

Atomic Theory

Our universe is formed of radiant energy and matter. Matter assumes different forms called *substances*. The science of chemistry attempts to describe the properties of substances and the reactions that convert them into other substances.

The Development of the Atomic Theory of Matter

Near the beginning of the 19th century, the **law of simple multiple proportions** was enunciated by the English physicist and chemist, *Dalton*, stating that the weights of the constituents (elements) of substances are in the ratio of small integers. Dalton hypothesized that each certain element consists of small, identical particles, which he called atoms, and explained the law of constant proportions by theorizing that atoms of particular elements combine in definite proportions to form specific compounds.

It was discovered later that some compounds could be decomposed by electric current and that a certain quantity of electric current was required to decompose a certain amount of a particular substance (compound). This led researchers to theorize that electricity consisted of units of charge that were particles (electrons), and that atoms contained such particles along with other oppositely charged particles (protons).

Late in the 19th century, *J.J. Thompson*, an English researcher, developed an experiment utilizing cathode rays to determine the charge to mass ratio of the electron. *R.A. Millikan*, an American, devised an experiment showing that all electrical charges are integral multiples of a definite, elementary unit, which he quantified:

$$\text{electron charge: } -1.6 \times 10^{-19} \text{ C}$$

Still, scientists did not have a clear idea of what the atom looked like. The English researcher, *Ernest Rutherford*, provided clearer focus when he bombarded a thin sheet of gold foil with alpha rays (beams of helium nuclei). If atoms were uniformly dense, as he expected, all of the rays would have passed directly through. That did not occur. He recorded a few large deflections, very few when compared to the total number of alpha particles emitted. He made sense of his results by postulating that most of the mass of the atom is concentrated in a very small particle, which he termed the *atomic nucleus*. The nucleus contains the positively charged protons (and also neutrons in most atoms) with electrons orbiting about it. Compared to the total volume of the atom, which is determined by the orbital space of the electrons, the volume of the nucleus is minute. For the most part, matter is filled with empty space!

Quantum Theory: The arrival of quantum theory marks a departure from classical Newtonian physics. Before the twentieth century, phenomena such as electrical charge or light were conceived of as continuously divisible quantities. With quantum theory, we have the principle that certain physical quantities can only assume discrete quantities. For example, charge cannot have magnitude less than $1.6 \times 10^{-19} \text{ C}$. Amounts of electrical charge, then, are always integral multiples of this quantity.

The initial introduction of quantum theory is credited to *Max Planck*. At the turn of the century, physics was unable to explain certain characteristics of the curves of energy against wavelength for light emitted when a *black-body* is heated up (A black-body is an

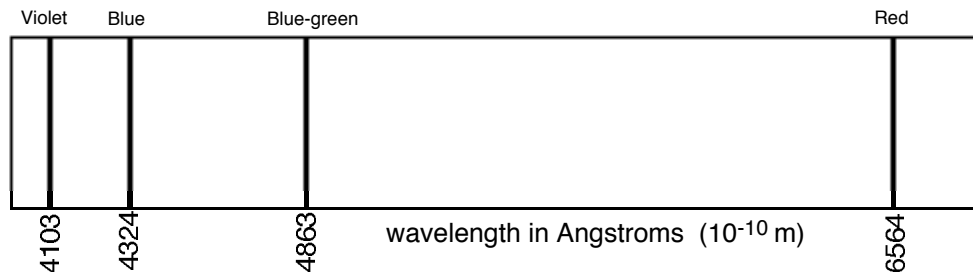
object that only absorbs and emits (does not reflect) electromagnetic radiation). Planck discarded the notion that the body could gain or lose energy continuously. He suggested that its energy could change only by discrete amounts. His explanation was that light energy comes in discrete packages called *quanta*, or *photons*. The energy of a quanta is proportional to the frequency of radiation:

$$E = h\nu$$

In the above equation, ν is equal to the frequency (Hz or sec^{-1}) and h is the constant of proportionality, an extremely important one, called *Planck's constant*:

$$\text{Planck's constant} = h = 6.63 \times 10^{-34} \text{ J s}$$

Bohr's Model of the Hydrogen Atom: When the atoms of a particular element are excited by high temperature or electrical energy, they give off light that can be diffracted into a distinctive pattern of lines. Instead of obtaining a **continuous spectrum**, containing light of all wavelengths, one obtains a **line spectrum**, where only particular wavelengths are represented. Below is the portion of the line spectrum in the visible region for the element hydrogen:



If the electron in orbit about the hydrogen atom obeyed the laws of classical physics, the emission spectrum of the hydrogen atom would be continuous like a rainbow. Electromagnetic waves, photons of light, are produced when a charge oscillates within an electric field, such as an electron in orbit within the positive proton's electric field. To account for the occurrence of the line spectrum, Bohr assumed that the hydrogen atom can only exist in certain discrete states. These he called the *stationary states* of the atom. The one representing the lowest possible energy for the atom is called the *ground state* and all others are called *excited states*. When an electron falls from an excited state to one of less energy, it releases a photon whose energy represents the difference between the two states. The equation describing this relationship is called the **Bohr frequency rule**:

$$h\nu = E'' - E'$$

Bohr explained the quantity of particular energy differences in the emission spectrum of hydrogen by postulating that the angular momentum of the electron has values that are integral multiples of $h/2\pi$. Or in other words, the angular momentum (mvr) = $n h/2\pi$ where $n = 1, 2, 3, \dots$. From this, Bohr derived the equation for the energy of a particular state:

$$E = - \frac{2\pi^2 m Z^2 e^4}{n^2 h^2}$$

m = mass of electron
 Z = atomic number
 e = charge of electron
 n = positive integer (1, 2, 3 . . .)
 h = Planck's constant

Quantum Numbers and Electron Orbitals: Innumerable difficulties were encountered when Bohr's theory was extended to more complicated (higher atomic number) atom systems. There are major flaws in the theory, especially in that according to the *Heisenberg Uncertainty Principle*, one cannot describe the exact orbit of an electron concurrently with its exact momentum, which Bohr's theory does.

These and other problems were resolved with the approach of *wave mechanics* developed by *Louis de Broglie* and *Erwin Schroedinger*. The currently accepted theory of the behavior of electrons in atoms, the theory characterizes electrons, like photons, as possessing both particle and wave nature. Schroedinger obtained a set of mathematical functions, called *wave functions*, which describe the spatial orientations and energies of electron waves (The mathematics is too complicated to analyze here). Each possible electron wave is called an *orbital*. Each orbital possesses a characteristic energy and describes the region of space around the nucleus that is the electron's most probable location.

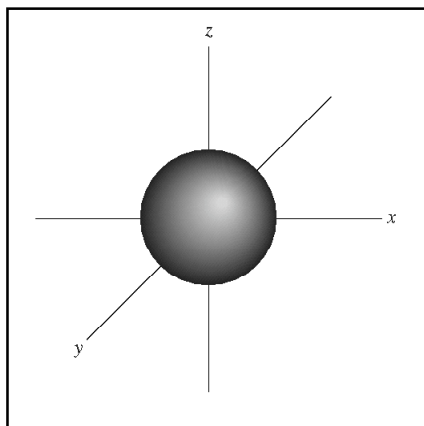
The allowed wave functions are characterized by three quantum numbers:

n = principle quantum number

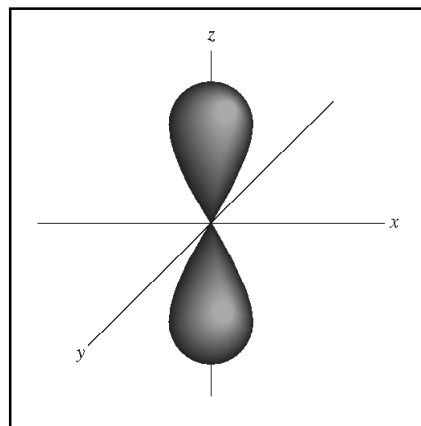
The energy of the electron in an atom mainly depends on the principle quantum number, n , which can have values 1,2,3 . . . The higher this number, the greater the energy of the electron and the larger the orbital. Orbitals with the same quantum number, n , are said to belong to the same *shell*. Electron shells are designated with the letters *K, L, M, N* and so on. 1 = *K*, 2 = *L*, 3 = *M*, 4 = *N*, etc.

l = angular momentum quantum number

This number may also sometimes be referred to as the *azimuthal quantum number*. It determines what type of *subshell* contains the electron. The number of possible values of this quantum number is constrained by the energy of the electron, determined mainly by the principle quantum number, n , and the higher the value of n , the greater the possible values of, l . For a given value of n , l can be any integer: 0,1,2 . . . $n - 1$. So an electron with principle quantum number $n = 1$ could have only one possible value for l (0), while an electron with principle quantum number $n = 2$ could have one of two possibilities (0 or 1). The angular momentum quantum number, l , determines the shape of the electron wave. Subshells are designated with letters corresponding to values of l : 0 = *s*, 1 = *p*, 2 = *d*, 3 = *f*, etc. Illustrated below are the characteristic shapes of orbitals found in an *s* or *p* subshell.



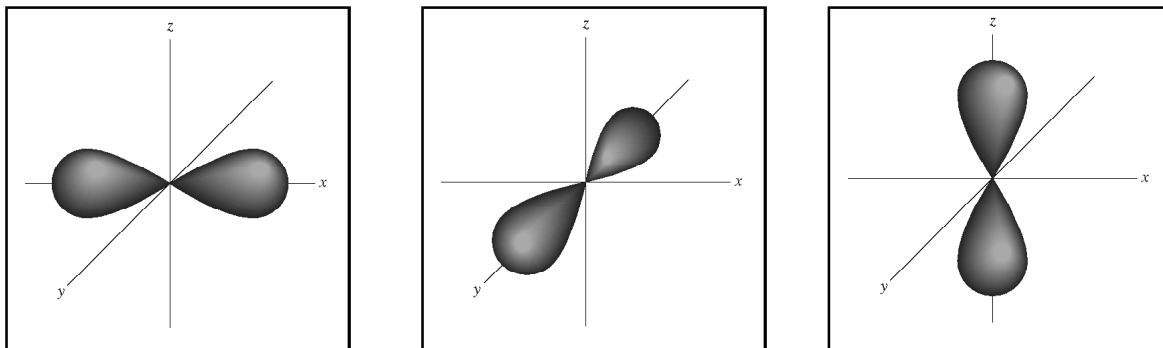
s orbital



p orbital

$m_l =$ magnetic quantum number

For an electron, this quantum number determines the specific orbital for a given set of quantum numbers n and l . The magnetic quantum number can have values of any integer between l and $-l$. For an s subshell ($l = 0$), m can only be 0, but for a p subshell ($l = 1$), m_l can be 1, 0 or -1. Therefore, an s subshell contains only one orbital while a p subshell contains three (and the d subshell has five). Orbitals of a given subshell are differentiated by their orientation in space. Pictured below are the shapes of the three p orbitals:



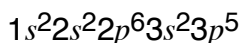
$m_s =$ spin quantum number

There is a fourth quantum number, which is not predicted by Schrodinger's wave equation. This number is m_s , the spin quantum number, which differentiates electrons within the same orbital. The spin quantum number arises because electrons rotate about an axis to produce a magnetic field that can have one of two orientations. There are two possible values of this quantum number, $+1/2$ or $-1/2$.

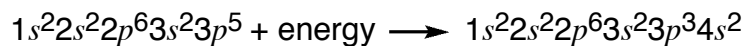
The Pauli Exclusion Principle: According to this principle, no two electrons within an atom can have the same four quantum numbers. A particular atomic orbital, determined by n , l , and m_l , can therefore contain only two electrons, because the spin quantum number, m_s , has only two possible values. We can see from this that each subshell can hold twice as many electrons as the number of orbitals in the subshell:

Subshell	Number of Orbitals	Maximum Number of Electrons
$s (l = 0)$	1	2
$p (l = 1)$	3	6
$d (l = 2)$	5	10
$f (l = 3)$	7	14

The Electron Configuration of Atoms: The *electron configuration* is a method of accounting for electrons among available subshells in an atom. For a particular subshell, the principle quantum number denoting the shell is given first. This is followed by the letter denoting the subshell. After this is written a superscript giving the amount of electrons in the subshell. According to the *Aufbau principle*, the ground state of an atom is represented by filling the subshells of lowest energy first. The *building-up order* is as follows: $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p$ etc. (This is very predictable up to $4s$, which proceeds $3d$. To obtain the order quickly, add the values of n and l . The subshell with the lowest total is filled first.) We give here as an example the ground state electron configuration of chlorine (atomic number = 17):



An *excited state* of the electrons of an atom occurs when the input of some type of energy causes one or more electrons to occupy orbitals other than the lowest available to them. For example with the chlorine atom:



Hund's Rule: Applied to ground states, this rule states that electrons entering a subshell will spread out over available orbitals with their spins in the parallel direction. In other words, within a subshell, every orbital will be occupied by one electron before any orbital is occupied by two, and the electrons in the singly occupied orbitals will have their spins in the same direction. The *orbital diagram* of oxygen (atomic number = 8) in the ground state would be as follows:

