

Atomic Theories

John Dalton's Atomic Theory:

In 1805, the English chemist/school teacher, John Dalton, created the modern theory to explain three important scientific laws: the law of definite composition, the law of multiple proportions and the law of conservation of mass.

John Dalton's Theory was that the smallest piece of matter was an atom that was indivisible, and that an atom was different from one element to another. All atoms of a particular element were thought to be exactly the same. Dalton's model of the atom was that of a featureless sphere which gave it the name "the billiard ball" model of the atom (See Figure 1). The success of this theory was that it could explain all three of these laws but much more.



Figure 1 – Dalton's billiard ball model of the atom

Joseph John (J.J.) Thomson's Atomic Theory:

The experimental studies of Svante Arrhenius and Michael Faraday with electricity and the chemical solutions of William Crookes with electricity and vacuum tubes suggested that electric charges were components of matter. J.J. Thomson's qualitative experiments with cathode rays resulted in the discovery of the electron, whose charge was later measured by Robert Millikan.

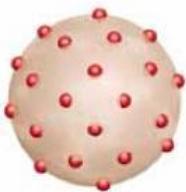


Figure 2 – Thomson's Raisin bun model of the atom

Thomson's model of the atom, which was created in 1897, was a hypothesis that the atom was composed of negative electrons embedded in a positively charged sphere. This was coined the raisin bun model of the atom with the raisins representing the electrons and the soft bun representing the positive material of the atom (See Figure 2).

Ernest Rutherford's Atomic Theory:

One of Thomson's students, Ernest Rutherford showed that some parts of the Thomson atomic theory were not correct. Rutherford developed an expertise with nuclear radiation which he later used to disprove the Thomson Theory. He worked with and classified nuclear radiation as alpha (α) particles, beta (β) particles and gamma (γ) radiation. The α -particles were determined to be the nucleus of a helium atom consisting of two protons and two neutrons. The β -particles, with their negative charges were discovered to be electrons. γ -Radiation is a version of high-energy electromagnetic radiation from the nucleus.

The experiment used to test the Thomson theory is popularly known as the gold foil experiment. A sample of radium was used to as a source of α -particles which was directed at a thin film of gold. The prediction that Rutherford made was based on Thomson's theory and stated that as the alpha particles were fired off from the radioactive sample, and would pass directly through the material (gold foil) and be deflected very little (see Figure 3). The hypothesis was refuted when Rutherford found that the alpha particles were not only deflected by small amounts, but some were deflected at huge angles and some even backwards (see Figure 4). The analogy that he used to describe this was, it was like firing a tank shell at a piece of tissue paper, and having it bounce off back to you. This had shown that Thomson's model of the atom could not be correct and was judged unacceptable.

Rutherford's analysis showed that all the positive charges in the atom had to be contained in a much smaller volume than was previously thought. He also began to hypothesize the existence of a nuclear (attractive) force to explain how so much positive charge could occupy such a small volume. The nuclear force that he hypothesized existed was later called the strong nuclear force and he said that the force had to be strong enough that it could overcome the strength of the electrostatic repulsive forces found within the nucleus of the atom from the positive charges. Rutherford's explanation of the evidence gradually gained widespread acceptance in the scientific community.

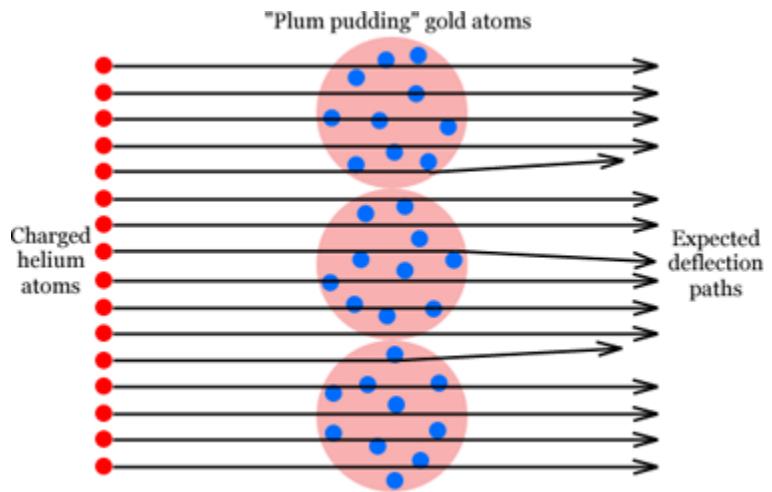


Figure 3 – Rutherford's prediction before the gold foil experiment. The charged helium nuclei pass right through the spaced out positive mass predicted by the Thomson model.

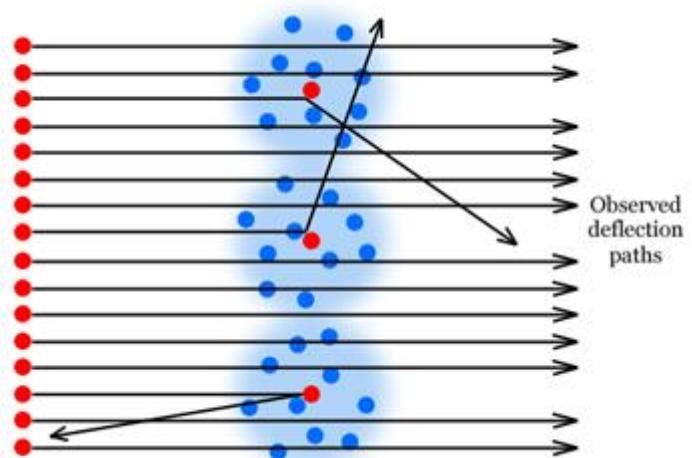


Figure 4 – Rutherford's observed results from the gold foil experiment. The charged helium nuclei are deflected and changed direction slightly or, after striking the nucleus, deflect at very large angles back towards the source of the α -particles.

Protons, Neutrons and Isotopes

The Thomson model included electrons as sub atomic particles but did not include the positive portion of an atom as a particle. Rutherford's model included electrons orbiting a positively charged nucleus that was very dense and very positive. Further studies completed by Rutherford, Thomson and other associates using cathode ray tubes found that the smallest positive charge possible was from ionized hydrogen gas (today we know this as the proton).

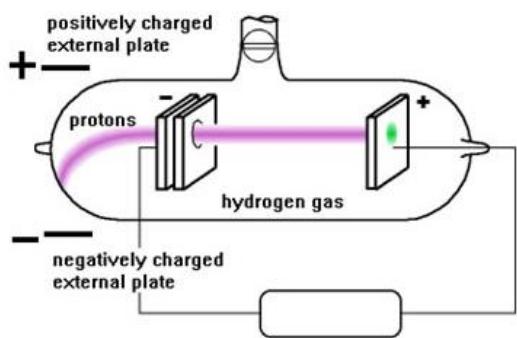


Figure 5 – A cathode ray tube showing the bending of the positive ray (hydrogen nuclei) bending away from the externally charged positive plate.

By bending the hydrogen positive rays in a magnetic field; the charge and mass of the hypothetical proton was determined (see Figure 5). The proton was shown to have a charge equal but opposite to that of the electron and a mass 1836 times greater than that of the electron.

Further analysis with radioactivity and mass spectrometry falsified Dalton's theory that all atoms of a particular element were identical. The evidence indicated that there were, for example, atoms of sodium that had different masses. Later, James Chadwick, working with Rutherford, was bombarding elements using α -particles to calculate the mass of nuclei. When the masses of the nuclei were compared to the sum of

the masses of the protons for elements, they found that they did not agree. In 1932, Chadwick completed his research involving the radiation effects caused by the α -particles bombardment and reasoned that the only logical and consistent theory that could explain these results involved the existence of a neutral particle in the nucleus (neutron).

The Origins of Quantum Theory

Black Body Radiation

As a solid is heated to higher and higher temperatures, it begins to glow. Initially, it appears red and then become white when the temperatures increase to higher levels. Since white light is a combination of all the colours, the light emitted by the hotter object, must be accompanied by, for example, blue light. The changes in the colours and the corresponding spectra do not depend on the composition of the solid.

When electronic instruments are used to measure the intensity (brightness) of different colours observed in the spectrum of the emitted light, a bell shaped curve is obtained (see Figure 6). The curve becomes higher and shifts towards higher-energy UV as the temperature increases. In 1900, Max Planck developed a mathematical equation to

explain the curve. He hypothesized that the energies of the oscillating atoms in the heated solid were multiples of smaller quantities of energy. In other words, energy is not continuous and is found in small quantized amounts.

Albert Einstein pointed out later that the light emitted by a hot solid is also quantized and thus comes in small bursts rather than a continuous stream of energy. The small burst or packet of energy is known as a quantum of energy.

Planck's equation for the energy of a photon of light is the product of Plank's constant (h) and the frequency (ν), of the light.

$$E = h \nu$$

E = Energy in joules (J)

h = Planck's Constant (6.67×10^{-34} J/Hz)

ν = Frequency (Hz)

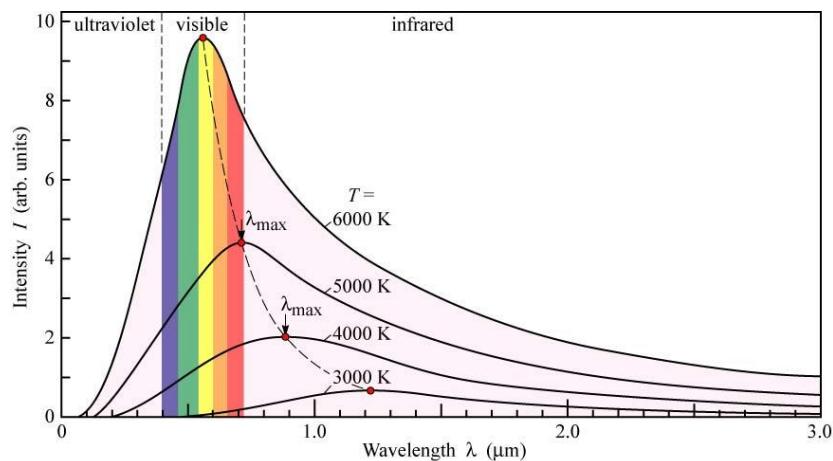


Figure 6 – The graph shows the spectral intensity distribution of Planck's black-body radiation as a function of wavelength for different temperatures

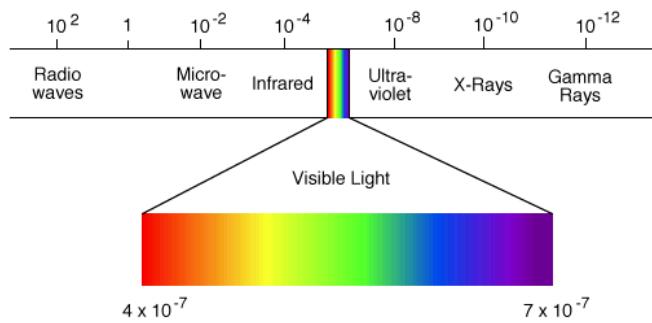
As the temperature of a solid increased, the proportion of each larger quantum becomes greater. The colour of a heated object is due to a complex combination of the number and kind of quanta.

The Photoelectric Effect

Greek philosophers believed that light was a stream of particles. Christian Huygens proposed that light can be best described as a wave. Isaac Newton, the famous English scientist, opposed Huygens view and continued to try to explain the properties of light in terms of minute particle which he called corpuscles.

Mounting evidence from scientists with reflections, refractions and diffraction favoured the wave hypothesis. James Maxwell proposed that light is an electromagnetic wave composed of electric and magnetic fields that can exert forces on charged particles. The electromagnetic wave theory, known as the classical theory of light, became widely accepted when new experiments supported this view.

The electromagnetic spectrum includes all forms of electromagnetic radiation from very short wavelength γ -rays to very long radio waves (see Figure 7).



The photoelectric effect is the release of electrons from a substance due to light striking the surface of a metal. Heinrich Hertz discovered this effect by accident in 1887. Albert Einstein used Max Planck's idea of a quantum of energy to explain the photoelectric effect. He reasoned that light consisted of a stream of energy in the form of small packets that he called quanta. These tiny packets of energy were later called photons.

Figure 7 – The electromagnetic spectrum of light with the wavelengths of light.

When we look at the energy that a photon carries, a photon of red light contains less energy than a photon of ultra-violet light. When photons strike electrons, as they would if light strikes an object, the energy of the photon is transferred to the electron. Some of this energy is used by the electron to break free from the atom and the rest is left over and converted to kinetic energy for the ejected electron.

The Bohr Atomic Theory

Atomic Spectra

Ernest Rutherford and other scientists had guessed that the electrons move around the nucleus as planets orbit the sun. An electron traveling in a circular orbit is constantly changing its directions, and thus accelerating. According to the classical theory, the orbiting electron should emit photons of electromagnetic radiation, losing energy in the process, and thus spiraling inwards towards the nucleus, collapsing the atom. This prediction was obviously incorrect as we are here reading this document.

Robert Bunsen and Gustav Kirchhoff worked together to invent the spectroscope. The spectroscope forms the basis of an analytic method called spectroscopy. They discovered that an element does not only produce a particular coloured flame but on examination through a spectroscope, also produces a bright line spectrum that was a characteristic of the element. The spectra of each element were a type of fingerprint identification system for each element. The line spectrum of an element is used as an analytic to identify unknown elements (see Figure 8).



Figure 8 - The above spectrum shows the spectral lines given off by the element hydrogen

Joseph von Fraunhofer investigated the absorption or dark line spectra both qualitatively and quantitatively. Kirchhoff was able to show that the dark lines in an element's spectrum were in the same position as the bright lines in the spectrum of an element (see Figure 9). This fact provides a powerful tool in determining the composition of planet's atmospheres far away in the universe.

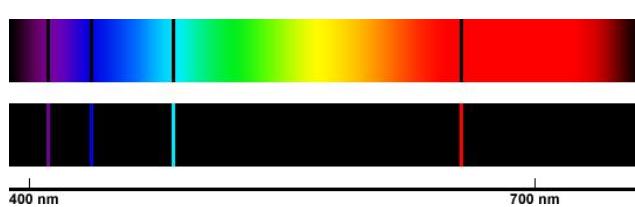


Figure 9 – This shows that the emission spectral lines (on bottom) are in the same position as the absorption spectral lines (on top).

Neils Bohr's model of the atom took into account the bright and dark line spectra of the element hydrogen and his theory stated that only certain quanta of light (certain photon energies) can be emitted or absorbed by an atom. He also reasoned that if the light that is released or absorbed by an atom was quantized, the energy of the electron inside the atom must also be quantized. In other words, electrons can only have certain energies. Bohr referred to these special energy states as stationary states, and the existing rules did not apply inside an atom.

Bohr postulated that electrons do not radiate energy as they orbit the nucleus. Each orbit corresponds to a state of constant energy (stationary state). He suggested that electrons "jump" from one orbit and energy level to another.

A transition from a higher energy state to a lower energy state means that the electron loses energy and this energy is released as a photon of light, explaining the bright line in the emission spectrum (see Figure 10). When some energy is absorbed, for example from a photon of light, the electron undergoes a transition from a lower energy state to a higher one, explaining the dark line in an absorption spectrum.

The Bohr model of the atom was also able to offer a reasonable explanation of Dmitri Mendeleev's periodic law and its representation in the periodic table.

According to the Bohr model:

- Each period in the periodic table results from the filling of electron energy levels in the atom (ex. Atoms in period three have electrons in three energy levels).
- A period comes to an end when the maximum number of electrons is reached for that particular level.
- The maximum number of electrons in each energy level is given by the number of elements in each period of the periodic table. (ex. 2,8,8,18 etc.).
- The last digit in the group number in the periodic table provides the number of electrons in the valence energy level.

Bohr was able to explain the visible spectrum for hydrogen and was able to predict the infrared and ultraviolet spectra for hydrogen. The failure of the Bohr model came from the fact that the theory works very well for the spectrum of hydrogen atoms, but does not work very well for any other atoms.

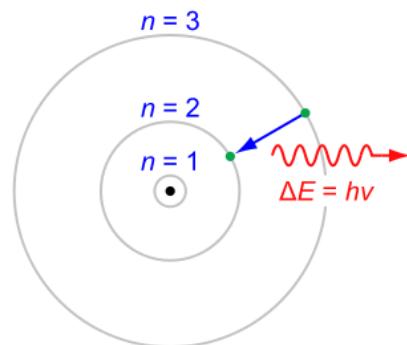


Figure 10 – The above atom shows an electron transitioning from a higher energy level to a lower energy level and emitting a photon with the energy equivalent to $\Delta E = h\nu$

The Quantum Mechanical Model of the Atom

In science, revisions to theories are constant, occurring as a result of the identification of weaknesses within current theories and then improving on those. Neils Bohr's postulates worked very well for the element hydrogen but did not apply when you had multi-electron elements. A revision to the Bohr model of the atom had to be made and three physicists were at the forefront of this new effort: Erwin Schrödinger, Louis de Broglie, and Werner Heisenberg. The new theory took into account wave mechanics and has more commonly been called quantum mechanics. Erwin Schrödinger and Louis de Broglie worked together to help determine the nature of electrons and their motions around the nucleus of the atom. They looked at the standing waves and how the motion of an electron bound to an atom must follow a similar motion (see Figure 11). The key to the standing waves was that they must occur in whole number ratios and the wavelengths must be finite. In other words, there are limitations to the wavelength of the standing waves. This had profound implications for the atom because it meant that electrons could only exist at given energy levels (orbitals) because if the wavelengths of the standing waves were not in the correct whole number wavelength ratios, then the electrons would fall and collide with the nucleus (see Figure 12). Schrödinger's work with the standing waves allowed him to create a mathematical equation that could be used to calculate the energy levels of electrons. This equation could then be used to identify regions in space where the electron could be localized.

The localization of the electrons and their motions about the nucleus were studied by Werner Heisenberg. He said that knowing the location and momentum that an object had at a macroscopic level was easy because we could see the object and measure both of these quantities at once. When you go down to the size of an atom, or even smaller in the case of electrons, it becomes exceedingly difficult to do this. The simple act of measuring these amounts would change the very nature of the amounts. In other words, the energy that is packed in one photon (so that you could look at the location of the electron) has enough energy in it to change the location and momentum of the electron itself. He proposed that knowing one of these quantities with certainty would mean that the others magnitude could not be known. The Heisenberg uncertainty principal states that it is impossible to know both the location and the momentum of an electron at the same time. The best that we can do is to think of these measurements as probabilities rather than certainties.

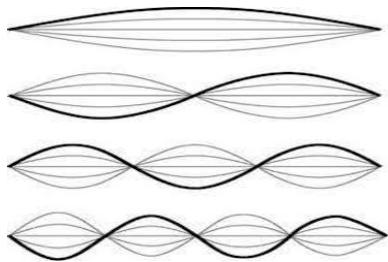


Figure 11 – The first four possible standing waves

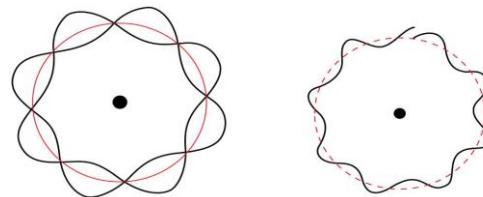


Figure 12 – The first picture shows the standing waves of an electron in the perfect ratio allowing the electron to exist at that energy level. The second picture shows a wave that is not in whole number wavelengths and would have destructive interference occurring.

The Quantum Numbers

Schrödinger's wave equation gave multiple wave functions for the various types of orbitals. Each of these types of orbitals has a set of four quantum numbers that can be used to describe the properties of the orbitals and the electrons within them. You may want to think of these quantum numbers as an address system for finding electrons within an atom. The analogy will become more apparent closer to the end of this section.

First Quantum Number- Principal Quantum Number (n)

The principal quantum number describes the energy level within an atom of a particular electron. The possible values of (n) are single digit whole numbers. Bohr's theory used only one quantum number (n) which is the main reason that it did not work well for elements other than Hydrogen

Second Quantum Number – Azimuthal Quantum Number (ℓ)

The second quantum number describes the shape of the orbital in which the electron is located. The possible values for (ℓ) range from zero to $n-1$. In other words, if the (n) value is a three, then the possible values are 0, 1, and 2. This number will determine the number of sub-levels and sub-shells that are present within the principal shell. The various sub-levels are designated as s, p, d, and f depending upon the value of (ℓ) and have different shapes depending on their designation (see Figure 13).

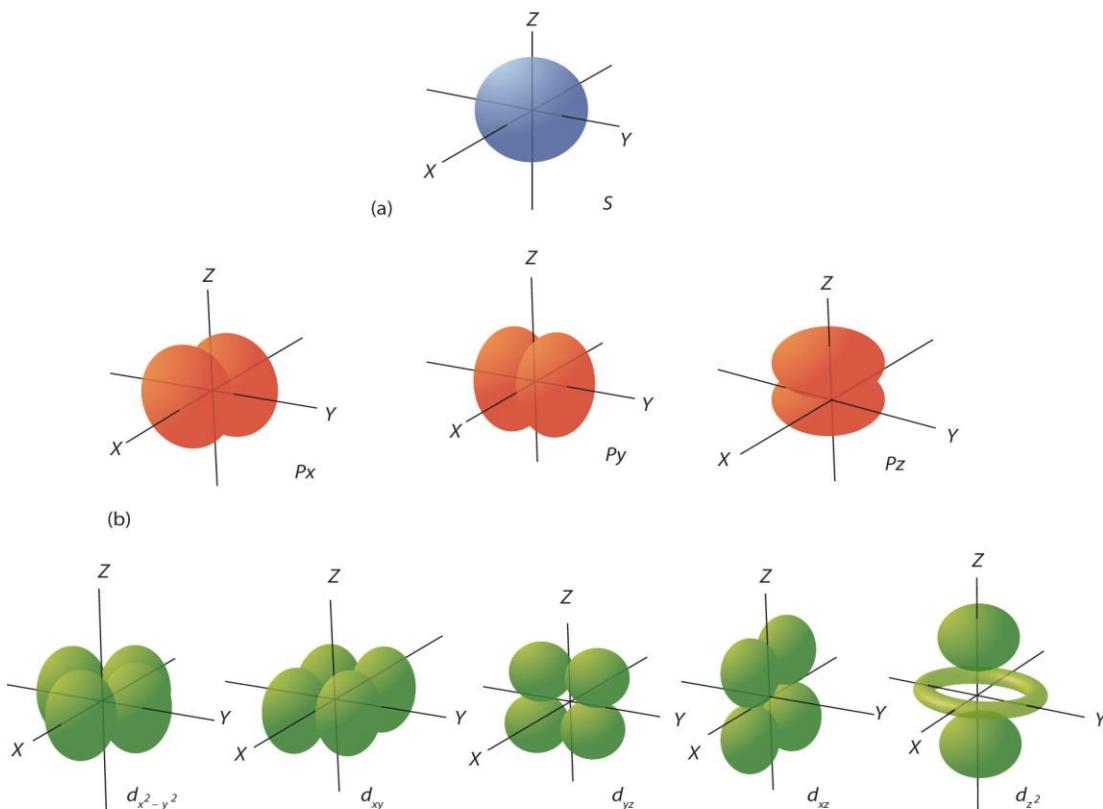


Figure 13 – Line one represents the s sub-shell in the spherical shape. Line two represents the p sub-shell containing three bilobate orbitals oriented along orthogonal x, y, and z axes. The third line represents the d sub-shell which are quadralobate and lie in the xy, xz and yz planes respectively so as to bisect the angles between the orthogonal axes. The d_{z^2} orbital forms a torus with bilobate shape aligned along the z axis.

Third Quantum Number – Magnetic Quantum Number (m_ℓ)

The third quantum number relates primarily to the orientation of the electron orbitals around the nucleus in space. This number ranges from $-\ell$ to ℓ . The larger the value of m_ℓ , the more variation in the atomic orbital orientation you can have (see Figure 13). For example, if you have a value $\ell = 1$ then the possibilities for the m_ℓ values can be -1, 0, and 1. This allows for five possibilities for the orientation of the electron orbitals (see Figure 14)

Fourth Quantum Number – Magnetic Spin Quantum Number (m_s)

The fourth and last quantum number relates to a property of an electron that can be best described as its spin. The spin of the electron can either exist as clockwise or anti-clockwise. The values associated with the magnetic spin quantum number (m_s) can be either $+\frac{1}{2}$ or $-\frac{1}{2}$. The electrons can only exist in single orbitals in pairs and the pairs of electrons must be of opposite “spin.” This is based on the Pauli Exclusion Principle which states that no two electrons can have the same four quantum numbers and thus cannot occupy the same space at the same time (see Figure 14)

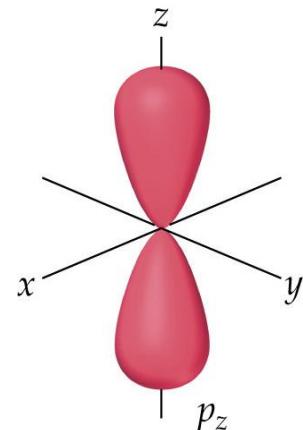


Figure 14 – The example orbital above represents the p_z orbital and would have a value of 1 in the example representing the third P orbital. The magnetic spin quantum number with the $+\frac{1}{2}$ or $-\frac{1}{2}$ values represents which side of the dumbbell the electron resides on.

Orbital Diagrams

In order to show the energy distribution of electrons in an atom, we have developed orbital diagrams that not only show which orbitals are filled, but also the location and energy of the electrons. They are helpful to us to understand where electrons are, and from where they can be removed or added to atoms. They are also a way of pictorially representing the four quantum numbers that we have learned about. There are some rules to consider before we begin with our orbital diagrams and these rules are fundamental rules when constructing our diagrams. Included in this are examples of energy level diagrams (see Figure 16). They cannot be broken!

Pauli Exclusion Principle:

The Pauli Exclusion Principle states that no two electrons in an atom can have the same four quantum numbers and as a result cannot occupy the same location in space. The electron repulsion pressures hold up and do not allow this to happen. This is also the reason that atoms can be so vast with over 99% of the atom open space, with infinitesimally small particles making up the atom, and yet be solid at the macroscopic level (it is why we do not fall through the floor as we stand here reading this page).

Aufbau Principle:

The Aufbau Principal states that electrons are placed in orbitals filling the lowest energy orbitals first (see Figure 15). They fill much how a stadium would fill at a concert, front rows first and then successively building from front to back. It also states that before electrons can occupy higher energy levels, the lower energy levels must be filled first. The word Aufbau comes from the German word to build up.

Hund's Rule

Hund's Rule states that orbitals must become half filled before it can start doubling up its electrons. This is a result of something called multiplicity which states that the most stable atoms are ones in which their orbitals are half filled and is a result of the equation: $2S + 1$. S represents the $\sum m_s$ for all electrons. Unpaired electrons will have a $+ \frac{1}{2}$ as a sum while paired electrons will have a value of 0 because of a $+ \frac{1}{2}$ and $- \frac{1}{2} = 0$. The higher the numbers from multiplicity, the more stable the atom.

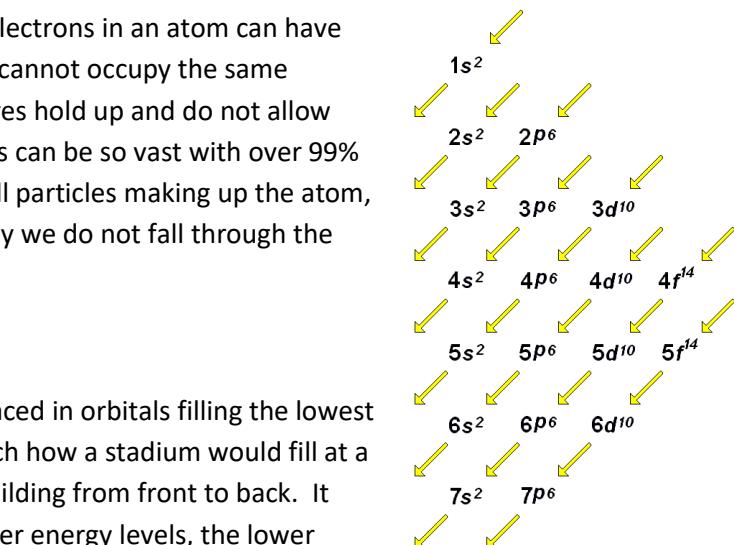


Figure 15 – The order in which orbitals are filled according to the Aufbau principle

Element	Total Electrons	Orbital Diagram				Electron Configuration
		1s	2s	2p	3s	
Li	3	↑↓	1			1s ² 2s ¹
Be	4	↑↓	1↓			1s ² 2s ²
B	5	↑↓	1↓	1		1s ² 2s ² p ¹
C	6	↑↓	1↓	1 1		1s ² 2s ² p ²
N	7	↑↓	1↓	1 1 1		1s ² 2s ² p ³
Ne	10	↑↓	1↓	1 1 1 1		1s ² 2s ² p ⁶
Na	11	↑↓	1↓	1 1 1 1 1	1	1s ² 2s ² 2p ⁶ 3s ¹

Figure 16 – A sample of orbital diagrams.

Electron Configurations

Electron configurations are methods of indicating the arrangements of electrons about a nucleus. A typical electron configuration consists of numbers and letters representing the energy level, orbital type and the number of electrons in the orbitals (see Figure 17).

To complete the electron configurations, you only need to determine the number of orbitals and energy levels that are occupied by the electrons and how many electrons exist within each energy level. To check that you have completed the electron configurations properly, the sum of the superscripts of all the orbital pieces should equal the total number of electrons. Below are sample electron configurations for some elements (see Figure 18).

Some of the electron configurations get rather long as you can see from the examples below. There is a shorter method to completing the electron configurations as well. You can create a shorter example by determining the closest noble gas (going backwards) from your element and place that gas's symbol in square brackets. Then add in the electron configurations as you would (see Figure 18). It is as if you are saying, the electron configuration for the noble gas and the valence shell electrons of the element of interest.

oxygen	$1s^2 2s^2 2p^4$
calcium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
lead	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^2$
nitrogen	$[He] 2s^2 2p^3$
chlorine	$[Ne] 3s^2 3p^5$
iron	$[Ar] 4s^2 3d^6$

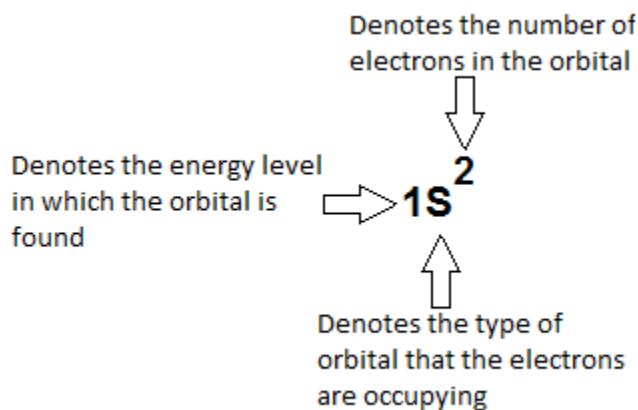


Figure 17 – This shows the standard format for the electron configurations with the energy level, type of orbital, and number of occupying electrons within the orbital.

Figure 18 – The diagram has three electron configurations in expanded form and three in condensed form.