ELECTRONIC STRUCTURE OF ATOMS

Elements that exhibit similar properties are placed together in the same column of the periodic table.

What is the fundamental reason for observation?

When atoms react, it is the electrons that interact. Understanding the behavior of electrons helps one answer the above question.

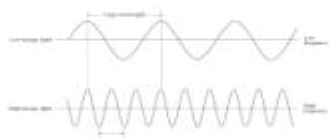
The arrangement of electrons in at atom is called its **electronic structure**.

First we must understand light. The light that we can see with our eyes, visible light, is a type of electromagnetic radiation.

Electromagnetic radiation carries energy through space and is therefor also known as *radiant energy.*

All types of electromagnetic radiation move through a vacuum at a speed of 3.0 x 10^8 M/sec.

The Wave Nature of light



The product of frequency of the radiation, ν, and wavelength, λ, equals the speed of light

$\nu \lambda = c$

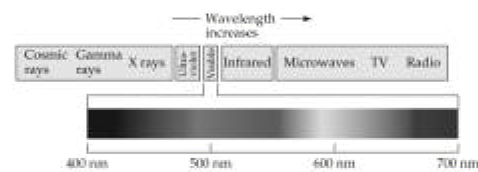


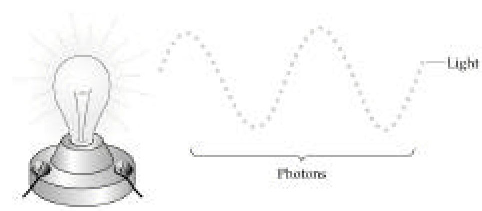
TABLE 6.1 Common Wavelength Units for Electromagnetic Radiation

Unit	Symbol	Length (m)	Type of Radiation
Angstrom	Å	10^{-10}	X ray
Nanometer	nm	10^{-9}	Ultraviolet, visible
Micrometer	μm	10^{-6}	Infrared
Millimeter	mm	10^{-3}	Infrared
Centimeter	cm	10^{-2}	Microwave
Meter	m	1	TV, radio

When solids are heated, they emit radiation, as seen in the red glow of an electric stove burner and the bright light of a tungsten light bulb.

The wavelength distribution of the radiation depends on the temperature, "red hot" object being cooler than a "white hot".

In the late 1800s physicists were studying this phenomenon, trying to understand the relationship between the temperature and the intensity wavelengths of the emitted radiation.



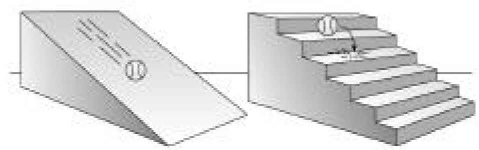
THE QUANTUM CONCEPT

1900, Max Planck proposed that radiant energy is not continuous, but rather, the radiation is emitted in small bundles. He assumed that energy can be released or absorbed by atoms only in "chunks" of some minimum size. Plank gave the name quantum (fixed amount) to the smallest quantity of energy that can be emitted or absorbed as electromagnetic radiation ($6.63x10^{-34}$J-s).

The energy, E, of a single quantum equals a constant times its frequency:

$$E = h\nu$$

The idea that energy is released in discrete unit is referred to as the quantum concept .

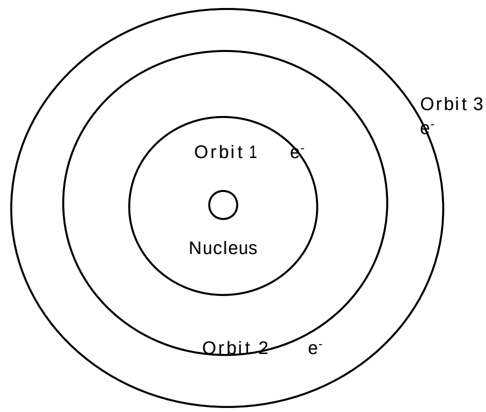


THE PHOTOELECTRIC EFFECT

In 1905 Albert Einstein used Plank's quantum theory to explain the photoelectric effect.

When a photon strikes a metal, its energy is transferred to an electron in the metal. A certain amount of energy is required for the electron to overcome the attractive forces that hold it within the metal.

The idea that the energy of light depends on its frequency helps us under stand the diverse effects that different kinds electromagnetic radiation have on matter.



BOHR'S MODEL OF THE HYDROGEN ATOM

1913, Bohr speculated that electrons orbit around the atomic nucleus just as planets circle around the Sun.

He suggested that the electron orbits were at a fixed distance from the nucleus and had a definite energy.

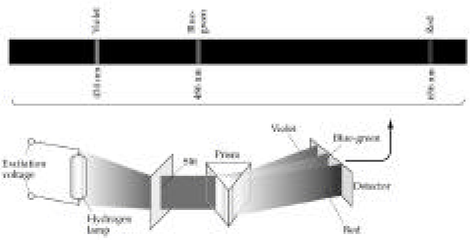
The electron was said to travel in a fixed-energy orbit that was referred to as an energy level.

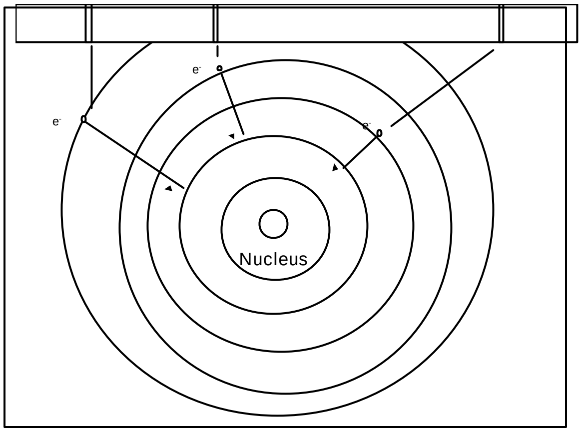
According to classical physics, however, an electrically charged particle that moves in a circular path should continuously lose energy by emitting electromagnetic radiation. As the electron loses energy, it should spiral into the nucleus.

Evidence For Electrons In Fixed-energy Levels

The collection of narrow bands of light energy is referred to as an **emission line spectrum**, and the individual bands of light are called spectral lines.

The concept of electron energy levels is supported by spectral lines.





Borh proposed that only orbits of certain radii, corresponding to certain definite energies, are permitted.

An electron in a permitted orbit has a specific energy and is said to be an "allowed" energy state.

An electron in an allowed energy state will not radiate energy and therefore will not spiral into the nucleus.

Bohr showed that the electron could circle the nucleus only in orbits of certain specific radii. The allowed orbits have specific energies, given by a simple formula:

$$E_n = (-R_H)\left(\frac{1}{n^2}\right) \qquad n = 1, 2, 3, 4, \ldots$$

The R_H is called the Rydberg constant and has the value of $2.18 x 10^{-18}$ J. The integer n, which can have values from 1 to infinity, is called the principal quantum number. Each orbit corresponds to a different value of *n*, and the radius of the orbit gets larger as *n* increases.

As n gets larger, the energy becomes successively less negative and increases. As n becomes infinitely large a point is reached in which the electron is completely separated from the nucleus. The energy for n= ∞ becomes

$$E_\infty = (-2.18\,x10^{-18}\,J)\left(\frac{1}{\infty^2}\right) = 0$$

The state in which the electron is removed is the reference, zero-energy state of the hydrogen atom.

Bohr made one more startling assumption: He assumed that the electron could "jump" from one allowed energy state to another by absorbing or emitting photons of radiant energy of certain specific frequencies.

The frequency,ν, of the radiant energy corresponds exactly to the energy difference between the two states.

If the electron jumps form an initial with energy E_i to a final state with energy E_f, the following equality will hold:

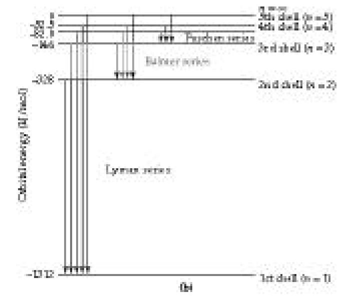
$$\Delta E = E_f - E_i = h\nu$$

$$E_n = \left(-R_H\right)\left(\frac{1}{n^2}\right)$$

$\Delta E = E_f - E_i = h\nu$

The above two equations can be combined to find the relationship between the frequency of absorbed or emitted light the principal quantum numbers of the two states.

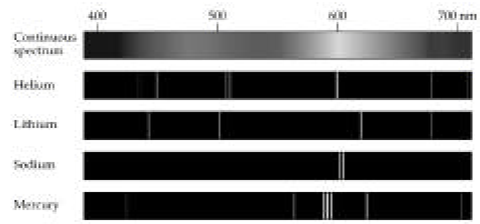
$$n = \frac{\Delta E}{h} = \left(\frac{R_H}{h}\right)\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$



Atomic Fingerprints

The study of emission spectra revealed that each element produced a unique set of spectral lines.

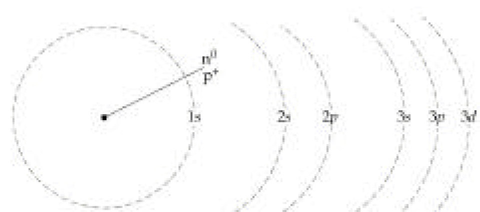
This observation indicated that the energy levels must be unique for atoms of each element. A line spectrum is used as an “atomic fingerprint.”



The model proposed by Niels Bohr was supported experimentally by the emission spectrum of hydrogen.

The emission spectrum of other elements besides hydrogen had far too many lines to interpret.

The model that eventually emerged had electrons occupying a **energy sub-level** within a main energy level. These energy sub-levels were designated s, p, d, and f in reference to the *sharp*, *principal, diffuse,* and *fine* lines in the emission spectra of the elements.

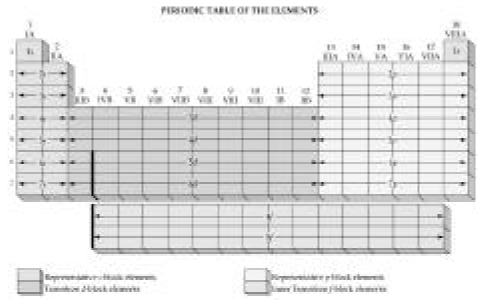


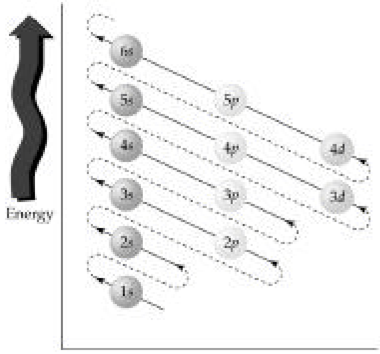
S sublevel = 2 e^-

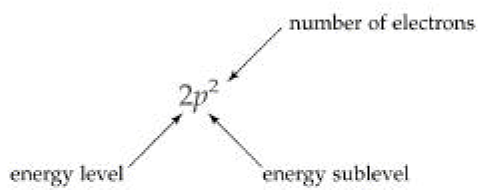
p sublevel = 6 e^-

D sublevel = 10 e^-

f sublevel = 14 e^-







Order of electron filling

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

The electron configuration of an atom is a shorthand statement for describing the location of the electrons by sublevel. First, the sublevel is written, followed by a superscript that indicates the number of electrons.

Ne: $1s^2$ $2s^2 2p^6$

Cl: $1s^2$ $2s^2 2p^6$ $3s^2 3p^5$

C: $1s^2$ $2s^2 2p^2$

Cu: $1s^2$ $2s^2 2p^6$ $3s^2 3p^6$ $4s^2 3d^9$

Order of electron filling

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

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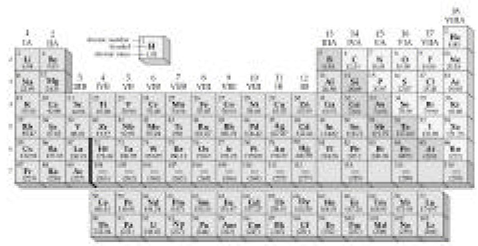
Cu: $1s^2$ $2s^2 2p^6$ $3s^2 3p^6$ $4s^2 3d^9$

VALENCE ELECTRONS

When an element undergoes a chemical reaction only the outermost electrons are involved. These electrons are the highest in energy and farthest from the nucleus. The outermost electrons are called **valence electrons**. The number of valence for an element can be determined from the periodic table.



THE WAVE BEHAVIOR OF MATTER

Following Bohr's development of a model for the hydrogen atom, the dual nature of radiant energy be came a familiar concept. Louis De Broglie suggested that the electron in its movement about the nucleus has associated with it a particular wavelength. The wavelength of the electron or of any particle depends on its mass, m, and velocity,v:

$$l = \frac{h}{mn}$$

THE UNCERTAINTY PRINCIPLE

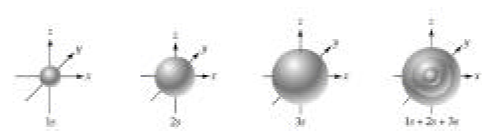
The German physicist Werner Heisenberg concluded that the dual nature of matter places a fundamental limitation on how precisely we can know both the location and the momentum of any object. When applied to the electrons in an atom, this principle states that it is inherently impossible for us to know simultaneously both the exact momentum of the electron and its exact location in space. Thus, it is not appropriate to imagine the electrons as moving in well-defined circular orbits about the nucleus.

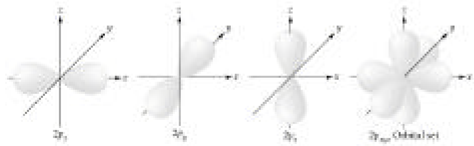
QUANTUM MECHANICS AND ATOMIC ORBITALS

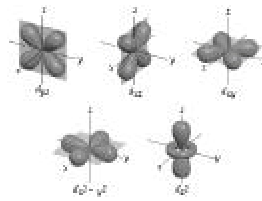
In 1926 Schrödinger proposed an equation that incorporates both the wavelike and particle-like behavior of the electron.

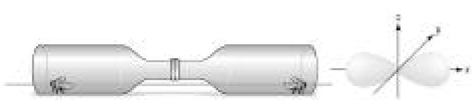
The complete solution to Schrödinger's equation yields a set of wave function and corresponding energies. These wave functions are called orbitals. Each orbital has a characteristic energy and shape.

This description gave rise to the quantum mechanical atom. A location within the atom where there is a high probability of finding a electron having a certain energy is called an orbital.









ORBITALS AND QUANTUM NUMBERS

The Bohr model introduced a single quantum number, *n*, to describe an orbit. The quantum mechanical model uses three quantum numbers, *n*, *l*, m_l to describe an orbital.

TABLE 6.2 Relationship Among Values of *n*, *l*, and m_l through $n = 4$

n	Possible Values of	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	1 *s*	0	1	1
2	0	2 *s*	0	1	
	1	2 *p*	1, 0, −1	3	4
3	0	3 *s*	0	1	
	1	3 *p*	1, 0, −1	3	
	2	3 *d*	2, 1, 0, −1,−2	5	9
4	0	4 *s*	0	1	
	1	4 *p*	1, 0, −1	3	
	2	4 *d*	2, 1, 0, −1, −2	5	
	3	4 *f*	3, 2, 1, 0,−1,−2,−3	7	16

Relationship Among Values of *n*, *l*, and m_l,

n	Possible Values of *l*	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitlas in Shell
1	0	1s	0	1	1
2	0 1	2s 2p	0 1,0,-1	1 3	4
3	0 1 2	3s 3p 3d	0 1,0,-1 2,1,0,-1,-2	1 3 5	9
4	0 1 2 3	4s 4p 4d 4f	0 1,0,-1 2, 1, 0,-1,-2 3, 2, 1, 0,-1,-2,-3	1 3 5 7	16

ELECTRON SPIN AND THE PAULI EXCLUSION PRINCIPLE

When scientists studied the line spectra of many-electron atom in detail, that noticed a very puzzling feature: lines that were originally thought to be single were actually closely spaced pairs. This meant that there were twice as many energy levels as there was supposed to be. They postulated that electrons have an property called electron spin. The quantum number m_s denotes electron spin and can have two values +½ and -½.

The Pauli exclusion principle states that not two electrons in an atom can have the same set of four quantum numbers n, l, m_l, and m_s.

For a a given orbital (1s, $2p_z$, and so forth), the values of n, l, and m_l, are fixed. Thus, if we want to put more than one electron in an orbital and satisfy the Pauli exclusion principle we must assign different m_s values to the electrons.

An orbital can hold a maximum of two electrons only if they have opposite spin.

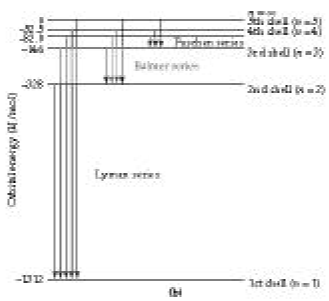
ORBITALS AND QUANTUM NUMBERS

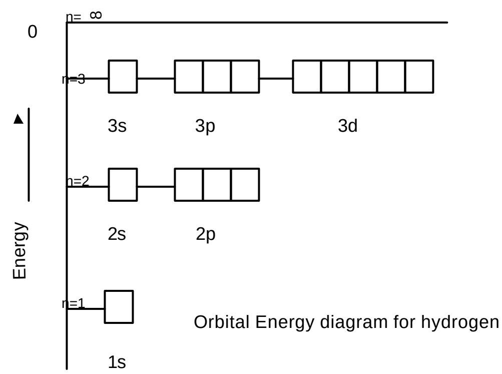
n = describes which primary energy level an electron is in.

l = describes the shape which the electron would trace out as it moves around the orbital that it's in.

m_l = describes the orientation of the orbital that the electron is in.

m_s = describes the spin of the electron.





Orbital Energy diagram for hydrogen

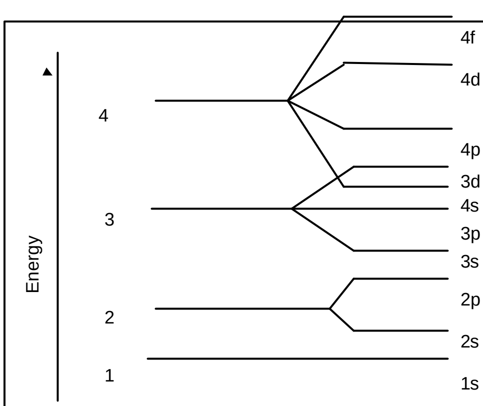
EFFECTIVE NUCLEAR CHARGE

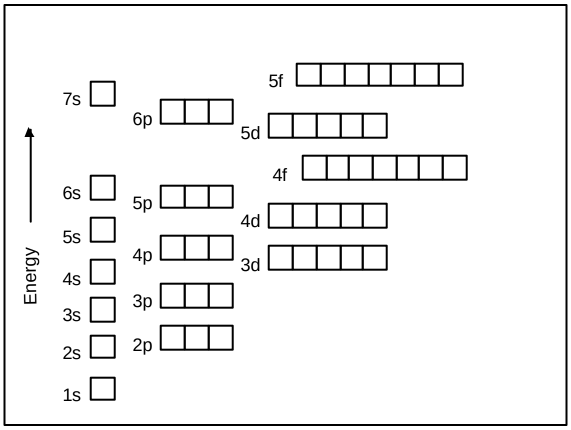
In a many electron atom, each electron is simultaneously attracted to the nucleus and repelled by the other electrons. The inner electrons are said to shield or screen the outer electron from the full charge of the nucleus.

The net positive charge attracting the electron is called the effective nuclear charge (Z_{eff}).

$$Z_{eff} = Z - S$$

Where Z equals the number of protons in the nucleus and S is the average number of electron that are between the nucleus and the electron in question.





HUND'S RULE

Within a given sublevel the order of filling is such that there is the maximum number of half-filled orbitals. The single electrons in these half-filled orbital have parallel spins.