Carbon,  ${}^6\text{C}$ , the distribution is  $1s^2 2s^2 2p_x^1 2p_y^1$  whilst
- Nitrogen,  ${}^7\text{N}$ , can be written as  $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$ .

This is a formulation of **Hund's Rule** which states that '*the lowest-energy configuration for an atom with electrons within a set of degenerate orbitals is that having the maximum number of unpaired electrons*'.

For convenience, and provided Hund's Rule is remembered, it is usual to ignore the x, y and z – notations such that the above three notations become:

- **Boron**,  ${}^5\text{B}$ :  $1s^2 2s^2 2p^1$
- **Carbon**,  ${}^6\text{C}$ ,  $1s^2 2s^2 2p^2$
- **Nitrogen**,  ${}^7\text{N}$ ,  $1s^2 2s^2 2p^3$

Continuing across Period 2, the electrons in the p – orbitals start pairing up and, for oxygen, fluorine and neon we have:-

- ${}^8\text{O}$      $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$     equivalent to     $1s^2 2s^2 2p^4$
- ${}^9\text{F}$      $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$     equivalent to     $1s^2 2s^2 2p^5$
- ${}^{10}\text{Ne}$      $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$     equivalent to     $1s^2 2s^2 2p^6$

Nobody would deny that this is cumbersome and there are two other ways to denote the electronic distribution.

## Linear notation

As a shortened version where the three p – orbitals are considered as one group so we can write the periodic electronic distribution of the second period, in two different ways. We can write it as used above but that is also tedious and it is prone to errors through a slip of the pen and so one way to record the electronic distribution is to write the symbol of the previous Noble Gas in square brackets and simply add the additional electrons afterwards. The two equivalent notations are shown below, separated by the vertical dashed line.

Element	Electronic configuration		Element	Electronic configuration	
${}_3\text{Li}$	$1s^2 2s^1$	[He] $2s^1$	${}_{11}\text{Na}$	$1s^2 2s^2 2p^6 3s^1$	[Ne] $3s^1$
${}_4\text{Be}$	$1s^2 2s^2$	[He] $2s^2$	${}_{12}\text{Mg}$	$1s^2 2s^2 2p^6 3s^2$	[Ne] $3s^2$
${}_5\text{B}$	$1s^2 2s^2 2p^1$	[He] $2s^2 2p^1$	${}_{13}\text{Al}$	$1s^2 2s^2 2p^6 3s^2 3p^1$	[Ne] $3s^2 2p^1$
${}_6\text{C}$	$1s^2 2s^2 2p^2$	[He] $2s^2 2p^2$	${}_{14}\text{Si}$	$1s^2 2s^2 2p^6 3s^2 3p^2$	[Ne] $3s^2 2p^2$
${}_7\text{N}$	$1s^2 2s^2 2p^3$	[He] $2s^2 2p^3$	${}_{15}\text{P}$	$1s^2 2s^2 2p^6 3s^2 3p^3$	[Ne] $3s^2 2p^3$
${}_8\text{O}$	$1s^2 2s^2 2p^4$	[He] $2s^2 2p^4$	${}_{16}\text{S}$	$1s^2 2s^2 2p^6 3s^2 3p^4$	[Ne] $3s^2 2p^4$
${}_9\text{F}$	$1s^2 2s^2 2p^5$	[He] $2s^2 2p^5$	${}_{17}\text{Cl}$	$1s^2 2s^2 2p^6 3s^2 3p^5$	[Ne] $3s^2 2p^5$
${}_{10}\text{Ne}$	$1s^2 2s^2 2p^6$	[He] $2s^2 2p^6$	${}_{18}\text{Ar}$	$1s^2 2s^2 2p^6 3s^2 3p^6$	[Ne] $3s^2 2p^6$

### Visual representation (*Arrows in Boxes*)

This is way of representing electrons in an orbital which is represented by a simple box. Each electron is represented by a half headed arrow. The first electron  $\uparrow$  points up whilst the second electron points down  $\downarrow$ .

Element	Atomic no.	Linear notation	Visual notation			Electrons in shells
			1s	2s	2p	
H	1	$1s^1$	$\uparrow$			1
He	2	$1s^2$	$\uparrow\downarrow$			2
Li	3	$1s^2 2s^1$	$\uparrow\downarrow$	$\uparrow$		2, 1
Be	4	$1s^2 2s^2$	$\uparrow\downarrow$	$\uparrow\downarrow$		2, 2
B	5	$1s^2 2s^2 2p^1$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	2, 3
C	6	$1s^2 2s^2 2p^2$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow \uparrow$	2, 4
N	7	$1s^2 2s^2 2p^3$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow \uparrow \uparrow$	2, 5
O	8	$1s^2 2s^2 2p^4$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow \uparrow$	2, 6
F	9	$1s^2 2s^2 2p^5$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow$	2, 7
Ne	10	$1s^2 2s^2 2p^6$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	2, 8

All of these methods of representing electronic distribution have particular value and have led to immediate explanations for well known but until then not understood, chemical phenomena:

There are many examples which demonstrate this and a few are now to be considered.



## The Significance of the Noble Gases to Electronic Distributions

The *Noble Gases* were known as the *Inert Gases* until the 1960s when the first compound of xenon was formed under extreme conditions. They were, however, not discovered until the turn of the 20<sup>th</sup> century and there is a simple reason for this. Essentially, they do not do anything: they are unreactive, colourless and odourless so there was no reason to suspect that they even exist. This remained the case until Sir William Ramsay began to investigate the composition of air since the measured quantities of nitrogen, oxygen and carbon dioxide did not add up to 100%. This led to the natural conclusion that air must contain at least one other gas and there was another curiosity: the density of nitrogen obtained from chemical compounds did not equal the apparent density of atmospheric nitrogen which was all that was assumed to remain after the removal of oxygen, water and carbon dioxide.

Ramsay sequentially removed oxygen, nitrogen and carbon dioxide. The oxygen was removed by passing the air over hot iron filings (forming solid iron(III) oxide), nitrogen by passing the remaining air over heated magnesium (forming solid magnesium nitride) and the carbon dioxide by bubbling the remaining air through lime water. The procedures were performed in a cycle of this chain of reactions and the air was repeatedly passed through this sequence for about three weeks. Eventually the remaining air was passed into an evacuated container and cooled under high pressure to collect the liquefied residual gases. The liquefied gas was gradually warmed up and each fraction collected separately.

The conclusions were stunning.

The gas with the lowest boiling point vaporised first and was collected. When analysed spectroscopically it was found to emit lines previously only known from spectroscopic analysis of sunlight. Ramsay had isolated the element previously only known in sunlight and named it *helium* after the Greek name for the sun: Helios. Ramsay isolated four other fractional gases and he named one *argon*, a combination of two Greek words for *lazy gas*. The others he discovered were neon, krypton and xenon. To Mendeleev's dismay, Ramsay then proposed a new column of the Periodic Table and he predicted the existence of *radon* which was subsequently discovered as a by-product of the radioactive decay of radium.

For the purposes of this volume, the significance of the newly discovered group was identified by Gilbert 'G.N.' Lewis. In 1916, Lewis, using the Bohr model observed that the inert gases all had two features in common: **all are unreactive and all possess a filled set of energy levels.**

Lewis suggested that there must be a correlation between lack of reactivity and the filled energy levels and proposed that filled energy levels conferred a particular stability on the atom hence leading to a lack of reactivity.

The solutions to the Schrödinger equation, which for our purposes are the electronic configurations, enable us to explain why Group I (alkali metals) elements only ever form singly positive ions e.g. for sodium  $\text{Na}^+$  and never an  $\text{Na}^{2+}$  ion or an ion of even higher charge.

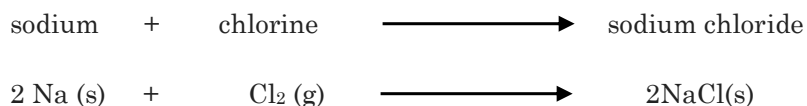
Following on from this we can also now consider why the halogens only form single, negatively charged, ions.

Considering the alkali metals first;

The chemical formation of sodium chloride is a magnificent demonstration of the power of chemistry:

A grey metal that will burn us (sodium) reacts with a yellow – green gas which can kill us (chlorine) to produce a white solid which we can safely put, within reasonable amounts on our food, sodium chloride, and it turned out that this was due simply to transfer of a single electron from each sodium atom to each chlorine atom of the Cl<sub>2</sub> molecule.

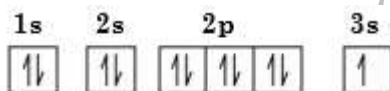
The word equation and the balanced symbolic equations are as follows



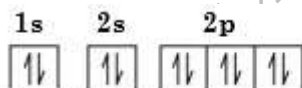
With the determination of the electronic distribution within the orbitals which were solutions to the Schrödinger wave equation, the reason for both suddenly became clear.

### Alkali metals

The *sodium* atom, atomic number 11, has the electronic distribution 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>1</sup>



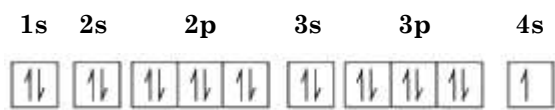
If it loses one electron then it assumes the electronic distribution of the *neon* atom:



The sodium ion becomes unreactive once the electron shells are all filled; in this case electron shells 1 and 2.

The concept of stability conferred by a Noble Gas electronic configuration was called by Lewis, the *Octet Rule* since the second energy level contains eight electrons explains the reactivity of the sodium atom, its stability as a Na<sup>+</sup> ion and its then complete lack of reactivity.

This explanation is reinforced by considering the same reaction with potassium which has the electronic configuration 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 4s<sup>1</sup> and as shown visually below.



One electron exists in an outer shell and when that is lost the K<sup>+</sup> ion has the same electronic configuration as argon and becomes unreactive. It is important to note that, although the 3<sup>rd</sup> energy level also contains five d – orbitals these are of higher energy than the 4s orbital which is filled before the d – orbitals are used.

The same occurs with lithium which loses one electron to become Li<sup>+</sup> which has the electronic configuration of helium.

It is now clear then that reactivity depends on the number of outer electrons.

When the atom or ion contains a filled set of electron shells then it goes quiet and becomes unreactive. There is a completely analogous set of descriptions of the behaviour of the Group II atoms which form 2+ ions.

## Halogens

Moving to the other side of the Periodic Table we can now consider the **halogens**.

For this purpose, the three most important halogens are fluorine, chlorine and bromine. All three atoms form single negatively charged ions  $X^-$  where  $X$  represents the atom.

The electronic configuration of the atoms are as follows:-

Element	Atomic number	Electronic configuration
Fluorine	9	$1s^2 2s^2 2p^5$
Chlorine	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
Bromine	35	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^6 5s^2 5p^5$

The halogens form only single charged anions,  $X^-$ , adopting the configuration of the subsequent Noble Gas.

*Fluorine* adopts the electronic configuration of *neon*, *chlorine* that of *argon* and *bromine* that of *krypton*:

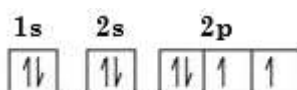
Atom	Ion	Noble Gas equivalent
Fluorine (F) $1s^2 2s^2 2p^5$	Fluoride (F <sup>-</sup> ) $1s^2 2s^2 2p^6$	Neon
Chlorine (Cl) $1s^2 2s^2 2p^6 3s^2 3p^5$	Chloride (Cl <sup>-</sup> ) $1s^2 2s^2 2p^6 3s^2 3p^6$	Argon
Bromine (Br) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^6 5s^2 5p^5$	Bromide (Br <sup>-</sup> ) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^6 5s^2 5p^6$	Krypton

This explains the instability of sodium (and the rest of the Group I, alkali metals) to create a stable and chemical unreactive material, *sodium chloride*, which we use in cooking as common, or table, salt.

It also explained why chlorine does not exist nature as single atoms but as a diatomic molecule,  $Cl_2$ , which will be addressed later.

These analyses can be extended to Group II, the alkaline earth metals, which form  $M^{2+}$  ions where  $M$  is the element and and to Group VI with the best example being oxygen.

Oxygen has the atomic number 8 and so has the electronic configuration,  $1s^2 2s^2 2p^4$  also visually depicted as:-



To adopt the configuration of the next Noble Gas, *neon*, the oxygen atom needs to acquire two electrons.

It does not matter where these electrons come from and it can be exemplified by two reactions:

1. If sodium is heated in oxygen then the product is sodium oxide  $\text{Na}_2\text{O}$ .



Two sodium atoms each want to lose an electron and oxygen wants to gain two.

Due to this transfer of electrons both sodium and oxygen adopt the stable, and consequently unreactive electronic distribution of neon. This explains the reaction and the formula of the product.

2. The second example is that of magnesium combusting in oxygen.



Each magnesium atom has two outer electrons which it wants to lose to assume the electronic distribution of neon whilst oxygen wants to acquire them to also adopt that stable configuration.

The same rules explain the formation of all ions of Group I (alkali metals) and Group II (alkaline earth) metals and why the former acquire a single positive charge whilst the latter form stable  $2^+$  ions. There is a consistency in all of these reactions and the theory demonstrates why metals lose electrons to acquire the electronic distribution of the previous noble gas configuration (as arranged in the Periodic Table) whilst non – metals gain electrons to acquire the distribution of electrons of the Noble Gas following the non-metal.

Bonding involving the transfer of one or more electrons from one atom to another results in compounds of high melting and boiling points and are water soluble. This type of bonding is **ionic bonding** and, although not particularly relevant to our investigation as we are looking at organic compounds, it does explain two of three phenomena observed with chemical substances:

1. Reaction between a metal and a non-metal produces a compound with high melting point, dissolves in water and when molten conducts electricity. This is also due to the fact that the product of the reaction comprises positive and negatively charged ions which attract each other and hold themselves together very tightly but when dissolved in water can carry an electric current. These simple ionic compounds form between a metal on the left of the Periodic Table and a non-metal on the right hands side.
2. No compounds of two metals exist (alloys of metals do, course, exist but they are physically mixed and not chemically combined and such compounds cannot exist since, if both metals wish to lose their outer electrons, where are they to go?
3. The third, so far unexplained phenomenon is that of low boiling, water insoluble organic compounds, formed from elements in the middle of the Periodic Table and, of course, hydrogen, which cannot be explained by the above electron transfer so there must be some other process at work and this is investigated next.