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CHEMISTRY 311 Introduction to Quantum Chemistry- 3Hr. **Text: (1)** Atkins: Physical Chemistry **(2)** http://www.umich.edu/~chem461/ (3) Cotton and Wilkinson: Advanced Inorganic Chemistry

Quantum Chemistry

Review of the Atomic Theory and Electromagnetic waves, (electronic structure, Bohr's theory of atoms), Introduction of quantum mechanical concepts by reviewing of experiments which cannot be explained by classical physics, the beginning of wave mechanics (wave equation, Hamiltonian equation, meaning of the wave equation), the hydrogen atom, the hydrogen atom orbitals, with a basic treatment of angular momentum (states derived from electronic configurations), hydrogen atom orbitals (s, p ,d f orbitals), The states derived from electronic configurations, electron spin, exclusion principle, Aufbau principle, Hund's rule, ionization energy and electron affinity.

1.0 Review of the Atomic Theory

John Dalton developed the atomic philosophy of the Greeks into a true scientific theory in the early years of the 19th Century by providing evidence for the existence of atoms and applied the atomic theory to chemistry, providing a physical picture of how elements combine to form compounds consistent with the laws of definite and multiple proportions. After over 2000 years of speculation and reasoning from indirect evidence, it is now possible in a sense to actually see individual atoms by using scanning tunnel spectroscopic methods. The word "atom" comes from the Greek "atomos", literally meaning indivisible." Others works in later years have shown that this not true. Michael Faraday's work had suggested the electrical nature of matter and the existence of subatomic particles. This became evident with the discovery of radioactive decay by Henri Becquerel in 1896|the emission of alpha, beta and gamma particles from atoms. In 1897, J. J. Thompson identified the electron as a universal constituent of all atoms and showed that it carried a negative electrical charge, now designated e$^-$.

Rutherford probed the interior of atoms by bombing a thin sheet of gold with a stream of positively-charged alpha particles emitted by a radioactive source. Most of the high-energy alpha particles passed right through the gold foil, but a small number were strongly detected in a way that indicated the presence a small but massive positive charge in the center of the atom (fig.1.) Rutherford proposed an atomic model that consist of an electrically-neutral atom of atomic number Z consists of a nucleus of positive charge +Ze, containing almost the entire the mass of the atom, surrounded by Z electrons of very small mass, each carrying a charge ¡e. The simplest atom is hydrogen, with Z = 1, consisting of a single electron outside a single proton of charge +e.
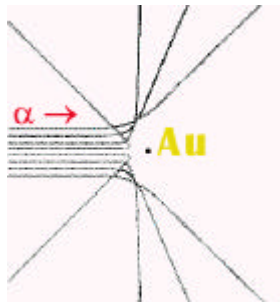
Figure 1. Rutherford trajectories of scattering of alpha particles by a gold nucleus

Chadwick clarified the structure of the nucleus of an atom by discovering the neutron. Therefore a nucleus of atomic number Z and mass number A was composed of Z protons and A¡Z neutrons. Nuclei diameters are of the order of several times 10¡15m. From the perspective of an atom, which is 10^5 times larger, a nucleus behaves, for most purposes, like a point charge +Ze. In the sixties, contributors like Murray Gell-Mann proposed that protons and neutrons each consist of three types of quarks with compositions "uud" and "udd", respectively. The up quark u has a charge of +2/3 e, while the down quark d has a charge of 1/3 e. Despite heroic experimental efforts, individual quarks have never been isolated, evidently placing them in the same category with magnetic monopoles. By contrast, the electron maintains its status as an indivisible elementary particle.

- Niel Bohr further developed the model of an atom by suggesting that that electrons moves in a circular orbit or shell around the nucleus

- The orbits are at a fixed distance and energy level from the nucleus
- Electrons arrange themselves in this orbit or shell
- The energy level increases as orbit distances increases from the nucleus
- There is an energy value associated with each orbit or shell
- The maximum number of energy level for a known atom is seven and is called the **principal energy (quantum) level with a symbol n**
- The principal energy level is labeled 1-7 or alphabetically from K to Q (KLMNOQ)
- Each energy level have a maximum number of electrons that can occupy it and is defined as **$2n^2$** as shown in the table below
-

1.2 Electromagnetic Waves

Heinrich Hertz in 1887 was the first to demonstrate experimentally the production and detection of the electromagnetic waves predicted by Maxwell specifically radio waves by acceleration of electrical charges. As shown in Fig. 2, electromagnetic waves consist of mutually perpendicular electric and magnetic fields, E and B respectively, oscillating in synchrony at high frequency and propagating in the direction of E x B.
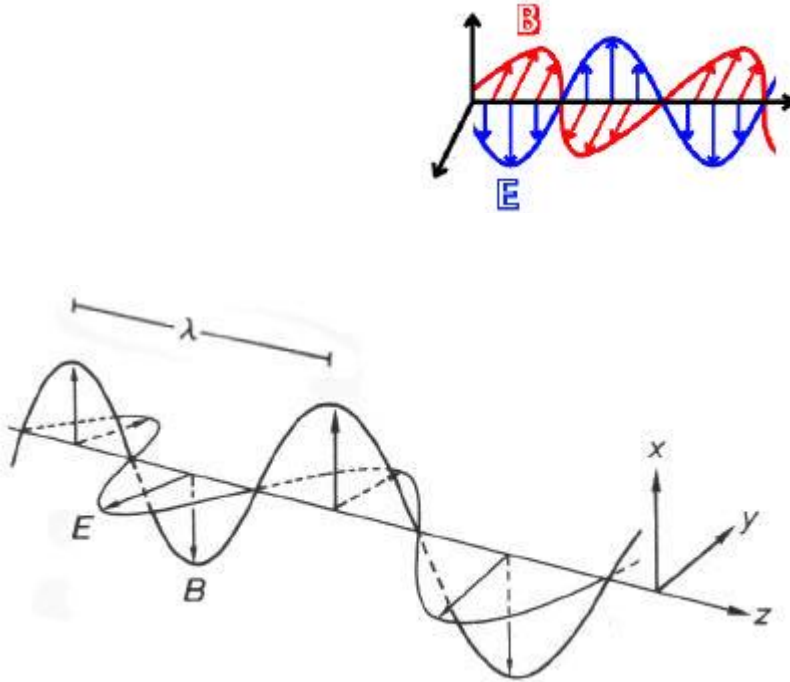
Figure 2. Schematic representation of monochromatic linearly-polarized electromagnetic wave

The wavelength ˏ λ is the distance between successive maxima of the electric (or magnetic) field. The frequency $\mathcal{P}$ represents the number of oscillations per second observed at a fixed point in space. The reciprocal of frequency $\tau = 1/\mathcal{P}=$ represents period of oscillation the time it takes for one wavelength to pass a fixed point. The speed of propagation of the wave is therefore determined by ˏ $\lambda = c\tau$ or in more familiar form ˏ

$$\lambda\,\mathcal{P}= c \quad (1)$$

where c = 2:9979x10^8 m/sec, usually called the speed of light, applies to all electromagnetic waves in vacuum. Frequencies are expressed in hertz (Hz), defined as the number of oscillations per second.

Electromagnetic radiation is now known to exist in an immense range of wavelengths including gamma rays, X-rays, ultraviolet, visible light, infrared, microwaves and radio waves, as shown in Fig.3
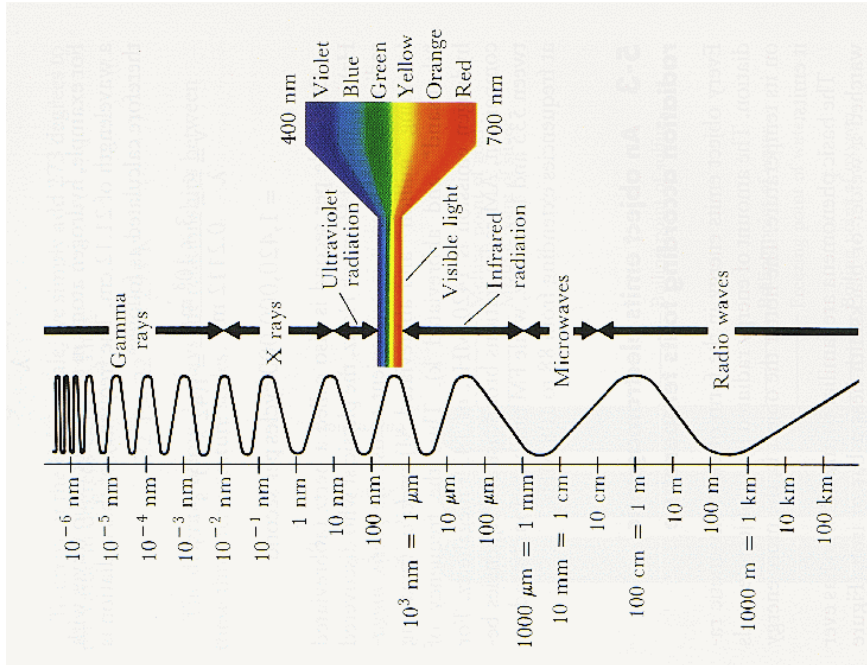
Figure 3 The electromagnetic spectrum, showing wavelengths of different types of radiation

Chapter 2 Review of Experiments Which Cannot be Explained by Classical Physics

2.1 Classical Physics

Newton introduced the idea or theory of *'determinism'*. Its most notable feature is the primacy of cause and effect relationships. Classical physics is causal; complete knowledge of the past allows computation of the future. Likewise, complete knowledge of the future allows precise computation of the past. (Chaos theory is irrelevant to this statement; it talks about how well you can do with incomplete knowledge.). Not so in quantum physics. Objects in quantum physics are neither particles nor waves; they are a strange combination of both. Given complete knowledge of the past, we can make only probabilistic predictions of the future. Given sufficient information about the present state of part of the universe, it should be possible, at least in principle, to predict its future behavior (as well as its complete history. For example, solar and lunar eclipses can be predicted centuries ahead, within an accuracy of several seconds. (But interestingly, we can't predict even a couple of days in advance if the weather will be clear enough to view the eclipse!) The other great pillar of classical physics is Maxwell's theory of electromagnetism.

2.2 The Origin of Quantum Theory

The origin of the development of the quantum theory started from three observations involving electromagnetic radiation which cannot be explained by classical physics, namely (1) blackbody radiation, which led to the contribution of Max Planck in 1900 2) the photoelectric effect, treated by Albert Einstein in 1905 and (3) the origin of line spectra, the hero being Neils Bohr in 1913. A coherent formulation of quantum mechanics was eventually developed in 1925 and 1926, principally the work of Schrodinger, Heisenberg and Dirac.

2.2.1 The Blackbody Radiation

A blackbody is an idealized perfect absorber and emitter of all possible wavelengths ¸ of the radiation. Fig. 4 shows experimental wavelength distributions of thermal radiation at several temperatures. Figure 4 shows that the maximum in the distribution determines the predominant color, which increases with increasing temperature. This relation is given by Wien's displacement law, which can be expressed as:

$$T \lambda_{max} = 2:898 \text{ x}10^6 \text{ nmK} \qquad (2)$$

where the wavelength is expressed in nanometers (nm). At room temperature (300K), the maximum occur around 10 µm, in the infrared region. In Figure 4, the approximate values of λ_{max} are 2900nm at 1000K, 1450nm at2000K and 500nm at 5800K, the approximate surface temperature of the Sun. The Sun's ¸max is near the middle of the visible range (380-750nm) and is perceived by our eyes as white light.
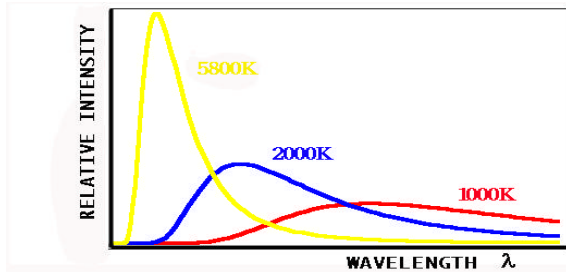
Fig. 4 Intensity distributions of blackbody radiation at three different temperatures

The total radiation intensity varies as T^4 (Stefan-Boltzmann law) so the total radiation at 2000K is actually $2^4 = 16$ times that at 1000K.

It was Max Planck that gave an explanation to the blackbody radiation phenomenon. He proposed that energies involved in absorption and emission of electromagnetic radiation did not belong to a continuum, as implied by Maxwell's theory, but were actually made up of discrete bundles, which he called "quanta." Planck's idea is traditionally regarded as marking the birth of the quantum theory. A quantum associated with radiation of frequency ν has the energy

$$E = h\nu = hc/\lambda \qquad (3)$$

where the proportionality factor h = 6:626 x 10^{-34} J sec is known as Planck's constant.
In summary, Planck is saying that energy is absorbed or released in multiple's amount of hν, 2hν, 3hν etc.

2.2.2. The Photoelectric Effect

A common device in modern technology is the photocell or "electric eye," which is used to run a variety of useful gadgets, including automatic door openers. The principle involved in these devices is the photoelectric effect, which was first observed by Heinrich Hertz. Visible or ultraviolet radiation impinging on clean metal surfaces can cause electrons to be ejected from the metal. Such an effect is not, in itself, inconsistent with classical theory since electromagnetic waves are known to carry energy and momentum. But the detailed behavior as a function of radiation frequency and intensity cannot be explained classically.
The energy required to eject an electron from a metal is called its work function ø. For example, sodium has ø = 1:82 eV.

The electron-volt is a convenient unit of energy on the atomic scale: 1 eV = 1.602x10^{-19}J. This corresponds to the energy which an electron picks up when accelerated across a potential difference of 1 volt. The classical expectation would be that radiation of sufficient intensity should cause ejection of electrons from a metal surface, with their kinetic energies increasing with the radiation intensity. Moreover, a time delay would be expected between the absorption of radiation and the ejection of electrons. The experimental facts are quite different. It is found that no electrons are ejected, no matter how high the radiation intensity, unless the radiation frequency exceeds some threshold value ν_o for each metal. For sodium ν_o = 4:39 x 10^{14}Hz (corresponding to a wavelength of 683 nm). For frequencies ν_o above the threshold, the ejected electrons acquire a kinetic energy given by

$$\tfrac{1}{2}mv^2 = h(\text{ƥ}- \text{ƥ}_o) = h\,\text{ƥ}- \text{ø} \; . \; (4)$$

There is a minimum frequency of light required to cause this emission for different metals. For example light with frequency $> 4.\,60 \times 10^{14}\ s^{-1}$ will cause Cesium to emit light. Anything less than this frequency will have no effect on Cesium.

Einstein explained the observation as follows: Each stream of light behaves as a packet of energy or as a particle called photon. Each photon has an energy $E = h\text{ƥ}$ which is quantized and can be absorbed by electrons on the surface of the metal. Electrons are held together by attractive forces in the bulk of the metal and needed a minimum amount of energy called the work function to overcome these attractive forces. So, if the photon energy is greater than or equal to this work function, electrons will be emitted from the surface of the metals as observed with photoelectric effect. Excess photon energy will be converted to kinetic energy for the electrons. A burst of light might be intense but if its frequency is less than the work function, it will not cause electron emission

2.2.3 Line Spectra

- There are 3 types of emission spectra: line, band, continuous which is useful in chemical analysis. In nature, many radiant lights like electric bulb, the sun, moon, and the stars emit light with many wavelengths. Also metals when heated to incandescence emit radiation of different wavelengths called black body radiation

- A **continuous** spectrum is produced when these wavelengths are separated into individual components that fade into each other. For example, if a light from a bulb is passed through a glass prism, the white light will be separated into its individual wavelength which appears as different colors that fades into each other
- Similar thing happens when the sun rays passes through raindrops in the atmosphere, the ray of light will be divided into different wavelengths which appears as different colors called the Rainbow
- **Band Spectrum**: Energy associated with each electronic energy state has associated quantized vibrational and rotational energy levels. The differences between these vibrational and rotational energy levels are much smaller than those between electronic energy levels and hence occur as bands of closely banded lines in between electronic energy levels. High resolution instruments can detect this band of spectra

 A continuous spectrum can also be produced by an incandescent solid or gas at high pressure. Blackbody radiation, for example, is a continuum. An emission spectrum can be produced by a gas at low pressure excited by heat or by collisions with electrons. An absorption spectrum results when light from a continuous source passes through a cooler gas, consisting of a series of dark lines characteristic of the composition of the gas

Gases heated to incandescence emit light with a series of sharp wavelengths. The emitted light analyzed by a spectrometer (or even a simple prism) appears as a multitude of narrow bands of color. These so called line spectra are characteristic of the atomic composition of the gas Classical electromagnetic theory can be used to explain that motions of electrical charges within atoms can be associated with the absorption and emission of radiation. What is interesting is how such radiation can occur for discrete frequencies, rather than as a continuum. The breakthrough that explained line spectra is credited to Neils Bohr in 1913. Bohr built on Einstein and Planck's idea and suggested that the energy levels of atoms belong to a discrete set of values En, rather than a continuum as in classical mechanics. When an atom makes a downward energy transition
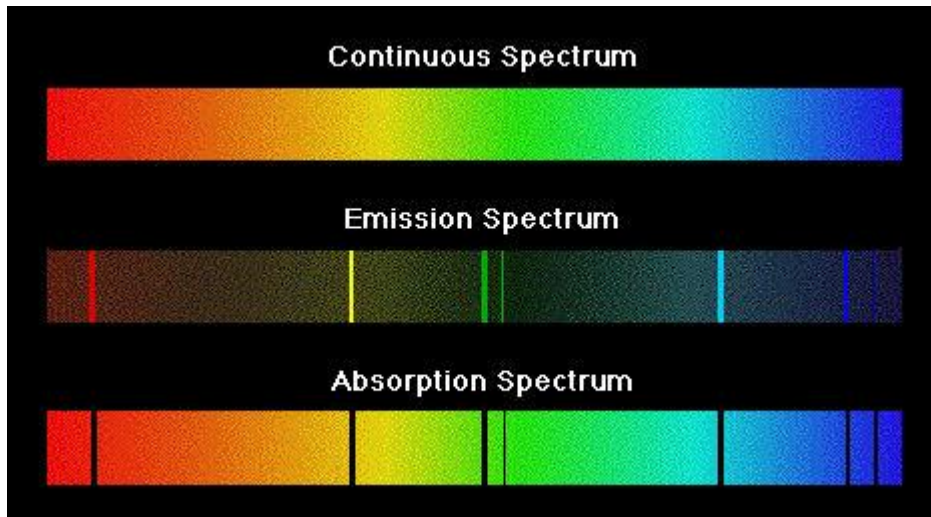

Figure 5 Continuous spectrum and two types of line spectra. From
http://csep10.phys.utk.edu/astr162/lect/light/absorption.html

from a higher energy level E_m to a lower energy level E_n, it caused the emission of a photon of energy

$$h\nu = E_m - E_n \quad (5)$$

This is what accounts for the discrete values of frequency ν in emission spectra of atoms. Absorption spectra are correspondingly associated with the annihilation of a photon of the same energy and concomitant excitation of the atom from E_n to E_m

When electric current is passed through a tube containing different gasses at reduced pressure, each gas emits different colors characteristics of such gases.
- Similar thing happens to some metals. For example, Na emits yellow light; Neon emits red-orange color used as street lights etc.
- If these lights are passed through a prism, few distinct color lines are seen instead of a continuous spread of colors. These lines represent different wavelengths and are called line spectrum of those metals or gases

- For example, the hydrogen atom shows 4 lines: violet (410nm), blue(434nm), blue-green(486nm), and red (656nm). Other lines were also found in the UV and IR region of the hydrogen spectrum
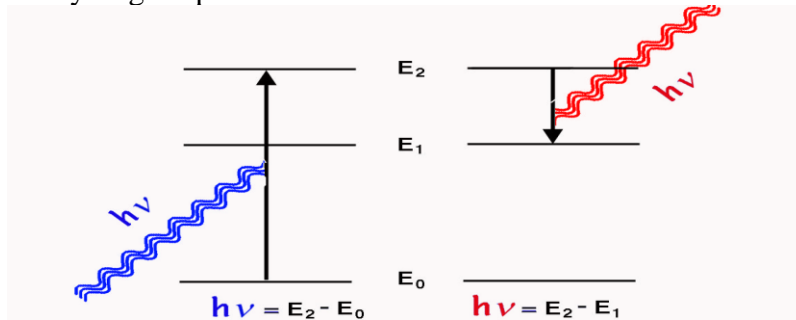

Fig. 6 Origin of line spectra. Absorption of the photon shown in blue causes atomic transition from E_0 to E_2. Transition from E2 to E1 causes emission of the photon shown in red.

- These lines fits into Balmer's series or the Rydeberg's equation
- $1/\lambda = (R_H)(1/n^2_1 - 1/n^2_2)$ n = 1,2 3 and $n_2 > n_1$
- λ = wavelength, R_H= Rydberg's constant (1.096776×10^7 m^{-1}), n_1 and n_2 are integers with $n_2 > n_1$
- This explains why there are line spectra, that is ; energy is quantized

2.2.4 Bohr's Theory of Atoms

Bohr postulated that the angular momentum of an electron about the nucleus can only take values which are multiples of n (principal energy levels) of h/2π, where h = Planck's constant. Bohr derived equations 6 and 7 for the radius and energy of the electrons in their various orbits around the nucleus

$$R = n^2h^2/Z^4\pi^2\mu e^2 \quad = n^2 a_o/Z \quad (6)$$

$$E = -Z^2\, 2\pi^2\mu e^4/n^2h^2 = -R/n^2 \quad (7)$$

Z = charge on the nucleus, h = plank's constant, e = the charge of the electron, μ = reduced mass of the electron (nearly the same as the actual mass, m, of the electron = mM/(m+M), M = mass of Nucleus), n = the number introduced to quantize the angular momentum and is called the quantum number, a_o = radius of the most stable orbit of the hydrogen atom and is called the Bohr radius = 0.529 Angstroms, R= Rydberg's constant

Bohr's theory also explains the appearance of line spectra (energy is quantized) of atoms. One can use equation 7 to calculate the energy needed to ionize the atom in its ground state, i.e. separate the electron and proton from each other. From the equation, the energy is simply R or I (the ionization energy). The equation can also be used to calculate the absorption or emission energy when an electron makes a transition either to a higher or lower energy level.

However, Bohr's theory cannot explain why electron (microscopic body) does not obey the same laws as obeyed by macroscopic bodies. A new theory has been developed for small bodies like an electron and is called wave mechanics.

Chapter 3   Wave Mechanics

3.1 Beginning of Wave Mechanics

The basic idea in wave mechanics is expressed by *Heinsberg Uncertainty Principles* that says that for a small molecule like an electron, it is impossible to know exactly where it is and where it is going at a definite time. It is the relative probability and its momentum at a certain time that can be specifically stated

We can start with a limited form of wave mechanics that deals with *stationary states*. A *stationary state* is a state that persists for a long time unless an external stimulus interacts with it. For example the energy states of the hydrogen atom are stationary states of the hydrogen system.

Wave mechanics indicate that any system (atom, molecule, electron, etc.) in free space can be described by a state or wave function, Ψ, which represents all the coordinates of all particles making up the system. The magnitude of Ψ depends on the positions in space of all the particles in the system.

Why is Ψ a wave function? De Broglie suggested that light or EMR behaves like a wave and as well as a particle hence small particles like an electron also behave like a wave and a particle. He suggested that

$$\lambda = h/p = h/mv \quad (1)$$

where p = momentum = mv and m = mass and v = velocity, h = Planck's constant
The physical reality of De Broglie theory is that a beam of electron can be diffracted by a grating (such as atoms in a crystal of gold) in the same way a beam of light is diffracted. Because system of small particles shows similar behavior like a wave under certain conditions, it is then possible to describes system of small particles with the same equation used to describe other known kind of waves e.g. standing waves of a vibrating string, EMR etc..
We shall start with wave equation for EMR and make some substitution that will enable us to convert to equations appropriate for matter. The substitutions are arbitrary but acceptable because they are based on physical reasoning and observation and lead to correct solutions to physical problems. Therefore, the wave equation is a postulate which allows us to apply it to atomic and molecular systems as started by Schrodinger.

3.2 The Wave Equation

The form of wave equation that applies to stationary states of a system can be represented as

$$H\Psi = E\Psi \quad (2)$$

Where *H = total energy of the system and E= the numerical value of that energy*

For all systems important to chemists, the total energy is the sum of the Kinetic energy (T) and potential energy (V)

$$H = T + V \quad (3)$$

H is called the Hamiltonian system

3.2.1 Application of the Hamiltonian System to Bohr's Model of the Hydrogen Atom

- We assume that stationary state with the electrons circulate around it. Then all the kinetic energy (T) of the system is just that of the electron represented by equation 4
$$T = \tfrac{1}{2}mv^2 \quad (4) \quad m = \text{mass of electron, } v = \text{electron velocity}$$

- The potential energy of the system is due to the electrostatic interaction (gravitational force is $\sim 10^{18}$ smaller) between the nucleus and the electron and is represented as
$$V = -e^2/r \quad (5)$$
where e = electronic charge of the electron and r = the radius of its orbit, the negative sign is because one charge is +e and the other –e.

- The Hamiltonian for hydrogen will therefore be represented as
$$H = T + V = \tfrac{1}{2}mv^2 - e^2/r \quad (6)$$

- Eqn. 6 can be written as $H = p^2/2m - e^2/r$ $\qquad (7)$

$p = mv$ and $p^2 = m^2v^2$ $\quad (8)$
$v^2 = p^2/m^2$ $\qquad (9)$
if $T = \tfrac{1}{2}mv^2$ $\qquad (10)$ we can put eqn. 9 in eqn. 10
$T = \tfrac{1}{2}m\, p^2/m^2 = p^2/2m$
Therefore $H = p^2/2m - e^2/r$ $\qquad (7b)$

- The next step is to convert classical description to wave mechanic form.
- The process is by taking the Hamiltonian of the classical equation
- Whenever momentum occurs in classical Hamiltonian, it is replaced with a derivative form:
$$h/2\pi i(\delta/\delta x + \delta/\delta y + \delta/\delta z) \quad (11)$$

- Therefore, the Hamiltonian for hydrogen atom in its wave form is

$$H = - h^2/8\pi^2 m \,(\delta^2/\delta x^2 + \delta^2/\delta y^2 + \delta^2/\delta z^2) - e^2/r \quad (12)$$

- Eqn. 12 can be substituted into the general wave equation 2
$$H\Psi = E\Psi \qquad (2)$$

$$H\Psi == [- h^2/8\pi^2 m \,(\delta^2/\delta x^2 + \delta^2/\delta y^2 + \delta^2/\delta z^2) - e^2/r]\,\Psi = E\Psi \quad (13)$$
which is the wave equation for a hydrogen atom

3.2.2 The Meaning of the Wave Equation

Equation 13 indicates that if we find the second derivative of a function, Ψ, multiply it by $h^2/8\pi^2 m$ and add $(- e^2/r)$ to it the result will be identical to E Ψ. That function will be the solution to the wave equation and is called the *wave function*. There will be many

different functions such as Ψ_1, Ψ_2…. Ψ_i solutions that gives values of energy equal to E_1, E_2….E_i

Equation 13 says we should take the second derivative of a function Ψ with respect to coordinates x,y, z indicates that Ψ is a function of these coordinates, that is $\Psi(x, y, z)$ must have specific values for any particular combination of the coordinates (x, y, z). In other words, at any point in space (where the proton/nucleus is the origin of the coordinate system) specified by the coordinates x, y, z, Ψ has a certain value.

The physical meaning of this value is that there is a relative probability that the electron will be found at a certain point in space at any given time.

The relative probability, P, of finding an electron at point (x, y, z) is given by

$$P = \Psi(x, y, z)^*(x, y, z) \qquad (14)$$

Ψ^* is the complex conjugate of Ψ and Ψ can have imaginary values. So for P to be real, we must multiply Ψ by its complex conjugate.

However, the probability of finding an electron at any point could be zero, small or large and not imaginary.

So if Ψ must be real, $\Psi = \Psi^*$ and therefore equation 13 only indicates that the probability equals the square of Ψ

If Ψ is real, then Ψ must satisfy the following requirements

(i)   It must have one value at each and every point i.e. whatever the value of (x, y, z), there must definitely be only one value or one probability of finding the electron at that point

(ii) Ψ cannot have an infinity (∞) value at any point

(iii)   Its absolute value at all points must be such that

$$\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \Psi(x, y, z)\, \Psi^*(x, y, z)\, dx\, dy\, dz = \int \Psi\, \Psi^* d\tau = 1 \ \ \text{(normalized)} \ (15)$$

The left term in eqn. 15 gives the sum of the probabilities of finding the electron at each point throughout all space and since there is only one electron that must be somewhere in space, this total probability must be equal to 1. The middle term in eqn. 15 is shorthand for the left term and τ is the general symbol for all coordinates. It is understood that the integration is all over the coordinates just as well as Ψ is a function of all coordinates.

When a wave function satisfies these criteria, the wave is said to be a normalized wave function.

When equation 13 is written in spherical polar coordinates it can be solved to obtain a set of wave functions. If we use, for example, the lowest energy, Ψ_1 which can be expressed as:

$$\Psi_1 = \exp(-r/a_o)/ \sqrt{\pi}\, a_o^{3/2}$$

Where r = distance fron nucleus, a_o = Bohr's radius

If Ψ_1 and Ψ_1^2 are plotted as a function of a_o as shown in figure 7, it shows that Ψ_1 has (1) a single value (2) never infinite (3) normalized

Fig. 1-1. Plot of ground state wave function ψ_1 and ψ_1^2 for hydrogen atom.

Fig. 1-2. A representation of the ground state wave function of the hydrogen atom.
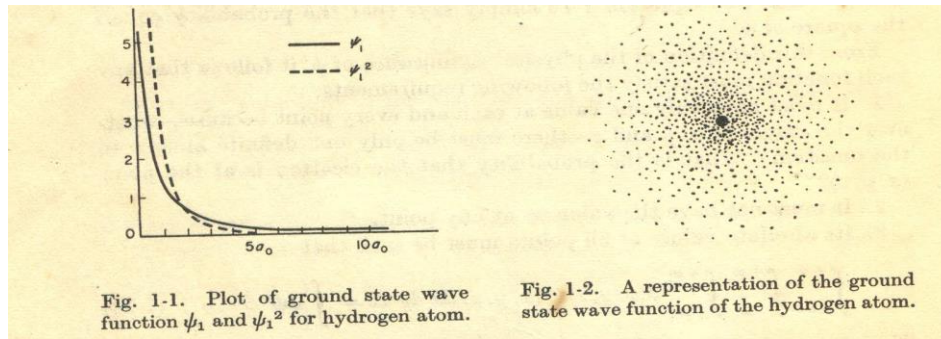
Figure 7 (a) Plot of ground state wave function Ψ_1 and Ψ_1^2 for hydrogen atom (b)

Representation of the ground State wave Function of the Hydrogen Atom

If we consider one atom and locate the various positions of the electron with respect to the nucleus we will obtain a picture similar to what is shown in Figure 7a If Ψ_1 and Ψ_1^2 are plotted as a function of a_o as shown in figure 7, it shows that Ψ_1 has (1) a single value (2) never infinite (3) normalized
. Similarly, if we consider the electron as a certain amount of negative charges and mass distributed around the nucleus as expressed in equation 14, what we 'should see' will be similar to Fig. 7b.

Figure 7 b (wave mechanical picture of a hydrogen atom ground state) can be compared with the pictures Bohr's atom. If the entire space around the nucleus is cut into very infinitesimally number of thin concentric spherical shells and then consider the probability of finding the electron in any of the concentric spheres. The total volume of the shell is $4\pi r^2 r^2 \Delta r$ and the probability of finding the electron within this shell is $(4\pi r^2 r^2 \Delta r) \Psi_1^2$. Plotting $(4\pi r^2 r^2 \Delta r) \Psi_1^2$ vs. r gives Fig. 8. The maximum $r_{max} = a_0$ where a_o= Bohr's radius (the radius of the lowest orbital of Bohr's hydrogen atom). Bohr model of the hydrogen suggest that electrons moves in a fixed orbital around the proton with a fixed radius= a_o, wave mechanics only talks about the probability of been found within the radius, r = a_o from the proton

Fig. 1-3. Probability density function, $4\pi r^2 \psi_1^2$, for the ground state orbital of the hydrogen atom.
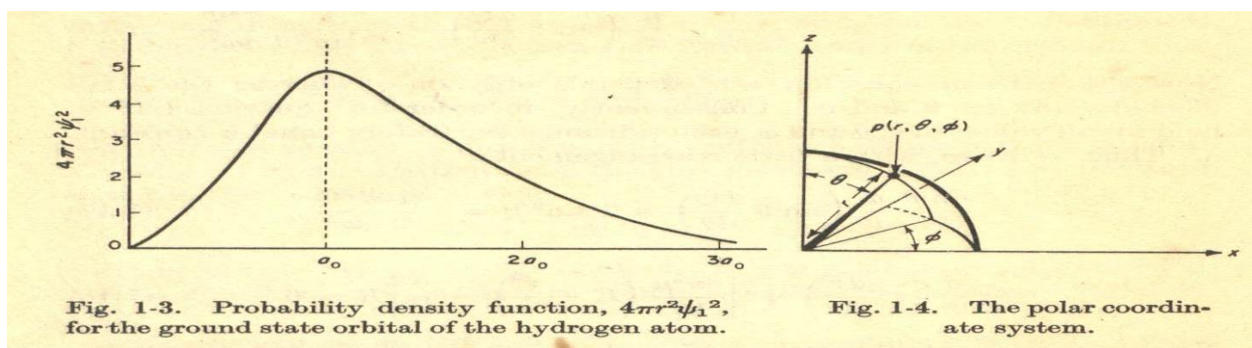
Fig. 1-4. The polar coordinate system.

Figure 8. Probability Density function $(4\pi r^2 r^2 \Delta r) \Psi_1^2$ vs. r (b) the polar coordinate of the system

Chapter 4 The Hydrogen Atom

4.1 **Solution to the Wave Equation**

The solution to the wave equation

$$H\Psi == [-h^2/8\pi^2 m \, (\delta^2/\delta x^2 + \delta^2/\delta y^2 + \delta^2/\delta z^2) - e^2/r] \, \Psi \ = E\Psi \ (1)$$

may be written in spherical polar coordinate, r, ø, θ. The coordinates are related to the Cartesian coordinates, x, y, z as shown in Figure (3-8b) and can be expressed as:

$$1/r^2 \cdot \delta/\delta_r(r^{2\delta}\Psi/\delta_r) + 1/r^2 \sin\theta \, \delta/\delta\theta(\sin\theta^\delta\Psi/\delta\theta) + 1/r^2\sin^2\theta \, \delta/\delta\theta(\sin\theta^\delta\Psi^2/\delta ø^2) + 8\pi^2 m/h^2(E + e^2/r)\Psi = 0 \quad (1)$$

Solution to the wave equation (1) can be expressed in a general form

$$\Psi = R(r) \, \Theta(\theta) \, \Phi(ø) \qquad\qquad (2)$$

Where Ψ is a general wave function of all the three coordinates r, Θ, ø, and a product of R(r) a function of only r , Θ(θ), a function of only of θ, and Φ(ø) a function of only ø. If we substitute these expressions in eqn. (1) and rearrange, then we will arrive at

$$1/R \, \delta/\delta_r(r^{2\delta}\Psi/\delta_r) + \ 8\pi^2\mu/h^2(E + e^2/r)r^2 = -1/ \, \Theta\sin\theta \, \delta/\delta\theta(\sin\theta^\delta\Theta/\delta\theta) - 1/ \, \Phi\sin^2\theta \, \delta^2\Phi/\delta ø^2 \quad (3)$$

The LHS of eqn.3 depends only on r and the RHS only θ and ø. For eqn. 3 to be true, for all r, θ, and ø, both the LHS and RHS must be equal to a constant, λ.

We can then rewrite eqn. 3 into two different equations, thus,

$$\text{Sin}\theta/\Theta \ \delta/\delta\theta(\sin\theta^\delta\Theta/\delta\theta) + \lambda\sin^2 \theta = 1/\Theta^{\delta 2}\Phi/\delta ø^2 \qquad (4)$$

$$1/r^{2\delta}/\delta_r(r^{2\delta}R/\delta_r) + \ [8\pi^2\mu/h^2(E + e^2/r) - \lambda/r^2]R = 0 \quad (5)$$

For eqn. 4 to hold we can rewrite it into two separate eqns:

$$\text{Sin}\theta/\Theta \ \delta/\delta\theta(\sin\theta^\delta\Theta/\delta\theta) + \lambda\sin^2 \theta = m^2 \qquad (6)$$

$$\delta^2\Phi/\delta ø^2 = m^2 \, \Phi \qquad\qquad (7)$$

Where m is also a constant

Solution to eqn. 7 is: $\Phi = (2\pi)^{-1/2\exp(im}$ ø)

Here m is either a positive integer or a negative integer, hence it a quantum number. All various forms of solutions of Φ are functions of the quantum number *l* and *m*. *l* may take positive integral values and *m* may take integral values from –*l* to +*l* for any value of *l*. For example if,

l= 1, 2, 3 m = [-1, 0, 1], [-2, -1, 0, 1, 2], [-3,-2,-1,0,1,2,3] respectively.

Likewise eqn.5 may be solved in terms of *l* which is related to λ that is expressed as

$$\lambda = l(l+1) \quad (8)$$

and also in terms of energy as:

$$E_n = -1/n^2(2\pi^2\mu^2e^4/h^2) \quad (9)$$

Where n is a quantum number called the principal quantum number with positive integers between 1 - ∞ and

$$l = (n-1), (n-2) \ldots.,0 \quad (10)$$

4.2 The Hydrogen Atom Orbitals

Some of the wave function which is solutions to the wave equation (4-1) are called *orbitals* which describes the spatial distribution of electron density around the nucleus. Each orbital is uniquely defined by the following sets of quantum number: n, l, and m.

General symbols are used to represent these orbitals and the orbital symbol consist of a number and a letter, e.g. 2*s*. The number represents the principal quantum number. The first four letters are arbitrary for historical reasons while the ones beyond *f* follow alphabetical order. The letters correspond to the value of *l* as follow:

l= 0, 1, 2, 3, 4 5,

s, p, d, f, g, h,

The three quantum numbers; *n, l, m* has physical meaning thus;

n= gives a measure of energy of an electron in an orbital as shown in *equation* 9. So, one can speak about the energy of an orbital. When *n*= 1, that indicates the lowest negative energy level. Energy value of the orbitals increases as the value of *n i*ncreases; i.e. the energy becomes less negative. The energy becomes zero when n = ∞ i.e. the electron is no more bounded to the nucleus beyond which there is a continuum of energy. Electrons in the continuum energy region have zero bounding energy and any arbitrary amount of kinetic energy. The difference between energy state *n*= 1 and *n* = ∞ is called the *ionization energy.* Transitions from any excited state (higher energy levels) to a common lower energy state give rise to a series of spectral lines which are characteristics of different atoms. An example of such transitions is shown in Figure 9 below.

n (Principal quantum number)
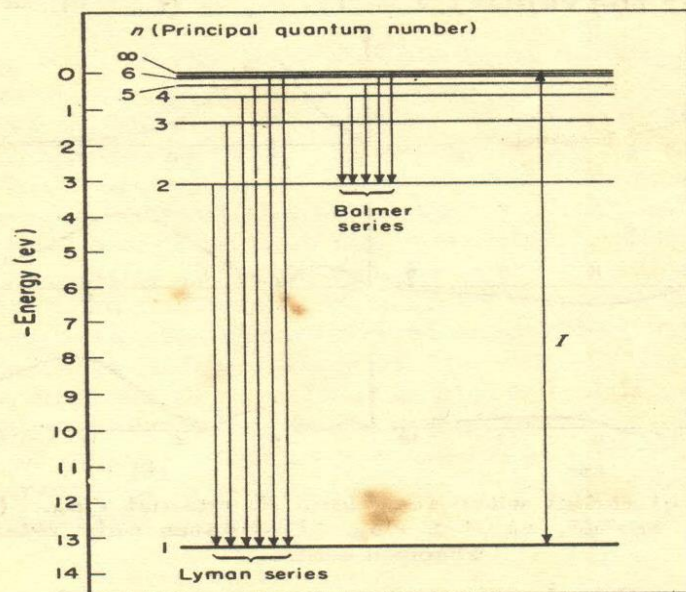
5. Simplified energy level diagram of the hydrogen atom, showing some of the spectral series.

Figure 9 Energy level diagram of Hydrogen atom showing some spectral lines

The number *n* also represents the radial distance of the electron density from the nucleus as shown in Figure 10 below.

The number *n* also represents the radial distance of the electron density from the nucleus as shown in Figure 10 below. The quantum number *l* is a measure of the classical angular momentum of the electron even though we cannot physically define it again in wave mechanics because we cannot define the position
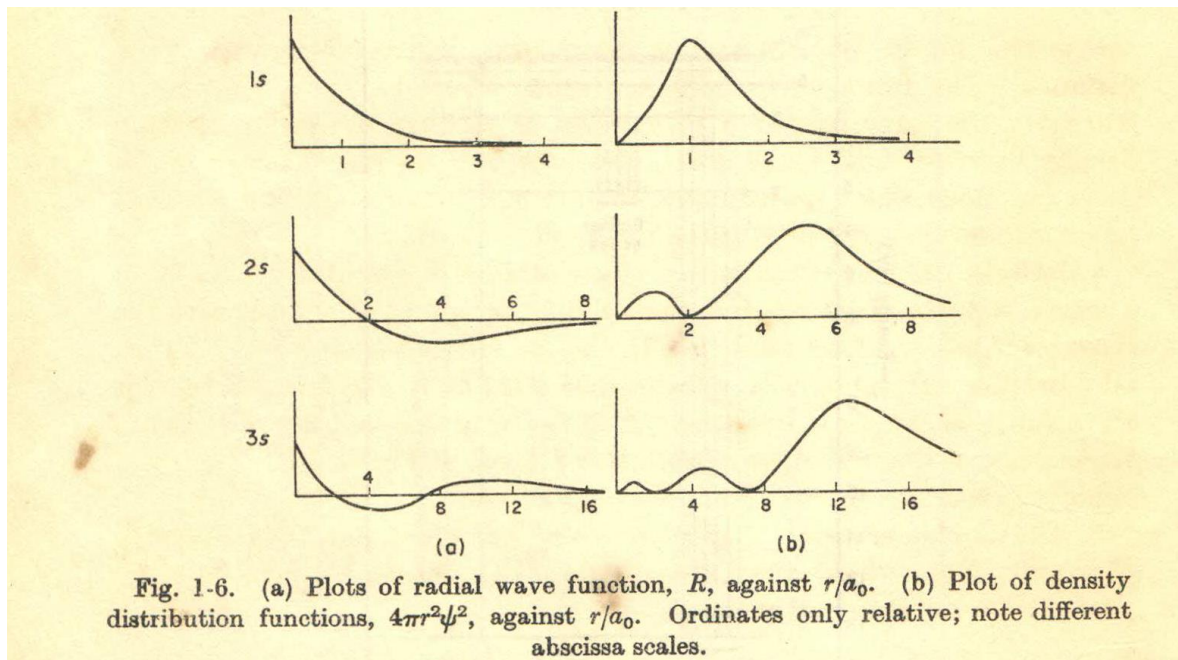
Fig. 1-6. (a) Plots of radial wave function, R, against r/a_0. (b) Plot of density distribution functions, $4\pi r^2\psi^2$, against r/a_0. Ordinates only relative; note different abscissa scales.

Figure 10. Plots of radial wave function

The quantum number l is a measure of the classical angular momentum of the electron even though we cannot physically define it again in wave mechanics because we cannot define the position and velocity of an electron at the same time any longer. We can only measure the orbital angular momentum which is given as $\sqrt{l(l+1)}h/2\pi$. *$h/2\pi$ is defined as a unit of angular momentum. So we can say the s(l=0) electrons has zero angular momentum and* p electrons (l=1) has $\sqrt{2}$ units of angular momentum etc.

The quantum number m tells us how the orbital angular momentum is oriented relative to some fixed direction. Sometimes the symbol m_l is used instead of m. m_l can only take the value $-l$ to l.

Table 4.1 shows the orbitals of a Hydrogen Atom and its quantum numbers

TABLE 1-1

Orbitals of a Hydrogen-like Atom

Quantum numbers			General symbol	Radial wave function[a]	Angular wave function	Explicit symbol
n	l	m				
1	0	0	$1s$	$2(Z/a_0)^{3/2}e^{-\rho}$	$(2\sqrt{\pi})^{-1}$	$1s$
2	0	0	$2s$	$2^{-3/2}(Z/a_0)^{3/2}(2-\rho)e^{-\rho/2}$	$(2\sqrt{\pi})^{-1}$	$2s$
2	1	0		$2^{-1}\cdot 6^{-1/2}(Z/a_0)^{3/2}\rho e^{-\rho/2}$	$2^{-1}\cdot 3^{1/2}\pi^{-1/2}\cos\theta$	$2p_z$
2	1	1	$2p$	„	$2^{-1}\cdot 3^{1/2}\pi^{-1/2}\sin\theta\cos\phi$	$2p_x$
2	1	−1		„	$2^{-1}\cdot 3^{1/2}\pi^{-1/2}\sin\theta\sin\phi$	$2p_y$
3	0	0	$3s$	$2\cdot 81^{-1}\cdot 3^{-1/2}(Z/a_0)^{3/2}(27-18\rho+2\rho^2)e^{-\rho/3}$	$(2\sqrt{\pi})^{-1}$	$3s$
3	1	0		$4\cdot 81^{-1}\cdot 6^{-1/2}(Z/a_0)^{3/2}(6\rho-\rho^2)e^{-\rho/3}$	$2^{-1}\cdot 3^{1/2}\pi^{-1/2}\cos\theta$	$3p_z$
3	1	1	$3p$	„	$2^{-1}\cdot 3^{1/2}\pi^{-1/2}\sin\theta\cos\phi$	$3p_x$
3	1	−1		„	$2^{-1}\cdot 3^{1/2}\pi^{-1/2}\sin\theta\sin\phi$	$3p_y$
3	2	0		$4\cdot 81^{-1}\cdot 30^{-1/2}(Z/a_0)^{3/2}\rho^2 e^{-\rho/3}$	$4^{-1}\cdot 5^{1/2}\pi^{-1/2}(3\cos^2\theta-1)$	$3d_{z^2}$
3	2	1		„	$2^{-3/2}\cdot 30^{1/2}\pi^{-1/2}\sin\theta\cos\theta\cos\phi$	$3d_{xz}$
3	2	−1	$3d$	„	$2^{-3/2}\cdot 30^{1/2}\pi^{-1/2}\sin\theta\cos\theta\sin\phi$	$3d_{yz}$
3	2	2		„	$4^{-1}\cdot 15^{1/2}\pi^{-1/2}\sin^2\theta\cos 2\phi$	$3d_{x^2-y^2}$
3	2	−2		„	$4^{-1}\cdot 15^{1/2}\pi^{-1/2}\sin^2\theta\sin 2\phi$	$3d_{xy}$

[a] $\rho = Zr/a_0$; Z = nuclear charge.

4.3 Sub Orbitals of Hydrogen Atom

The angular part of the wave function is very important in determing the shape of a suborbital.

s-orbital: There is an *s* orbital in every principal energy leverl, i.e. in every group of orbitals with the same principal quantum number. All *s*-orbital is spherical in shape since they all have an angular wave function that is independent of θ and ø. The spatial properties of the suborbitals are shown in Fig. 11. The *s*-orbital can contain a maximum of two electrons with opposite spins
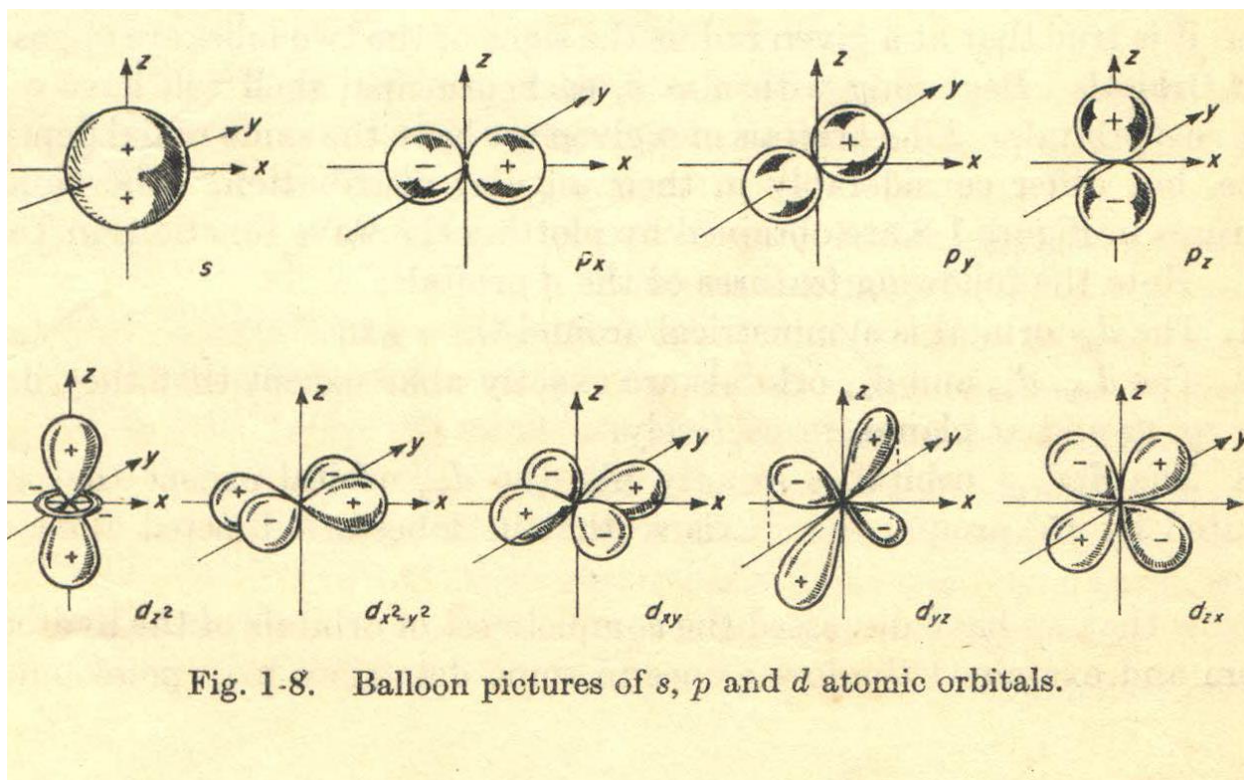
Fig. 1-8.   Balloon pictures of s, p and d atomic orbitals.

Figure 11. Ballon pictures of the *s, p, and d* atomic orbitals

***p-* orbitals**: *p-* orbitals begin when $n = 2$. Each principal orbital has three degenerate orbitals labelled p_x, p_y, p_z. The *p-* orbitals depend on θ and ø and hence are not spherical in shape. They form dumbell shape (figure 8) with two lobes with opposite signs. Each principal energy level have a p- orbital. Each degerate orbital can contain a maximum of two electrons, making a total of six electrons for these orbitals

***d*-orbital:** The *d*-orbital appears when $n = 3$ and above. The *d*-orbitals have five degenerate orbitals with different angular distribution or spatial orientation. The five degenerate orbitals are labeled as: d_z^2, d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ and can contain a maximum of ten electrons.

f-orbital: The f-orbital appears when n = 4 and above. The f-orbital have seven degenerate orbitals with different angular distribution or spatial orientation. The seven degenerate orbitals are labeled as: f_z^2, f_{xy}, f_{xz}, f_{yz}, $f_{x^2-y^2}$, $f_{x^2-z^2}$, $f_{y^2-z^2}$ with a maximum of 14 electrons.

4.4 Electron Spin

Electrons have inherent angular momentum called the *spin*. The *spin* has a unit of *h/2π* and its value is equal to:

$$\sqrt{s(s+1)}$$

where *s* is the *spin quantum number* that takes the value of $\pm\frac{1}{2}$ with reference to a reference direction. By analogy to m_l there is a quantum number defined as m_s whose value is limited to $\pm\frac{1}{2}$.

Therefore, the complete state of an electron can be defined by four quantum numbers namely, *n, l, m_l, m_s*.

The spin of an electron is described simply by the classical concept of a spherical electron rotating about an axis through its center which makes it have an inherent magnetic moment. The direction of its moment coincides with the direction of the m_s vector. Therefore, when two electrons occupy degenerate energy levels at the same time, their magnetic moment must be opposite each other. Hence, every electron that does not have another electron with the opposite magnetic moment (not paired) will contribute to the magnetism of the atom or molecule in which it occurs and its value will be proportional to the number of unpaired electrons in that atom or molecule.

Example: $^{14}_{7}N = 1s^2 2s^2 2p^{3\cdot}$- has 3 unpaired electron i.e. a multiplicity of 3 while

$^{16}_{8}O = 1s^2 2s^2 2p^4$- has 2 unpaired electron i.e. a multiplicity of 2 so we expect nitrogen to be more magnetic than oxygen.

If one electron occupies a *p, d* or higher orbitals, it will have both orbital and spin angular momenta which may combine together in two ways, thus; $l + s$ or $l\text{-}s$ to give a total angular momenta of

$$\sqrt{j(j + 1)} \text{ where } j = l + s \text{ or } l\text{-}s$$

The energy of the atom will be different for the two values of *j*.

Example: for an electron in a p-orbital it has $l = 1$ and $s = \pm 1/2$, then $j = \sqrt{j(j + 1)}$

$j = l+s = 1 + 1/2 = 3/2$ or $j = l\text{-}s = 1-1/2 = 1/2$ so total momenta is

$j = \sqrt{3/2(3/2 + 1)} = \sqrt{3.75}$ or $j -\sqrt{1/2(1/2 + 1)} = \sqrt{0.75}$

4.5 The Exclusion Principle

The four quantum numbers that totally describes the state of an electron is *n, l, m_l, m_s*. There is a need to add one more restriction on the behavior of electrons that is called the *Pauli's exclusion principle (PEP)* when describing multi-electron atoms. PEP says:

> (i)The maximum number of electrons in a degenerate orbital is two (ii) the two electrons in a degenerate orbital have opposite quantum spin number (+/-). Each spin is represented

$\uparrow\downarrow$

by half headed arrows (   ). (iii) no two electron have all four principal quantum numbers the same

4.6 The Aufbau Principle: Configuration of Many Electron Atoms

Electron configuration means how electrons are arranged in the various orbitals of a many electron atom. This is called the Aufbau principle and it simply states that: electrons of an atom are arranged in a set of orbitals in the order of decreasing stability while making the process obey the Pauli's exclusion principle or in other words, electrons are filled into orbitals in order of increasing energy value: 1s<2s<2p<3s<sp<4s<3d<4p<5s<4d<5p<6s<4f<5d etc

The alternative way of knowing the order of the energy level is shown below. The electronic arrangement can be written in the format shown below by following the direction of the arrow

- 1s
- 2s   2p
- 3s   3p   3d
- 4s   4p   4d   4f
- 5s   5p   5d   5f
- 6s   6p   6d   6f
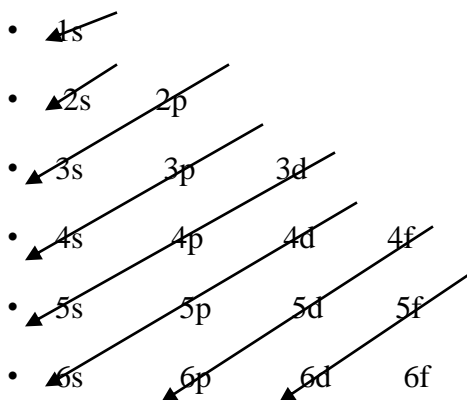
For example, hydrogen has one electron which occupies the 1s orbital, which is the most stable orbital with the least energy value. The next element is Helium with two electrons. If we start the nucleus represented by He^{2+}, and start adding the electrons, the first electron will go to the 1s orbital with the following sets of quantum numbers; n =1, l= o, m_l = 0, m_s= +½. The atom is He^+ to give hydrogen- like atom. The next electron will go the next stable orbital which is still the same orbital 1s without flouting Pauli's principle. The quantum number for the second electron is: n =1, l= o, m_l = 0, m_s= -½. The symbol for these two electrons is $1s^2$ and the electrons is said to be *paired* and *diamagnetic*. The next element is Lithium with three electrons. The first two electrons fills up the 1s suborbital to form $1s^2$ and the third electron therefore goes to the next stable orbital, which is the 2s orbital. So the configuration of Li will be: $1s^2 2s^1$

4.7 The Hund's rule (the principle of maximum multiplicity): degenerate orbitals are singly filled before pairing up. As a result, an atom tends to have as many unpaired electrons as possible. In order words, electrons avoid repelling each other by seeking out empty shells to fill up first instead of pairing up.

Following Aufbau's principle of filling energy levels with electrons, when we get to Boron with five electrons, the configuration becomes: $1s^2 2s^2 2p^1$. The next element is carbon with six

electrons. The sixth electron has the option of pairing up with the fifth electron or remains unpaired by filling the next degenerate p-orbital. Here, the Hund's rule is obeyed and the electron remains unpaired by filling the next degenerate p-orbital. Then the configuration for carbon will be: $1s^2 2s^2 2p^2$. The next element is nitrogen with seven electrons. The seventh electron remains unpaired and goes to the next degenerate orbital making nitrogen to have three unpaired electrons. Pairing of the p-electrons starts with the next element which is oxygen (eighth electron pairs up with one of the p electrons).

Chapter 5   The States Derived from Electronic Configuration

5.1 Russell-Saunders Coupling Rule

Generally, the electronic configuration on an atom does not correspond to a single state of the atom or ion. A state of an atom is characterized by three values that include (i) energy (ii) orbital angular momentum (iii) spin angular momentum. A state so defined is called by the spectroscopist a multiplet state.

These three characteristics of a state have magnitudes which are determined by the way the three quantities for each electron combine to produce the resultant quantities for the entire group of electrons. This combination process is difficult to understand even for the simplest atom. But observations from experiments have shown that nature follows a simple scheme of combination or coupling to arrive at the resultant quantities. This scheme is called the Russell-Saunders or LS coupling scheme

Each electron has a set of quantum numbers: *n, l, m$_l$, m$_s$*. We use *l* as $\sqrt{l(l+1)}$ to represent the orbital angular momentum of a single electron, so also we can use L as $\sqrt{L(L+1)}$ to represent the total orbital angular momentum for an atom. The symbol M$_L$ can be used to represent a component of L for an atom in a certain direction and is similar to m$_l$ for an electron. In like manner, we can use a quantum number S to represent the total electron spin angular momentum which is given by $\sqrt{S(S+1)}$ for an atom just like we use *s* as $\sqrt{s(s+1)}$ for a single electron. S may take integral values starting with 0 but *s* only takes the value of $\pm\frac{1}{2}$ for a single electron. The components of S in a certain direction are represented by the symbol M$_s$ which is analogous to m$_s$ for an electron.

In quantum mechanics, the **Russell-Saunders term symbol** is an abbreviated description of the ***angular momentum quantum numbers*** in a multi-electron atom. Each energy level of a given electron configuration is described by its own term symbol, assuming LS coupling. The ground state term symbol is predicted by Hund's rules

Symbols for the states of atoms are similar to the symbols for the orbitals of a single electron. L is the total orbital quantum number in spectroscopic notation. Thus, we use capital letters, S, P, D, F, G, H etc to represent states with L = 0, 1, 2, 3, 4 , 5 etc

The first 17 symbols of L are:

$$L = 0 \; 1 \; 2 \; 3 \; 4 \; 5 \; 6 \; 7 \; 8 \; 9 \; 10 \; 11 \; 12 \; 13 \; 14 \; 15 \; 16 \; ...$$

$$S \; P \; D \; F \; G \; H \; I \; K \; L \; M \; N \; O \; Q \; R \; T \; U \; V \text{ (continued alphabetically)}$$

The nomenclature (*S, P, D, F*) is derived from the characteristics of the spectroscopic lines corresponding to (*s, p, d, f*) orbitals: sharp, principal, diffuse, and fundamental; the rest being named in alphabetical order. The complete symbol for a state of an atom indicates the total spin but not in terms of S but in terms of M_s called the *spin multiplicity*. The *spin multiplicity* is obtained with the formula 2S+1 and is indicated in the state symbol as a left superscript to the symbol L. For example

For M_L= 4, S = ½, the symbol is ^2G – doublet G state

For M_L = 2, S= 3/2, the symbol is ^4D – quartet D state

States with spin multiplicities of 1, 2 ,3, 4, 5, 6 etc are called singlet, doublet, triplet, quartet, quintet and sextets states

As we did with single electron, the total angular momentum is expressed as $j = (l + s)$ we can do so for an atom with the total angular momentum $J = (L + S)$. Usually the J values are written as a right subscript to the symbol of the state of an atom. For example,

L	M_s	J	Symbol
2	3/2	7/2	$^4D_{7/2}$

The ***term symbol*** is also used to describe compound systems such as mesons or atomic nuclei, or even molecules (see molecular term symbol). In that last case, Greek letters are used to designate the (molecular) orbital angular momenta.

For a given electron configuration

The *combination of an S value and an L value is called a **term***, and has a statistical weight (i.e., number of possible microstates) of $(2S+1)(2L+1)$;

A *combination of S, L and J is called a **level***. A given level has a statistical weight of $(2J+1)$, which is the number of possible microstates associated with this level in the corresponding term;

A *combination of L, S, J and M_J determines a single **state***.

As an example, for $S = 1$, $L = 2$, there are $(2\times1+1)(2\times2+1) = 15$ different microstates corresponding to the ^3D term, of which $(2\times3+1) = 7$ belong to the $^3D_3$ ($J = 3$) level. The sum of $(2J+1)$ for all levels in the same term equals $(2S+1)(2L+1)$. In this case, J can be 1, 2, or 3, so $3 + 5 + 7 = 15$.

5.2 Possible States of an Atom

To actually determine the possible states of an atom, it is right to define

$$M_L = m_l{}^1+m_l{}^2+m_l{}^3+\ldots\ldots m_l{}^n \text{ and}$$

$$M_S = m_s{}^1+m_s{}^2+m_s{}^3+\ldots\ldots m_s{}^n$$

It is not necessary to consider all the electrons in an atom when calculating M_L and M_s because for all electrons in completely filled sub-orbitals (s, p, d, f etc) all the total angular momentum and total spin angular momentum will cancel each other out, i.e. it will have a value of zero and do not contribute to the total angular momentum. Therefore, we only need to concern ourselves with those electrons in partially filled orbitals or that are unpaired. If all shells and sub shells are full then the term symbol is $^1S_0$.

5.2.1 Ground state term symbol

It is relatively easy to calculate the *term symbol for the ground state of an atom using Hund's rules*. It corresponds with a state with maximal S and L.

Start with the most stable electron configuration. Full shells and sub-shells do not contribute to the overall angular momentum, so they are discarded.

If all shells and sub shells are full then the term symbol is $^1S_0$.

Distribute the electrons in the available orbitals, following the Pauli Exclusion Principle. First, fill the orbitals with highest m_l value with one electron each, and assign a maximal m_s to them (i.e. $+\frac{1}{2}$). Once all orbitals in a sub shell have one electron, add a second one (following the same order), assigning $m_s = -\frac{1}{2}$ to them.

The overall S is calculated by adding the m_s values for each electron. That is the same as multiplying ½ times the number of **unpaired** electrons. The overall L is calculated by adding the m_l values for each electron (so if there are two electrons in the same orbital, add twice that orbital's m_l).

Calculate J as follow:

if less than half of the sub shell is occupied, take the minimum value $J = |L - S|$;

if more than half-filled, take the maximum value $J = L + S$;

if the sub shell is half-filled, then L will be 0, so $J = S$.

As an example, in the case of <u>fluorine</u>, the electronic configuration is $1s^2 2s^2 2p^5$.

1. Discard the full sub shells and keep the $2p^5$ part. So there are five electrons to place in sub shell p ($l = 1$).

2. There are three orbitals ($m_l = 1, 0, -1$) that can hold up to $2(2l + 1) = 6$ electrons. The first three electrons can take $m_s = \frac{1}{2}$ (↑) but the Pauli Exclusion Principle forces the next two to have $m_s = -\frac{1}{2}$ (↓) because they go to already occupied orbitals.

m_l		
+1	0	−1
m_s: ↑↓	↑↓	↑

3. $S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} - \frac{1}{2} - \frac{1}{2} = \frac{1}{2}$; and $L = 1 + 0 - 1 + 1 + 0 = 1$, which is "P" in spectroscopic notation.

4. As fluorine 2p sub shell is more than half filled, $J = L + S = \frac{3}{2}$. ***Its ground state term symbol is then $^{2S+1}L_J = {^2P}_{3/2}$.***

For a p\`\`\`\`\`\`\`\`\`\`\`\`\`\`artly filled shell, there is always more than one way of assigning m_l and m_s values to all the electrons in that shell. All ways must be considered except those that are prohibited by exclusion principles or are redundant. If we use $m_s = \pm\frac{1}{2}$, For a three electron shell, the first electron can be assigned the quantum numbers $m_l = 1$ and $m_s = \frac{1}{2}$, the second electron can be assigned the quantum numbers $m_l = 2$ and $m_s = -\frac{1}{2}$ and the third one $m_l = 0$ and $m_s = +\frac{1}{2}$ which can be written as: $1^+, 2^-, 0^+$. This specification for the state of each electron is called a *microstate*

Let us consider the two configurations $2p^3p$ (4 electrons with one paired and two unpaired electrons) and $2p^2$ (the two electrons are unpaired). The two electrons of the $2p^3p$ configuration have different principal quantum numbers, so we are free to assign quantum numbers m_l and m_s to them with no restriction. Assignment such as $(1^+, 1^+)$ and $(0^+, 0^+)$ are possible and are physically different states. For the $2p^2$ electrons, these pairs are physically identical since there is no physical distinction between the 1st and 2nd electrons.

For the $2p^3p$ configuration there are 6x6 = 36 microstates while 6 of these microstates are prohibited by the exclusion principle for the $2p^2$ configuration. The remaining 30 microstates consist of some pairs that are physically redundant. Overall there are 15 possible microstates as shown in the table 5.1 below. From this table, we can deduce the possible values of L and S. The

table shows that the minimum and maximum values of M_L are ± 2 each of which is associated with an $M_S = 0$. This state is described by L $=2$ and S $= 0$ which is a ^1D state. This state also have microstate with $M_S = 0$ and $M_L = 1, 0, -1$. If we remove these 5 states of ^1D state's from Table 5.1 we are left with the microstates in Table 5.2. It does not matter which state is removed because microstates in the same box always mix together to give new ones. However, the number of microstates in a box alway remain the same. There are nine microstates with $M_L = 1$, 0, -1 and $M_S = 1, 0, -1$ where L $= 1$ and S $= 1$ which is a ^3P state. There is only one state with $M_L= 0$ and $M_S = 0$ which is ^1S state. In conclusion, the permitted states of any np^2 configuration are ^1D, ^3P, ^1S states

Table 5.1 Tabulation of Microstates for a p^2 Configuration

M_L	M_S	M_S	M_S
	1	0	-1
2		$(1^+, 1^-)$	
1	$(1^+, 0^+)$	$(1^+, 0^-)(1^-, 0^+)$	$(1^-, 0^-)$
0	$(1^+, -1^+)$	$(1^+, -1^-)(0^+, 0^-)(1^-, -1^+)$	$(1^-, 1^-)$
-1	$(-1^+, 0^+)$	$(-1^+, 0^-)(-1^-, 0^+)$	$(-1^-, 0^-)$
-2		$(-1^+, -1^-)$	

Table 5.2

M_L	M_S	M_S	M_S
	1	0	-1
2			
1	$(1^+, 0^+)$	$1^-, 0^+)$	$(1^-, 0^-)$
0	$(1^+, -1^+)$	$(0^+, 0^-)(1^-, -1^+)$	$(1^-, 1^-)$
-1	$(-1^+, 0^+)$	$(-1^-, 0^+)$	$(-1^-, 0^-)$
-2			

For the $2p^3p$ configuration there are 36 microstates as shown in table 5.3

Table 5.3 Tabulation of Microstates for a $2p^3p$ Configuration

M_L	M_s	M_s	M_s
	1	0	-1
2		$(1^+, 1^-)$	
1	$(1^+, 0^+)$	$(1^+, 0^-)(1^-, 0^+)$	$(1^-, 0^-)$
0	$(1^+, -1^+)$	$(1^+, -1^-)(0^+, 0^-)(1^-, -1^+)$	$(1^-, 1^-)$
-1	$(-1^+, 0^+)$	$(-1^+, 0^-)(-1^-, 0^+)$	$(-1^-, 0^-)$
-2		$(-1^+, -1^-)$	

5.2.2 Term symbols for an electron configuration

The process to calculate all possible term symbols for a given electron configuration is a bit longer.

First, calculate the total number of possible microstates N for a given electron configuration. As before, we discard the filled (sub) shells, and keep only the partially filled ones. For a given orbital quantum number l, t is the maximum allowed number of electrons, $t = 2(2l+1)$. If there are e electrons in a given sub shell, the number of possible microstates is

$$N = \binom{t}{e} = \frac{t!}{e!\,(t-e)!}.$$

As an example, lets take the carbon electron structure: $1s^2 2s^2 2p^2$. After removing full sub shells, there are 2 electrons in a p-level ($l = 1$), so we have

$$N = \frac{6!}{2!\,4!} = 15$$ different microstates

. Second, draw all possible microstates. Calculate M_L and M_S for each microstate,

$$M = \sum_{i=1}^{e} m_i$$

with where m_i is either m_l or m_s for the i-th electron, and M represents the resulting M_L or M_S respectively:

	m_l				
	$+1$	0	-1	M_L	M_S
	$\uparrow$	$\uparrow$		1	1
all up	$\uparrow$		$\uparrow$	0	1
		$\uparrow$	$\uparrow$	-1	1
	$\downarrow$	$\downarrow$		1	-1
all down	$\downarrow$		$\downarrow$	0	-1
		$\downarrow$	$\downarrow$	-1	-1
	$\uparrow\downarrow$			2	0
	$\uparrow$	$\downarrow$		1	0
one up	$\uparrow$		$\downarrow$	0	0
one down	$\downarrow$	$\uparrow$		1	0
		$\uparrow\downarrow$		0	0
		$\uparrow$	$\downarrow$	-1	0

$$\downarrow \quad \uparrow \;\big|\; 0 \;\; 0$$

$$\downarrow \; \uparrow \;\big|\; {-1} \;\; 0$$

$$\uparrow\downarrow \;\big|\; {-2} \;\; 0$$

Third, count the number of microstates for each M_L—M_S possible combination

M_S

M_L	+1	0	−1
+2		1	
+1	1	2	1
0	1	3	1
−1	1	2	1
−2		1	

Fourth, extract smaller tables representing each possible term. Each table will have the size $(2L+1)$ by $(2S+1)$, and will contain only "1"s as entries. The first table extracted corresponds to M_L ranging from −2 to +2 (so $L = 2$), with a single value for M_S (implying $S = 0$). This corresponds to a ^{1}D term. The remaining table is 3×3. Then we extract a second table, removing the entries for M_L and M_S both ranging from −1 to +1 (and so $S = L = 1$, a ^{3}P term). The remaining table is a 1×1 table, with $L = S = 0$, i.e., a ^{1}S term.

S=0, L=2, J=2 S=1, L=1, J=2,1,0

^{1}D$_2$ ^{3}P$_2$, ^{3}P$_1$, ^{3}P$_0$ S=0, L=0, J=0

M_s   **M_s** ^{1}S$_0$

0   **+1 0 −1**   **M_s**

M_l	0
+2	1
+1	1
0	1

M_l	+1	0	−1
+1	1	1	1
0	1	1	1
−1	1	1	1

M_l	0
0	1

$$
\begin{array}{c|c}
-\mathbf{1} & 1 \\
\\
-\mathbf{2} & 1 \\
\end{array}
$$

Fifth, applying <u>Hund's rules</u>, deduce which is the ground state (or the lowest state for the configuration of interest.) Hund's rules should not be used to predict the order of states other than the lowest for a given configuration. If only two equivalent electrons are involved, there is an "Even Rule" which states " For two equivalent electrons the only states that are allowed are those for which the sum $(L + S)$ is even".

Assignment: Prove that an np^3 configuration will give rise to ^4S, ^2P, and ^2D states and nd^2 will give rise to ^3F, ^3P, ^1G, ^1D and ^1S states respectively.

5.2.3 Configuration for States with more than Five Electrons

Determining the configuration for elements with more than five electrons using the L-S coupling scheme will be cumbersome, hence a new scheme called ***Hole formalism*** has been devised. This method involves looking at a partially filled shell of n electrons to be treated as n electrons or N-n **positrons,** where N is the total capacity of the shell. As far as electrostatic interaction is concerned, it does not matter whether they are all positively or negatively charged since the energies of interaction are all proportional to the product of two charges.

The several states derived from a particular configuration have different energies which are not easy to evaluate by theoretical calculations. The differences in the energies of these states are small and are in the order of typical energies of a chemical bonds and chemical reactions. For example , the energies of the ^1D and ^1S excited states of the carbon atom in the configuration of $1s^2 2s^2 2p^2$ are ~25 and ~56 kcal/mole respectively above the ^3P ground state.

Each state is represented by the scheme ^{2s+1}L and each state also has sub states. The energy difference between the sub states are generally an order of magnitude less than the energy difference between each state itself and can be ignored in ordinary chemical reactions. However, for heavy metals (Lanthanides) this energy difference between sub states are comparable to the energy difference between the states and hence the LS coupling scheme becomes inadequate. Other schemes like the *jj* coupling will need to be applied to determine the states of each configuration.

5.3 Ionization Potential

If there is sufficient energy to do the work, it is possible to remove electrons from an atom, ion or molecule. The energy needed to do this work without leaving the detached electron with any kinetic energy is called the ***ionization potential*** denoted by the letter *I*. The energy to remove the first electron is called the *first ionization energy;* the second is called the second ionization

energy etc. In general, the algebraic sum of all ionization potentials is *positive*. Ionization potential forms the minimum for alkali metals and the maximum for the noble gases as we go across the periodic table except for mercury. However there are some irregularities in this sequence, despite a sharp rise going from alkali metals to the noble gases. This is explained by the ability of the electrons to shield and interact with each other as the shell is gradually filled up

5.4 Electron Affinity

It is possible to attach an electron to an atom, ion or molecule. The energy released while doing this is called the ***electron affinity*** of the specie denoted by the symbol *A*. Electron affinities may be positive or negative (when specie does not want an extra electron but is forced to take it). The accuracy in measuring electron affinity is low because they are often measured by indirect methods unlike ionization potential which is measured by spectroscopic methods. The halogens have the highest electron affinity because they only require adding on one electron to achieve the noble gas configuration. The alkali metals have the lowest electron affinity because the only electron in their outermost shell is not well bounded to their nuclei; hence, they are easy to remove. Ideally the electron affinity of an atom is numerically equal to the ionization potential of the corresponding anion.