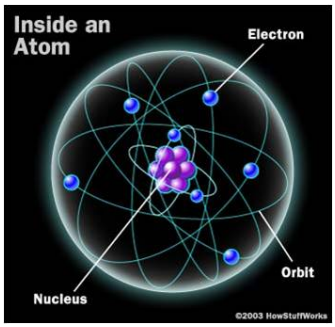
HISTORY OF THE ATOM FROM DEMOCRITUS TO BOHR AND SCHRÖDINGER



DEMOCRITUS'S ATOMIC THEORY

This is the Greek philosopher Democritus who began the search for a description of matter more than 2400 years ago. He asked: Could matter be divided into smaller and smaller pieces forever, or was there a limit to the number of times a piece of matter could be divided?

His theory: Matter could not be divided into smaller and smaller pieces forever, eventually the smallest possible piece would be obtained. This piece would be indivisible. He named the smallest piece of matter "atomos," meaning "not to be cut."

To Democritus, atoms were small, hard particles that were all made of the same material but were different shapes and sizes. Atoms were infinite in number, always moving and capable of joining together.

DALTON'S ATOMIC THEORY

John Dalton (1766-1844) was such a brilliant youth that he became an English shool teacher when barely 12 years old.

He proposed the Atomic theory of matter based on his experimental observations. The main postulates of Dalton's atomic theory are as follows.

To Dalton :

- **All matter is made of atoms. Atoms are indivisible and indestructible.**
- **All atoms of a given element are identical in mass and properties.**
- **Compounds are formed by a combination of two or more different kinds of atoms.**

- **A chemical reaction is a rearrangement of atoms.**

- **Atoms can be neither created nor destroyed.**

The Billiard Ball

THOMSON'S ATOMIC THEORY

Thomson's atomic theory proposed a model of atom which is known as plum pudding model or Christmas pudding or chocolate chip cookie model.

Till the end of the nineteenth century the concept of atom was similar to a small solid billiard ball.

In the year 1897 Joseph John Thomson (1856–1940) totally changed the view of an atom by discovering electron. Thomson's atomic theory suggested that the atom is not indivisible as it was of smaller pieces – electrons and protons.

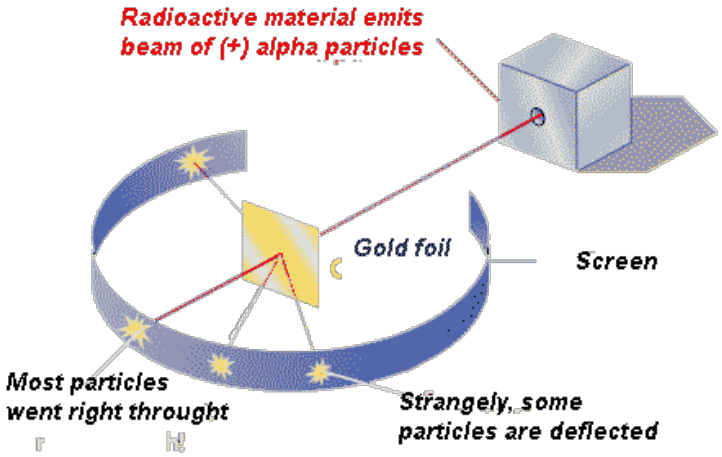
- **An atom consists of a sphere of positive charge with negatively charged electron embedded in it.**

- **The positive and the negative charges in an atom are equal in magnitude, due to which an atom is electrically neutral. It has no over all negative or positive charge.**

The Plum Pudding

RUTHERFORD'S ATOMIC THEORY

100 years ago, on March 7, 1911, Ernest Rutherford (1871–1937) presented a paper to the Manchester Literary and Philosophical Society accurately describing the structure of the atom. Based on an experiment he had performed - with totally unexpected results - he realized that the atom must have almost all of its mass concentrated at its center, in a nucleus, with the vast majority of the atom consisting chiefly of empty space.



Two years earlier, in 1909, he had conducted an experiment with two other scientists, in which they studied the deflection angles of "alpha particles" that they shot through a microscopically thin layer of gold. Alpha particles are just helium atoms stripped of their 2 electrons.

He showed that while the nucleus contains virtually all of the mass of the atom, it only takes up one-billionth of the volume of the atom, an inconceivably tiny amount. Much smaller particles - electrons - orbit the nucleus at a great distance, relatively speaking.

Structure of the Atom 3: The Rutherford Model

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Rutherford analogized his version of the atom, in contrast to the Thomson's atom, to a fly in a cathedral; it has since become known as the planetary model because electrons orbit the nucleus like planets around the Sun.

BOHR'S ATOMIC THEORY

Bohr

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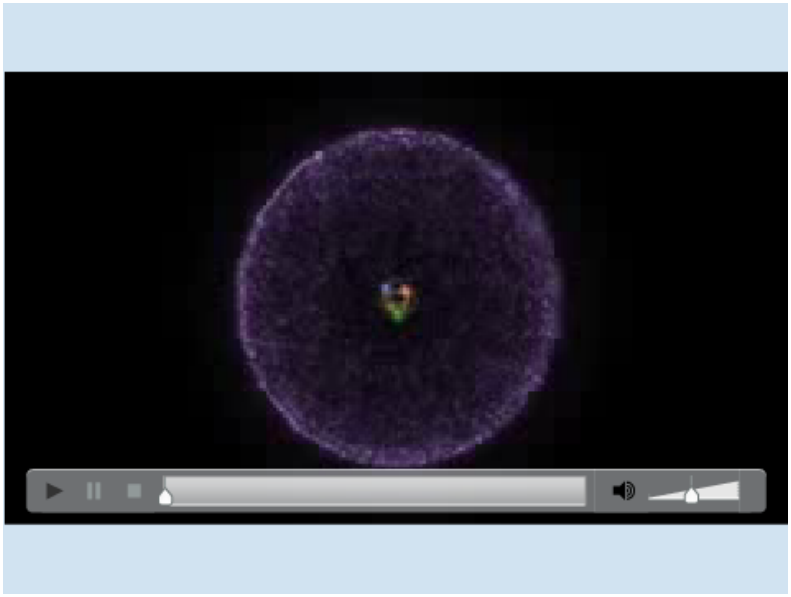
Neils Bohr (1885–1962) refined Rutherford's model in 1913 by proposing that electrons:

- **orbit the nucleus without losing energy;**
- **could move only in fixed orbits of specific energies.**
- **Electrons with low energy would orbit closer to the nucleus while electrons with high energy orbit further from the nucleus.**

In 1932, James Chadwick identified the neutron. The particle proposed by Rutherford as having significant mass and no charge. With the discovery of the neutron three subatomic particles were identified that would help explain observations made at the atomic level. One observation was the existence of radioactive variances of the same element.

How could two atoms of the same element have identical chemical properties but one be radioactive and the other not? A British scientist Frederick Soddy who made this observation called varieties of the same element isotopes.

Chadwick was now able to explain the existence of isotopes through his discovery of the neutron. Isotopes of the same element have the same number of protons and electrons but differ in the number of neutrons found in their nucleus.



The Quantum Model of the Atom

Although the Bohr model adequately explained how atomic spectra worked, there were several problems that bothered physicists and chemists:

- **Why should electrons be confined to only specified energy levels?**
- **Why don't electrons give off light all of the time?**
- **As electrons change direction in their circular orbits (i.e., accelerate), they should give off light.**
- **The Bohr model could explain the spectra of atoms with one electron in the outer shell very well, but was not very good for those with more than one electron in the outer shell.**
- **Why could only two electrons fit in the first shell and why eight electrons in each shell after that? What was so special about two and eight?**

Obviously, the Bohr model was missing something!

In 1924, a French physicist named Louis de Broglie suggested that, like light, electrons could act as both particles and waves. De Broglie's hypothesis was soon confirmed in experiments that showed electron beams could be diffracted or bent as they passed through a slit much like light could. So, the waves produced by an electron confined in its orbit about the nucleus sets up a standing wave of specific wavelength, energy and frequency (i.e., Bohr's energy levels) much like a guitar string sets up a standing wave when plucked.

Another question quickly followed de Broglie's idea. If an electron traveled as a wave, could you locate the precise position of the electron within the wave? A German physicist, Werner Heisenberg, answered no in what he called the uncertainty principle:

- **To view an electron in its orbit, you must shine a wavelength of light on it that is smaller than the electron's wavelength.**
- **This small wavelength of light has a high energy.**
- **The electron will absorb that energy.**

- **The absorbed energy will change the electron's position.**

We can never know both the momentum and position of an electron in an atom. Therefore, Heisenberg said that we shouldn't view electrons as moving in well-defined orbits about the nucleus!

With de Broglie's hypothesis and Heisenberg's uncertainty principle in mind, an Austrian physicist named Erwin Schrödinger derived a set of equations or wave functions in 1926 for electrons. According to Schrodinger, electrons confined in their orbits would set up standing waves and you could describe only the probability of where an electron could be. The distributions of these probabilities formed regions of space about the nucleus were called orbitals. Orbitals could be described as electron density clouds. The densest area of the cloud is where you have the greatest probability of finding the electron and the least dense area is where you have the lowest probability of finding the electron.

Electrons can be labelled using the subshell and orbital or by using the four quantum numbers:

- **n : principal quantum number**
- **l : azimuthal or angular quantum number**
- **m_l : magnetic quantum number**
- **m_s : spin quantum number**

Principal Quantum Number, n

The principal quantum number, n, is always a positive integer and describes the SIZE of the orbital. Since the distance from of an electron from the nucleus is directly proportional to the energy of the electron (as described in the Bohr model), the principal quantum number is also a measure of the orbital.

Azimuthal or Angular Quantum Number, l

The azimuthal or angular quantum number describes the SHAPE of the orbital.

- **The s orbitals are spherical (l = 0).**
- **The p orbitals are polar (l = 1).**
- **The d orbitals are clover-leaf shaped (l = 2).**

Magnetic Quantum Number, m_l

The magnetic quantum number, m_l, describes an orbital's ORIENTATION in space.

- **For s orbitals (l = 0), there is only one orientation possible, so m must equal 0.**
- **For p orbitals (l = 1), there are three possible orientations, so m can be -1, 0, or 1.(see picture below)**
- **For d orbitals (l = 2), there are five possible orientations, so m can be -2, -1, 0, 1, or 2.**

Spin Quantum Number, m_s

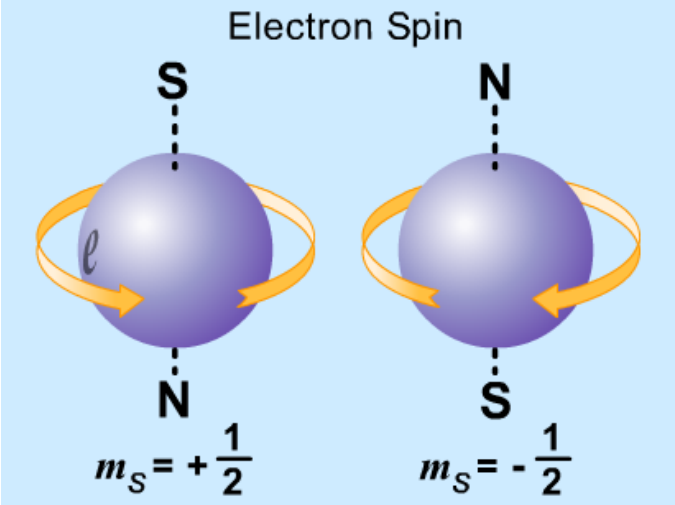
The spin quantum number, m_s, tells us the SPIN or direction (clockwise or counter-clockwise) in which an electron spins. If there are two electrons in any one orbital, they will have opposite spins, that is, one will have for m_s a value of +½ (↑) and the other will have a value of -½ (↓).
The maximum number of electron in any one orbital is two.

Rules for Allowable Combinations of Quantum Numbers

The three quantum numbers (n, l, and m) that describe an orbital must be integers.

- **"n" cannot be zero. "n" = 1, 2, 3, 4...**
- **"l" can be any integer between zero and (n-1). e.g. If n = 4, l can be 0, 1, 2, or 3.**

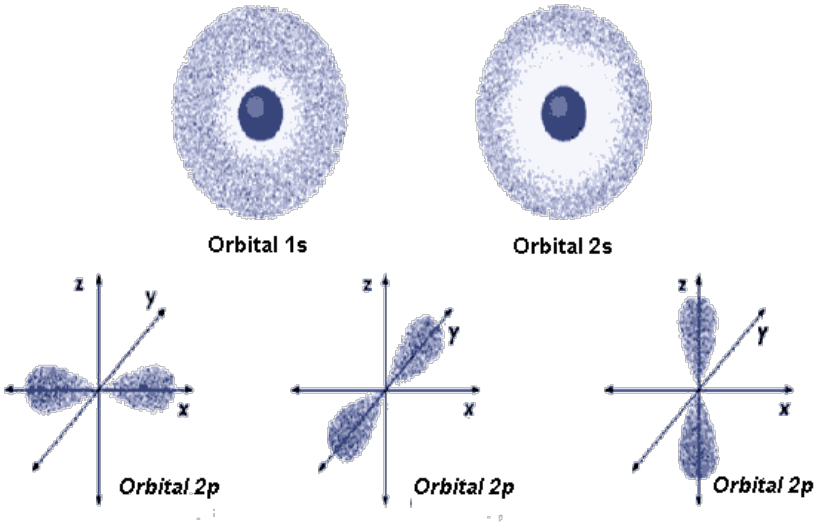
- **"m" can be any integer between -l and +l. e.g. If l = 2, m can be -2, -1, 0, 1, or 2.**
- **"s" is arbitrarily assigned as + or -, but for any one subshell (n, l, m combination), there can only be one of each.**



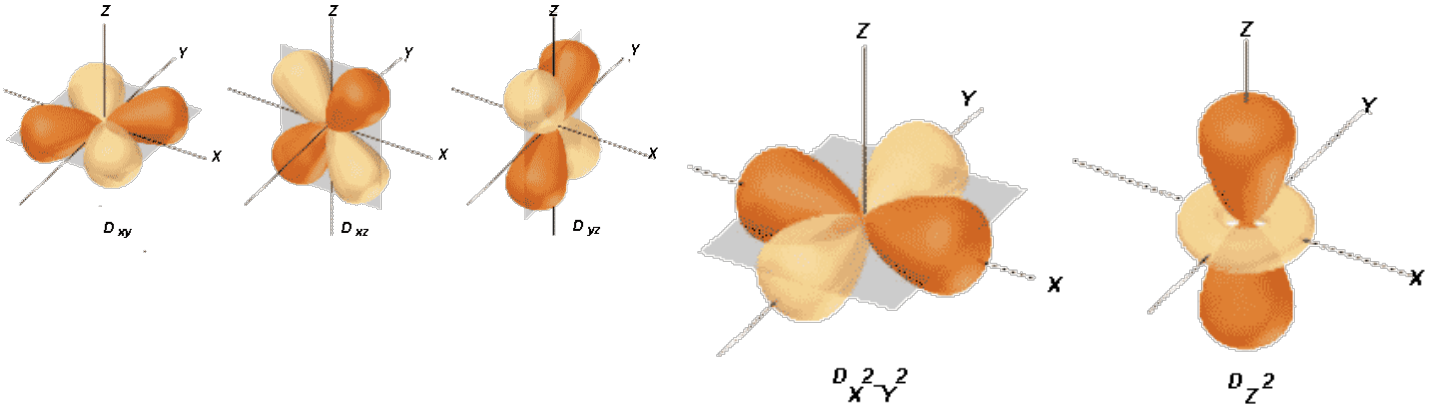
TYPES OF ORBITALS: s,p,d y f

Corresponding to the fixed number n indicating the energy level, you have the following orbitals:

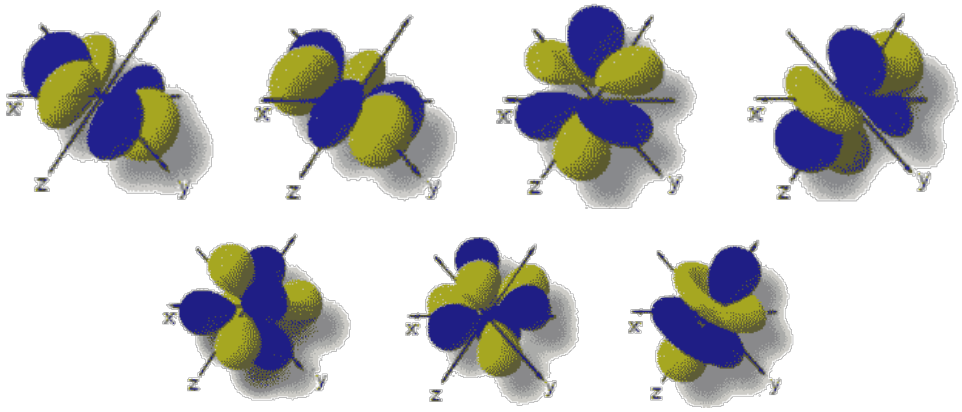
l = 0 orbital s (can hold up to $2e^-$) **l = 1, l = -1 orbital p (can hold up to $6e^-$)**



l = 2 orbital d (can hold up to $10e^-$)

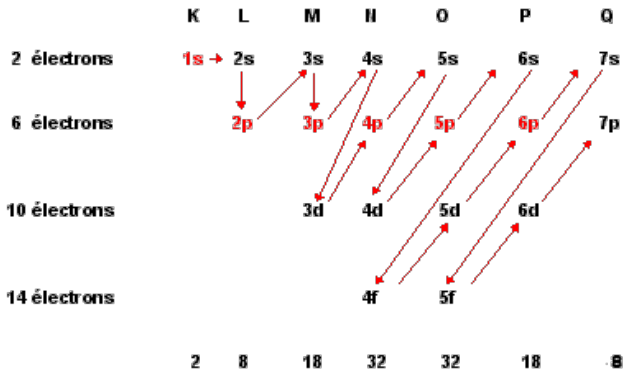


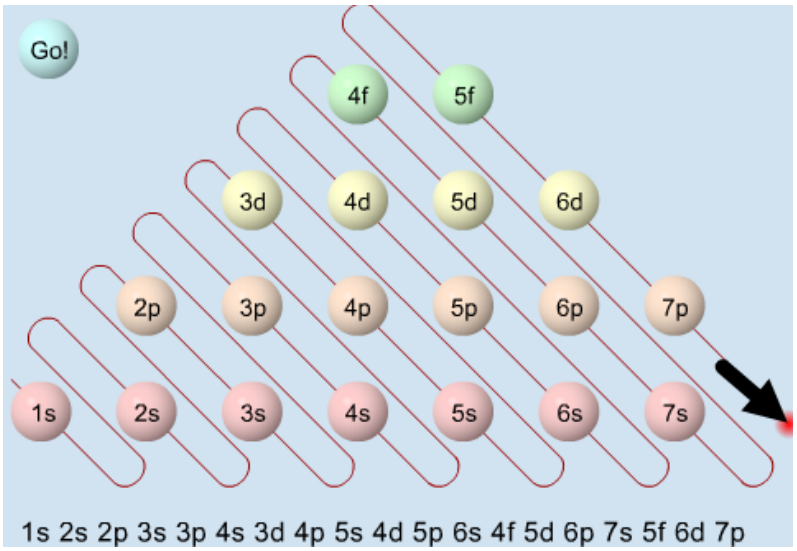
l = 3 orbital f (can hold up to 14e$^-$)



DIAGONAL RULE

In chemistry, the Diagonal Rule (also known as Madelung's Rule or Aufbau Principle) is a guideline explaining the order in which electrons fill the orbital levels. The $1s^2$ orbital is always filled first, and it can contain 2 electrons. Then the $2s^2$ level is filled, which can also hold 2 electrons. After that, electrons begin to fill the $2p^6$ orbital, and so on. The diagonal rule provides a rule stating the exact order in which these orbitals are filled, and looks like this:





There are some exceptions to the to the diagonal rule:

The first is chromium (Z = 24), the diagonal rule predicts the an electron configuration of [Ar]3$d^4$4s^2 but experimentally we find it to be [Ar]3$d^5$4s^1.

The next exception found is that of copper (Z = 29), the predicted electron configuration is [Ar]3$d^9$4s^2 but experimentally we find it to be [Ar]3d^{10}4s^1. .

The reason for these and other exceptions are not completely understood, but it seems that a half-filled 3*d* subshell in the case of chromium or a completely-filled 3*d* subshell in the case of copper lend a special stabilty to the observed electron configurations. There is no need to dwell on these exceptions, the point to remember is that the diagonal rule predicts the correct electron configuration most of the time and that the energy of the predicted electron configuration is very close to the ground state energy.

For more information, click on orbit and on history_of_the_atom

Please, address any remarks or comments to Prof Mokeur

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