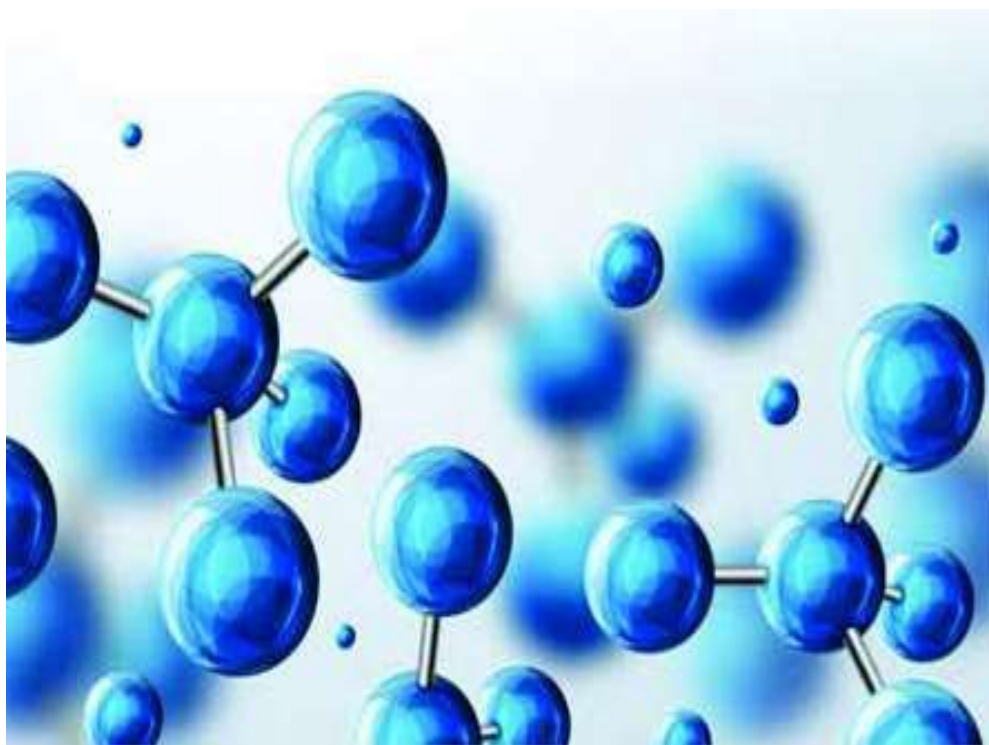




General Chemistry

1. INTRODUCTION

Atoms are the building blocks of which all matter in the universe is made. In everyday life we are familiar with many kinds of structures made of building blocks that we can see. For example, the wall of your house is constructed of bricks bound together with mortar. If we stand at a distance, we do not see the individual bricks, only the total structure can be seen; but, if we approach more closely, we can see the shape and size of each individual brick together with the layer of mortar that binds each brick to its neighbors. By way of contrast, in observing structures made of atoms we are always standing at a distance, we are always so far away that we can not see the sizes and shapes of individual atoms. In fact, as we understand more about the fundamental laws that govern the behavior of matter, we believe that it will never be possible to construct any instrument that will enable us to see atoms distinctly in the same way that we can see bacteria through a microscope. But, through many decades of experiments in chemistry and physics, indirect evidence has been accumulating that proves beyond any doubt that atoms do exist, and that all matter is made of atoms and atoms themselves are constructed of many particles.

Many of the fundamental particles are now recognized to be the basic building blocks of all atoms. Under ordinary

conditions, three fundamental particles are of major importance in chemistry. These particles are: the **electron**, mass = 0.000555 amu (on the scale on which that of ^{12}C is 12.00000) and charge -1.6021×10^{-19} C or -1 (relative scale); the **proton**, mass = 1.00728 amu and charge equal but opposite to that of the electron and **neutron**, mass = 1.00867 amu and charge zero.

In addition to these three fundamental particles, many other particles, such as quarks, positrons, neutrinos, pions and muons, have also been discovered. It is not necessary to study their characteristics to learn the fundamentals of atomic structure that are important in chemical reactions.

Although this evidence does not give us directly a picture of atoms, it does enable us to deduce their shapes and structure. Now we are going to use our previous knowledge to construct a mental picture for the atom. For our immediate purpose, the important conclusion is that sometimes, as in the collision of gaseous atoms, we find that atoms behave as elastic spheres with diameters of the order of $1/100\ 000\ 000$ cm (10^{-8} cm). At other times the atoms behave as if they were made up of electrons moving in orbits like planets around the sun. At still other times, when taking part in chemical combination or chemical reaction, the behaviour of the atom suggests that its outer part is made up of an

electron cloud the shape of which is determined by what is called ***wave mechanics***. The evidence indicate that, at the center of the atom there is an extremely small subatomic particle called the ***nucleus*** which contains a positive charge equivalent to but opposite in sign to the negative charge of the electron cloud. The nucleus also contains nearly all the mass of the atom and its atomic energy. It is roughly one-billionth (10^{-12}) centimeter in diameter. This gives us an idea of the infinitesimally small size of the atomic nucleus.

2. ATOMIC STRUCTURE

2.1. The nuclear atom

Rutherford (1912) put forward the nuclear model of the atom. According to this model, the atom consists of a positively charged nucleus with electrons revolving around it different orbits, like the planets around the sun. if Newton's laws of motion and the laws of physics were applicable on the atomic scale we would expect that atoms would no longer exist. It was clear even in 1913 that something in this analysis was wrong or at least inapplicable to electrons in atoms, because simply atoms are exist.

2.2. Wave theory and electromagnetic radiation

All types of electromagnetic radiation (radiant energy), Figure (2.1) can be described in the terminology of waves.

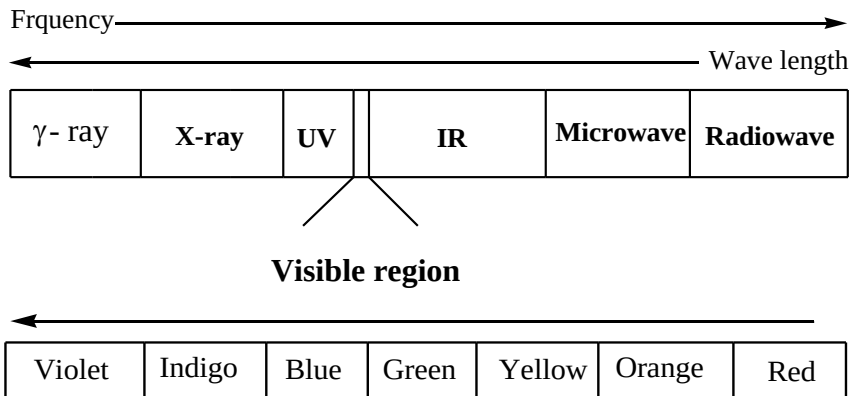


Fig.2.1.The electromagnetic spectrum

The significant feature of wave motion is its repetitive nature, as shown in Figure (2.2). The wave length λ (lambda), is the distance between two adjacent point of the wave. The frequency is the number wave crests passing a given point per unit time, it is represented by the symbol ν (nu) and usually expressed in cycles /second or Hertz (1 Hz = 1 cycle per second) and the height of the wave is the amplitude. E and H are vectors representing the electric and magnetic fields, respectively. The wavelength and the frequency for a given wave are related to each other by the known equation;

$$\lambda \nu = c$$

where c is the velocity of electromagnetic radiations and its value is 2.998×10^8 m/sec.

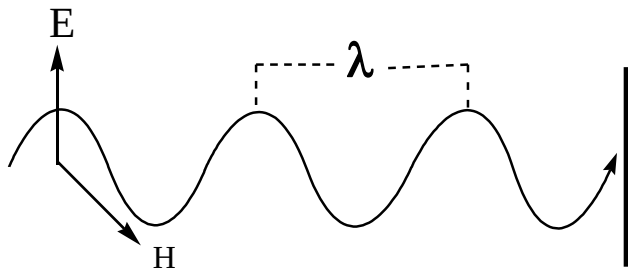


Figure (2.2): The electromagnetic wave

A unit which is particularly useful and commonly used in the infrared region is the wave number, $\tilde{\nu}$, which is the number of

waves contained in a length of one centimeter. The wave number value for an electromagnetic wave is given by the relationship

$$\bar{\nu} = \frac{1}{\lambda} = \frac{c}{\lambda}$$

2.3. HYDROGEN ATOMIC SPECTRA

When atomic hydrogen is heated to a very high temperature (discharge tube), it emits light with a characteristic color that contains only certain wavelengths of light, this is called the hydrogen emission spectra. The spectra was found to consist of sharp lines (hence, the name of line spectra) as shown in Figure (2.3).

In 1885, Balmer stated that, the wave number of the lines in the visible region (Balmer series) can be calculated using the empirical relation;

$$\bar{\nu} = R \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

where **R** is known as Rhydberg constant = 109678 cm⁻¹, and **n** is an integer greater than 2, i.e., 3, 4, 5, 6, ...∞, corresponding the first, second, third, fourth,.....etc, respectively.

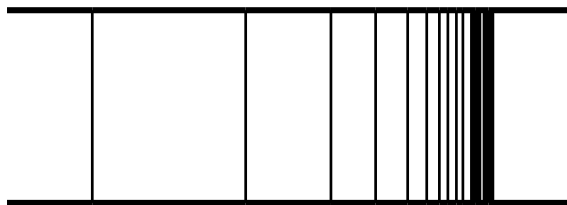


Figure (2.3): Atomic spectra of hydrogen in the visible region

Later it was discovered that, four other series of lines in the ultra violet and infrared regions known as Lyman (UV), Paschen (IR), Brackett (IR), and Pfund (IR) can be established by the general empirical relation, Rhydberg equation.

$$\bar{\nu} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where n_1 and n_2 are integers and n_2 is always greater than n_1 . The wave number of the lines in the mentioned series can be calculated using Rhydberg equation, as summarized in Table (2.1).

**** Calculate the wavelength of the third line in the Brackett series for hydrogen. (2.16612 x 10⁻⁴ cm)***

**** Calculate the energy required to remove an electron from the lowest energy level of the hydrogen atom to produce H⁺(the ionization potential). (2.18 x 10⁻¹⁸ J)***

**** Calculate the energy liberated when an electron drops from the fifth to the second energy level in hydrogen. (4.58 X 10⁻¹⁹ J)***

Table (2.1): Series of lines in the hydrogen spectra

Series	n ₁	n ₂				
		1 st line	2 ^{ed} Line	3 ^{ed} line	4 th Line	 α
Lyman	1	2	3	4	5	 ∞
Balmer	2	3	4	5	6	 ∞
Paschen	3	4	5	6	7	 ∞
Brackett	4	5	6	7	8	 ∞
Pfund	5	6	7	8	9	 ∞

2.4. ORIGINS OF QUANTUM THEORY

Quantum theory originated in 1900 in the mind of Max Planck, a professor at the University of Berlin, who was concerned with explaining the energy radiated by hot black bodies. Professor Planck discovered that experiment and theory could be brought into agreement by assuming that energy could be absorbed or

emitted only as packages that he called quanta (singular quantum), hence the name of quantum theory. The concept of quantization of energy was applied by Einstein (1905) to explain the photoelectric effect and by N. Bohr to explain the spectrum of atomic hydrogen.

Einstein proposed that light is propagated through space in definite quanta called photons. The energy of these photons is given by the relation

$$E = h \nu$$

Where **h** is Planck constant = 6.62×10^{-34} Js.

2.5. Bohr's theory of the hydrogen atom

Bohr's theory was intended to explain the spectrum of atomic hydrogen, that is, to explain why hydrogen absorbs and emits light of only well-defined wavelengths. Bohr use the concept of the quantum theory which state that "light is not emitted or absorbed in any amount but only in quanta of energy equals $h \nu$ " and assumed that the hydrogen atom can exist only in certain energy states or in another expression he assumed that the electron can move around the proton (the nucleus of hydrogen atom) in

only certain definite circular orbits called energy levels. The angular momentum of such orbits is given by the relation

$$mvr = \frac{nh}{2\pi}$$

where **m** and **v** are the mass and velocity of the electron, respectively, **r** is the radius of the circular orbit and **n** is an integer called ***the quantum number*** and can take any value of 1, 2, 3, 4, 5, ... ∞

He further assumed that one of these orbits has the minimum energy allowed for a hydrogen atom and is the most stable state of the atom (the ground state). An electron in this orbit cannot lose energy. Bohr according to this assumption was able to calculate the radius and energy of the various orbits (energy levels), see appendix (1, 2).

Bohr also assumed that light can be emitted or absorbed when the electron transfer between two levels of different energy, as shown in Figure (2.4).

$n = \infty$ (ionization)

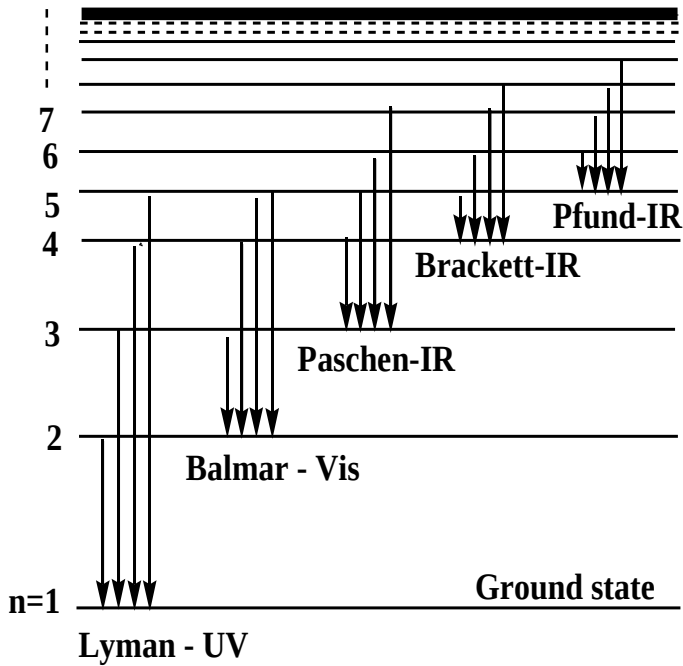


Figure (2.4): Energy level diagram for the hydrogen atom

According to the last assumption Bohr was able to derive an equation agrees with the empirical Rhydberg equation, see appendix (3).

2.6. Modification of Bohr's theory

Further investigation of the spectrum of hydrogen with spectroscope of high resolving power showed that Bohr's theory did not account for all of the details or so called fine structure of

the spectrum. Therefore, several improvements in the original theory were made by Bohr, Wilson, and Sommerfeld. One of these improvements led to propose the existence of elliptical orbits in addition of circular orbits and more than one quantum number is required to describe fully the electronic structure and the spectrum of hydrogen atoms, see Figure (2.5).

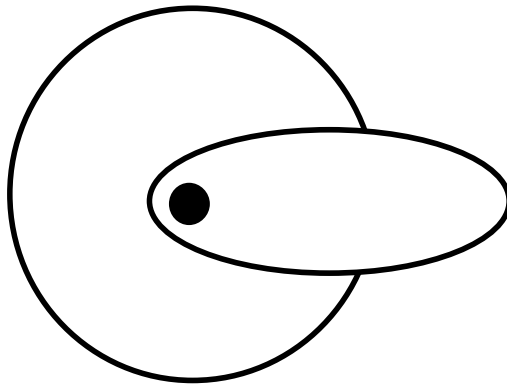


Figure (2.5): Orbits of Bohr-Sommerfeld atom for $n = 2$

Bohr's theory was, however, unable to account for the more complex spectra of atoms other than hydrogen (many-electron atoms). The simple model of an electron moving in a closed circular or elliptical orbit is so naïve regarding to the actual motion of the electrons. Complete explanation of the observed spectra had to await the development of the quantum theory.

2.7. Dual nature of the matter

The quantum theory was introduced the term duality in properties for light, light (electromagnetic radiation) as a wave behaves also as particles. The particle of light was named quantum or photon.

In 1924 **L. de Broglie** advanced the hypothesis that such a dual nature is characteristic not only for light but it applies as well to all the particles. He showed that, from the quantum theory equation $E = h \nu$ and from the known equation of relativity theory $E = mc^2$, thus we have

$$mc^2 = h \nu \text{ or } mc = h \nu / c$$

where mc is the momentum p of the photon or an equivalent particle. Thus

$$mc = h / \lambda \text{ or } \lambda = h / mc \text{ or}$$

$$\lambda = h / p$$

De Broglie said that the last equation should apply to electrons, if we substitute for the mass (9.1×10^{-28} gm) and velocity (5.9×10^8 cm/sec) of the electron, we get

$$\lambda = \frac{6.62 \times 10^{-27} \text{ erg sec}}{9.1 \times 10^{-28} \text{ gm} \times 5.9 \times 10^8 \text{ cm/sec}}$$

$$= 1.2 \times 10^{-8} \text{ cm} = 1.2 \text{ \AA}$$

De Broglie's theory and the resulting equation were regarded as pure speculation by the skeptical. But in 1927 Davisson and Germer found that electrons are scattered by crystals in a way similar to X-ray, and showed that the wavelength of moving electrons was in complete agreement with the de Broglie equation.

****Calculate the de Broglie wavelength for a 150 gm ball moving 60 km /hour.***

On this basis, Bohr orbits would correspond to waves like as those pictured in Figure (2.6). The circumference of the orbit must be an integral multiple of the wavelength of the electron in order to avoid destructive interference. If this occurs there would be no electron in such orbit; hence we write

$$2 \pi r = n \lambda$$

substitution for $\lambda = h / mv$ gives

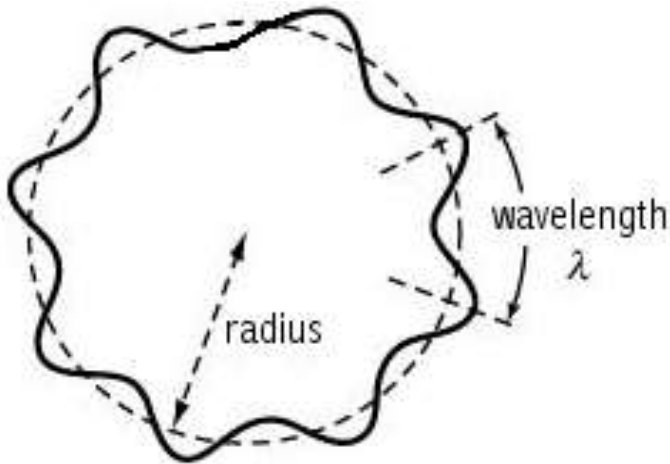
$$2 \pi r = nh / mv$$

from which we get

$$mvr = nh / 2\pi$$

which is the same as Bohr postulation as shown before.

n = number of wavelengths



n must be an integer

Figure (2.6): electron waves in circular orbit.

2.8. Heisenberg Uncertainty Principle

The Bohr theory succeeded it provide both a simple physical picture of the motion of an electron in an atom and a method of calculating its possible energies. Any new theory must

do all this, but it must also account for diffraction effects and reduce the number of arbitrary assumptions required by the older theory.

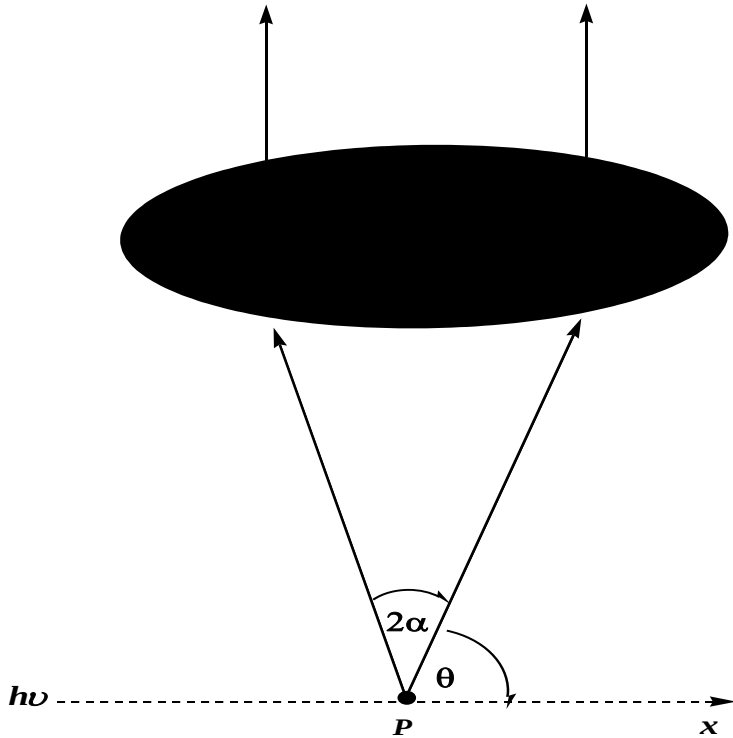


Figure (2.7): The γ - ray microscope

Heisenberg uncertainty principle states that, it is impossible to determine simultaneously and precisely, both the position and the momentum of an electron. Suppose we have devise a hypothetical experiment to measure the position and velocity of an

electron. We could set two " γ - ray" microscopes and measure the time taken for the electron to pass from one to the other. P , in Figure (2.7), represents the electron. It can be observed if a photon incident upon it is scattered into the aperture of the microscope, i.e. within the cone of angle 2α . Now a photon of frequency ν will have an associated wavelength:

$$\lambda = c / \nu$$

thus,

$$c / \nu = h / p \text{ , whence}$$

$$P = h \nu / c$$

If the photon is scattered in a direction making an angle θ with the x axis, the electron will receive a component of momentum along the x axis of,

$$\frac{h\nu}{c} (1 - \cos \theta)$$

and since the electron will be detected for any value of the angle between $90^\circ \pm \alpha$, the momentum may have any value between

$$\frac{h\nu}{c} [1 - \cos (90 - \alpha)] \quad \text{and} \quad \frac{h\nu}{c} [1 - \cos (90 + \alpha)]$$

i.e. between

$$\frac{h\nu}{c} (1 - \sin \alpha) \quad \text{and} \quad \frac{h\nu}{c} (1 + \sin \alpha)$$

If we define this spread of values as the ***uncertainty*** in the value of ***p***, and denote it by Δp , then

$$\Delta p = \frac{2 h \nu}{c} \sin \alpha$$

We could try to reduce this uncertainty by making α small, i.e. by using a microscope of smaller aperture, but the accuracy with which an object can be located by a microscope is defined by the Rayleigh equation for the resolving power

$$\Delta x = \frac{c}{\nu \sin \alpha}$$

where Δx is the uncertainty in x , the coordinate defining the position of the electron. Thus a smaller aperture, while decreasing the uncertainty in the momentum, would increase the uncertainty in position. In this experiment

$$\Delta p \cdot \Delta x = \frac{2 h \nu}{c} \sin \alpha \cdot \frac{c}{\nu \sin \alpha}$$

$$= 2 h$$

In general, the product $\Delta \mathbf{x} \cdot \Delta \mathbf{p}$ is of the order of magnitude of the Planck constant, h . this is one way of expressing the Heisenberg uncertainty principle.

We can illustrate its importance by a rough calculation. Suppose that we could locate the position of an electron with an uncertainty of 0.1 pm, i.e. $\Delta \mathbf{x} = 10^{-13}$ m. substituting values of $\Delta \mathbf{x}$ and h in the above equation we obtained

$$\Delta \mathbf{p} = 2 \times 6.6 \times 10^{-34} / 10^{-13}$$

$$= 13.2 \times 10^{-21} \text{ kg m s}^{-1}$$

This uncertainty in momentum would be quite negligible in macroscopic systems, but it is far from negligible in systems containing electrons since we are then dealing with masses of the order of 10^{-30} kg. Precise statements of the position and momentum of electrons have to be replaced by statements of the probability that the electron has a given position and momentum. The introduction of probabilities into the description of electronic

behavior is a direct consequence of the Heisenberg uncertainty principle.

2.9. Quantum mechanics

According to the Heisenberg Uncertainty Principle it is impossible to specify simultaneously the exact position and momentum of an electron circling around its nucleus. This principle is a logical consequence of the wave properties and the high speed of the electrons. For this reasons we became familiar to describe the motion of an electron not in a closed orbit as stated by Bohr but by the probability of finding the electron or electron cloud (electron density) in a definite space or more convenient by **orbital**. The successful application of quantum-mechanical methods to a number of important problems in chemistry has given rise to a new branch of that science – quantum chemistry.

The starting point for much of quantum mechanics is the Schrodinger wave equation (1927). This equation describes an electron in the field of the nucleus as a three-dimensional wave based on the ideas suggested by de Broglie. If the de Broglie relationship is valid and if the motion of the electron is analogous to a system of standing waves Schrodinger formulated the

following equation to describe the behavior of the electron in the hydrogen atom.

$$-\frac{h^2}{8\pi^2m} \left(\frac{\partial^2 \varphi}{\partial x^2} + \frac{\partial^2 \varphi}{\partial y^2} + \frac{\partial^2 \varphi}{\partial z^2} \right) + V\varphi = E\varphi$$

where ψ is called the wave function and the square of the wave function represents the probability of finding an electron in a certain volume in the atom. The Schrodinger equation can be arranged to the form

$$\left[-\frac{h^2}{8\pi^2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V \right] \varphi = E\varphi$$

and shortened to

$$\hat{H} \psi = E \psi$$

$\hat{H}$ is called a "Hamiltonian Operator" and it defines the operation or sequences of operations to be performed on the function ψ . The result of carrying out these operations on the function ψ is the same as multiplying ψ by the electronic energy E .

This equation is also called the **wave equation** for the electrons and is need not to be understood (very much mathematics are involved) to read this book.

The function $\psi (x, y, z)$ is called an **atomic orbital**. It is analogous to the function $f (x)$ which represents the amplitude in the case of the vibration of a stretched string. We can, therefore refer to ψ as amplitude function. Now if the behavior of electrons is represented by a wave equation, we can equate the square of the function, ψ^2 representing the amplitude in the wave equation with either (a) the electron density, or (b) the probability that the electron will be found in a given volume element. We thus get a physical significance for the function $\psi^2 (x, y, z)$, in that

$$\psi^2 dx . dy . dz = \psi^2 dv$$

measures the probability that the electron will be found in the volume element dv surrounding the point whose coordinates are (x,y,z) .

Suppose we could photograph the position of an electron at any particular instant ; three-dimensional photography would enable us to assign coordinates, x, y, z to the electron and to plot it as a point. Now the electron is in rapid motion and a photograph

taken a fraction of a second later would reveal the electron in a new position. Several millions of photographs would produce an array of dots in our diagram which would resemble a cloud, dense in regions which a large number of points are crowded together, diffuse in regions where there are very few points. This is pictured in Figure (2.8).

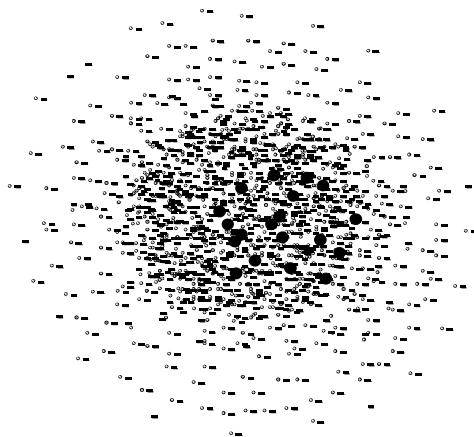


Figure (2.8): Electron cloud of the hydrogen atom in the ground state

2.9.1. Acceptable solutions – the quantum numbers

There is an infinite number of solutions to Schrodinger equation but only some of these are acceptable giving what we called the quantum numbers.

Principle quantum number, n , it's the most important quantum number with respect to the energies of electrons in atoms. It describes the main energy level an electron occupies in an atom. The Principle quantum number can take any positive integer.

$$n = 1, 2, 3, 4, 5, 6, 7, 8, \dots \infty$$

Azimuthal quantum number, l , is also called the **angular momentum quantum** number because it determines the angular momentum of the electron and the shape of the electron cloud. In other words the *azimuthal quantum number* describes the sublevel that an electron may occupy. Within each energy level, l may take integral values from 0 up to and including $(n-1)$. We usually give a letter notation to each value of l , each corresponds to a different kind of sublevel. For instance, if $n = 4$, l might be 0, 1, 2, 3 corresponding to ***s, p, f, d*** sublevels, respectively. This letter notations are historically quoted from the characteristics of spectral emission lines produced by electrons occupying these orbitals: ***s***: sharp, ***p***: principle, ***d***: diffuse, ***f***: fundamental.

For the 1st energy level $n = 1$: $l = 0$ i.e., only ***s*** sublevel

2^{ed} energy level $n = 2$: $l = 0, 1$ i.e., there are ***s*** and ***p***

3^{ed} energy level $n = 3$: $l = 0, 1, 2$ i.e., there are ***s, p*** and ***d***

The magnetic quantum number, m , it describes the orientation of the electron cloud in space. The magnetic quantum number can have all the integral values from $-l$ through 0 up to and including $+l$ ($m = -l \dots 0 \dots +l$). The permissible values of m depend on the value of l , for example when $l = 1$ which designates the p sublevel, there are three values of m : -1, 0, 1. there are thus three distinct electron clouds associated with the p sublevel. We refer to these values as three orbitals p_x , p_y , and p_z . According to this conclusion, the d sublevel contains 5 orbitals and the f sublevel contains 7 orbitals.

The spin quantum number, s , refers to the spin of an electron on its own axis and the orientation of the magnetic field produced by this spin. This spin can be in either of two directions; hence, there are two possible values of the spin quantum number; $1/2$ or $-1/2$. The values of n , l , and m describe a particular atomic orbital. Each atomic orbital can accommodate no more than two electrons, one with spin = $1/2$ and another with spin = $-1/2$.

The Pauli Exclusion Principle must also be considered in connection with the quantum numbers assigned to electrons in atoms. This principle state that "**no two electrons in the same atom can have the same set of four quantum number**" and is therefore,

roughly analogous to the classical principle that two bodies cannot be in the same place at the same time. Pauli Exclusion Principle leads to a restriction of a maximum of two electrons in any orbital. For example, if we choose $n = 1$, $l = 0$ and $m = 0$, we are taking about **1s** orbital, we are able to have only two electrons with different values of the spin quantum number $s = 1/2$ or $s = -1/2$. This limits the number of electrons in any given orbital to two, and it also requires that the spins of these two electrons be in opposite directions. The maximum number of electrons that can be in any shell or subshell is determined by the allowed quantum numbers and the Pauli Exclusion Principle, as stated in Table (2.2).

Table (2.2): The permissible values of quantum numbers
(number of electrons through $n = 3$)

n	l	m	s	symbol	Total number of electrons
1	0	0	$+\frac{1}{2}, -\frac{1}{2}$	1s	2
2	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2s	2
	1	+1 0 -1	$+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$	2p	6
					8
3	0	0	$+\frac{1}{2}, -\frac{1}{2}$	3s	2
	1	+1 0 -1	$+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$	3p	6
	2	+2 +1 0 -1 -2	$+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$ $+\frac{1}{2}, -\frac{1}{2}$	3d	10
					18

2.9.2. Atomic orbitals

An orbital is the space in which there is a high probability of finding the electron and is determined by a set of quantum numbers n , l , m .

s Orbitals. As shown from Table 2.2, for every principle quantum number (principle shell) there is an s orbital with $l = 0$ and $m = 0$. As shown in Figure (2.9), the electron probability density at a given distance from the nucleus is plotted against distance from the nucleus for the first three s orbitals (the electron clouds are three dimensional and only cross-sections are shown). It is clear from the Figure that $1s$ does not contain any **node** (node is a region in which the electron probability density is equal to zero), while $2s$ and $3s$ contain one and two nodes, respectively. The number of nodes for a given s orbital is always $(n-1)$.

It should be noted that, the following diagrams (atomic orbitals) represent the angular functions. In these diagrams + and – donate the algebraic signs of the angular function, which determine their symmetry, and have nothing to do with electrical charges.

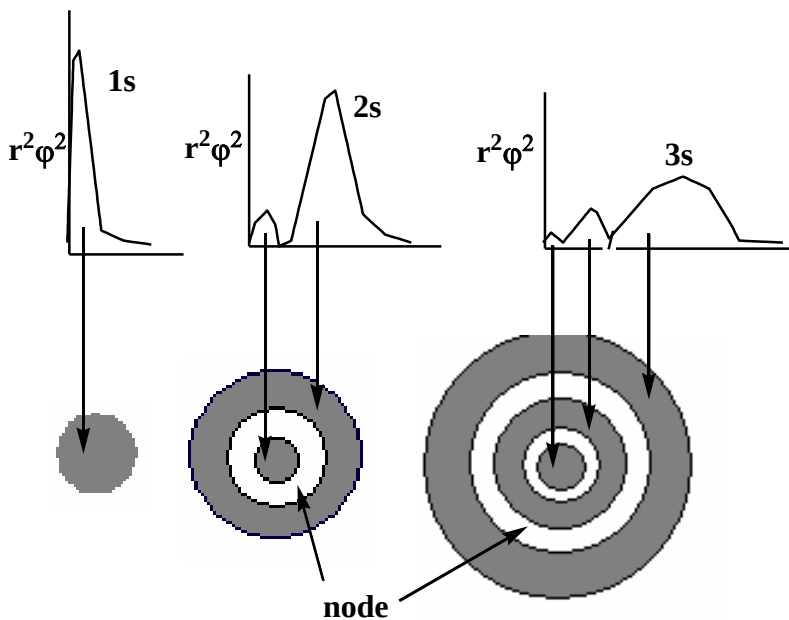


Figure (2.9): Electron probability density distribution for s orbitals

We describe an s orbital as spherically symmetric, as shown in Figure (2.10).

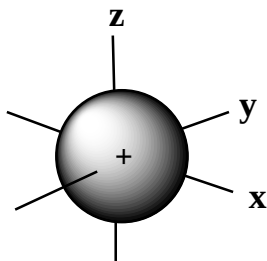


Figure (2.10): s atomic orbital

p Orbital. Beginning with the second ($n = 2$) energy level each level contains a ***p*** sublevel ($2p, 3p, 4p \dots$) with $l = 1$. Each of this sublevel contains a set of three atomic orbitals (three allowed values of m , 1, 0 and -1). The three mutually perpendicular ***p*** orbitals in each set are referred as ***p_x***, ***p_y*** and ***p_z*** to indicate the axis along which each of the three two-lobed orbitals is directed, as shown in Figure (2.11).

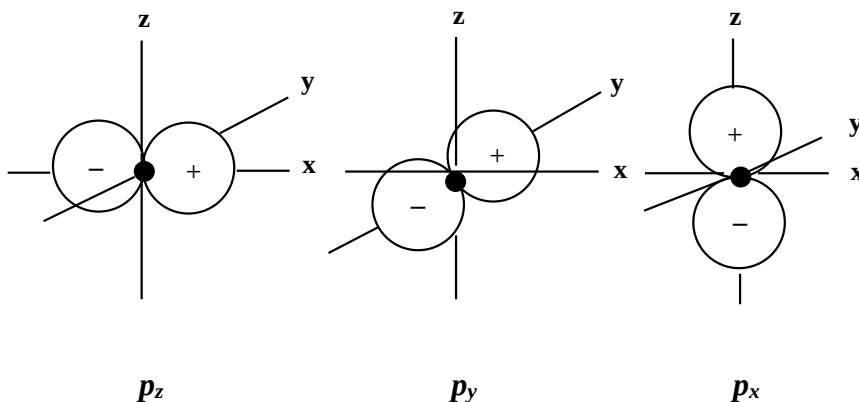
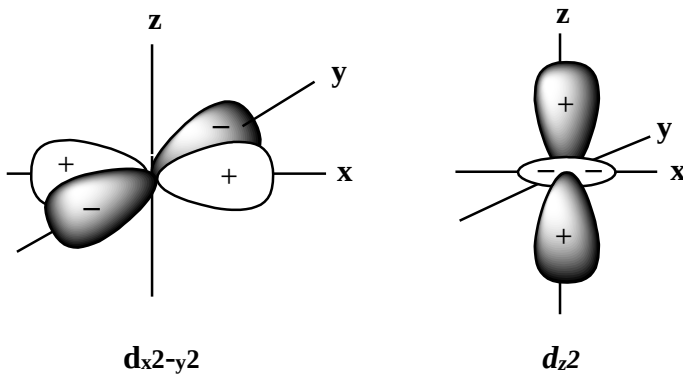


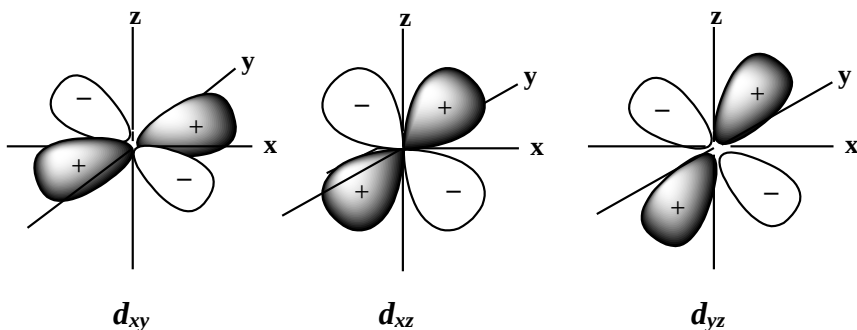
Figure (2.11): *p* atomic orbital

d Orbital. Beginning with the third energy level ($n = 3$), each level contains a ***d*** sublevel ($3d, 4d, 5d, \dots$) with $l = 2$. Each ***d*** composed of five orbitals (five allowed values of m , 2, 1, 0, -1 and -2). The shapes of the five ***d*** orbitals are given in Figure (2.12). The ***d_{z2}*** is symmetrical around the ***z*** axis. The ***d_{x2-y2}*** is symmetrical around the ***x*** and ***y*** axes, where the four lobes are directed along the

axes. The d_{xy} , d_{xz} and d_{yz} are exactly alike except that they lie in the xy , xz and yz planes, respectively.



The lobes are directed along the axes



The lobes are directed between the axes

Figure (2.12): d atomic orbitals

f* Orbital.** Beginning with the fourth energy level ($n = 4$), each level contains a fourth sublevel called ***f, with $l = 3$. Each ***f***

contains a set of seven atomic orbitals, corresponding to the seven allowed values of m (3, 2, 1, 0, -1, -2, and -3). The shapes of the seven f orbitals are given in Figure (2.13).

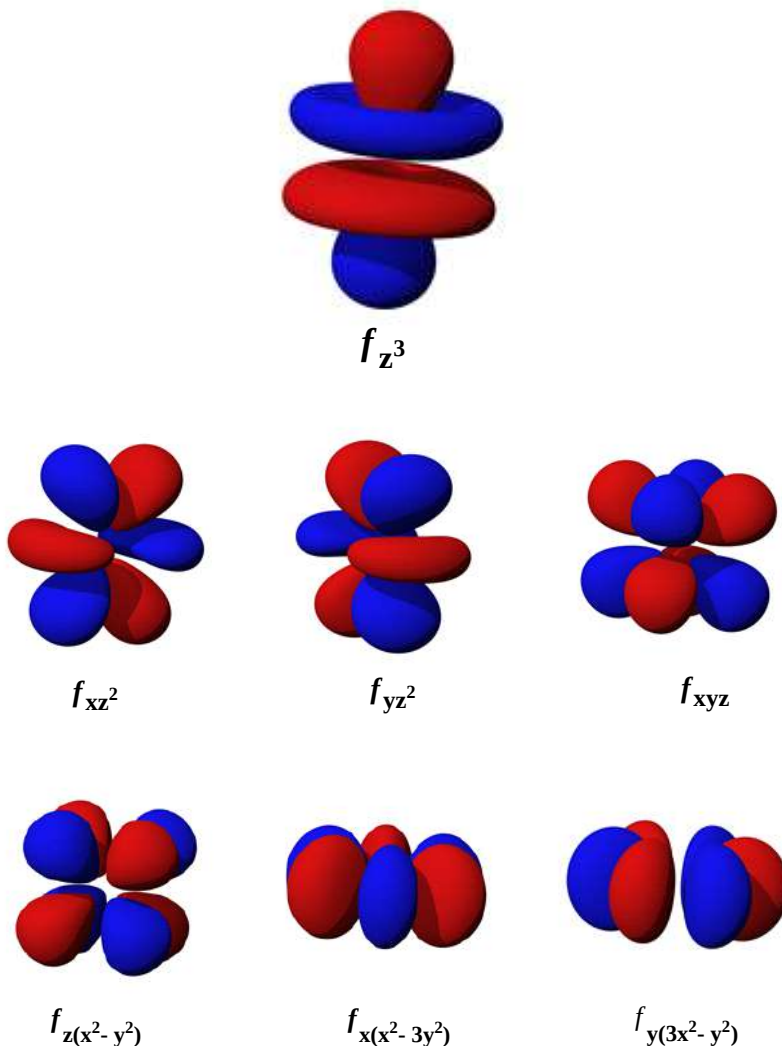


Figure (2.13): f atomic orbitals

Let us summarize in some of the information we have developed to this point. The principle quantum number n indicates the energy level. The number of sublevels per energy level is equal to n , the number of atomic orbitals per energy level is n^2 , and the maximum number of electrons per energy level is $2n^2$, as summarized in Table (2.3).

Table (2.3): *The number of sublevels, atomic orbitals and electrons per energy levels for the first four principle quantum numbers*

Energy level, N	Number of sublevels n	Number of atomic orbitals n^2	Max. number of electrons, $2n^2$
1	1	1 (1s)	2
2	2	4 (2s, three 2p`s)	8
3	3	9 (3s, three 3p`s, five 3d`s)	18
4	4	16 (4s, 4p, 4d, 4f)	32

2.9.3. Electronic configurations of atoms

To examine the way of distribution of electrons between atomic orbitals in different elements in their ground state (electronic structure or configuration), we must first consider two other useful rules in addition to the already discussed Pauli Exclusion Principle.

Hund's rule. Electrons must occupy all the orbitals of a given sublevel (energetically equivalent or *degenerate* orbitals) singly before pairing begins and these unpaired electrons have parallel spins.

Aufbau principle. The total energy of the atom is as low as possible. The usual order of filling (Aufbau order) of the orbitals of an atom is given in Figure (2.13), and Figure (2.14) gives an easy way to remember the Aufbau order.

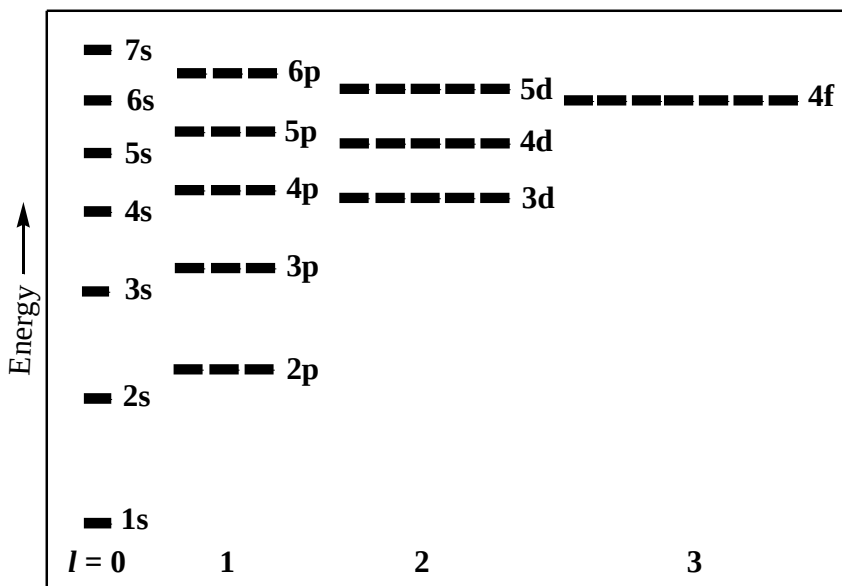


Figure (2.13): Energy levels of atomic orbitals

A hydrogen atom has one electron, and we want to characterize that electron by means of quantum numbers. We are mostly interested in the lowest energy state, for which $n = 1$. For $n = 1$, l can only be zero, and therefore, $m = 0$. The spin quantum number, s can be either $+1/2$ or $-1/2$. This information can be summarized by writing $1s^1$ where 1 indicates the lowest (1^{st}) energy level, s indicates that $l = 0$ and the superscript ^{1} indicates the number of electrons (one in this case).

We can build a helium atom by adding the proper nuclear particles (one proton and two neutrons) and one electron to an

atom of hydrogen, and the electronic configuration can be represented by $1s^2$. The two electrons in this case have the same n , l and m but they differ in the spin quantum number, one electron has $s = +1/2$ and the other has $s = -1/2$ (spin paired). Remember that, Pauli Exclusion Principle prohibits both electrons from having identical set of quantum numbers.

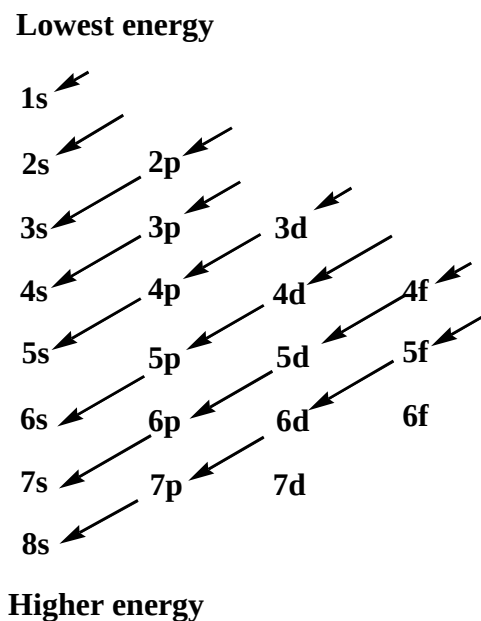


Figure (2.14): Aufbau order of filling atomic orbitals

The next element is lithium with three electrons. The third electron can not have $n = 1$ because all the allowed values of l , m and s when $n = 1$ have been used by the first two electrons. The

third electron must have $n = 2$ and can have $l = 0$, $m = 0$ and $s = +1/2$ or $-1/2$. The electronic configuration of Li is thus represented as $1s^2 2s^1$. Similarly, the electronic configuration of beryllium (Be) which has four electrons, is represented by $1s^2 2s^2$.

Boron contains five electrons. Four of these electrons are characterized by $1s^2 2s^2$. Remember, we are still in the second energy level, $n = 2$, the next lowest energy level is characterized by $n = 2$ and $l = 1$, see Table (2.2). When $l = 1$, the allowed values of m are $+1$, 0 and -1 ; and for each value of m there are two allowed spin quantum numbers. For the fifth electron in boron, we choose $n = 2$, $l = 1$, $m = -1$ and $s = -1/2$. The electronic configuration is then $1s^2 2s^2 2p^1$. It should be noted that $m = -1$ and $s = -1/2$ have been chosen arbitrarily. We would as well have chosen $m = 0$ or $+1$ and $s = +1/2$, but it is a customary to choose the smallest.

For carbon atom, the sixth electron can be described by $n = 2$, $l = 1$, $m = 0$ and $s = -1/2$, and the configuration becomes $1s^2 2s^2 2p^2$. Here, we used another allowed value of m to get a spin parallel state for the last two electrons, according to **Hund's rule**. By analogy to carbon, we can predict that the highest energy electron (the seventh) in nitrogen atom has the following set of quantum numbers $n = 2$, $l = 1$, $m = +1$ and $s = -1/2$ with spin

parallel to the last two electrons, giving the configuration $1s^2 2s^2 2p^3$.

The eighth, ninth and tenth electrons of oxygen, fluorine and neon respectively, take the other allowed value of spin quantum number $+1/2$ in which spin pairing occurs. The expected electronic configurations for these atoms are $1s^2 2s^2 2p^4$, $1s^2 2s^2 2p^5$ and $1s^2 2s^2 2p^6$, respectively.

The next elements show electron occupancy similar to that discussed previously in accordance with Aufbau order with some exceptions. The electronic configurations for all of the known elements are summarized in Table (2.4). As you have noticed from the Table that, the electronic configurations of $_{24}\text{Cr}$ and $_{29}\text{Cu}$ is an exception from the Aufbau order. Both have one electron in the 4s orbital and half-filled and filled 3d orbital, respectively. Calculation from quantum mechanics indicates that half-filled and filled sets of equivalent orbitals have a special stability.

It should be mentioned here that, the electronic configurations described here refer to the isolated atoms or ions in the gaseous state. The configuration may well be different if the ion is in a solid structure or in solution.

*Table (2.4): Electron configurations for the ground states of the elements (numbers in parentheses **are uncertain**).*

Ele- ment	At. No.	1	2	3	4	5	6	7
		s	s p	s p d	s p d f	s p d f	s p d f	S
H	1	1						
He	2	2						
Li	3	2	1					
Be	4	2	2					
B	5	2	2 1					
C	6	2	2 2					
N	7	2	2 3					
O	8	2	2 4					
F	9	2	2 5					
Ne	10	2	2 6					
Na	11	2	2 6	1				
Mg	12	2	2 6	2				
Al	13	2	2 6	2 1				
Si	14	2	2 6	2 2				
P	15	2	2 6	2 3				
S	16	2	2 6	2 4				
Cl	17	2	2 6	2 5				
Ar	18	2	2 6	2 6				
K	19	2	2 6	2 6	1			
Ca	20	2	2 6	2 6	2			
Sc	21	2	2 6	2 6 1	2			
Ti	22	2	2 6	2 6 2	2			
V	23	2	2 6	2 6 3	2			
Cr	24	2	2 6	2 6 5	1			
Mn	25	2	2 6	2 6 5	2			
Fe	26	2	2 6	2 6 6	2			

Element	At. No.	1	2	3	4	5	6	7
		s	s p	s p d	s p d f	s p d f	s p d f	S
Co	27	2	2 6	2 6 7	2			
Ni	28	2	2 6	2 6 8	2			
Cu	29	2	2 6	2 6 10	1			
Zn	30	2	2 6	2 6 10	2			
Ga	31	2	2 6	2 6 10	2 1			
Ge	32	2	2 6	2 6 10	2 2			
As	33	2	2 6	2 6 10	2 3			
Se	34	2	2 6	2 6 10	2 4			
Br	35	2	2 6	2 6 10	2 5			
Kr	36	2	2 6	2 6 10	2 6			
Rb	37	2	2 6	2 6 10	2 6	1		
Sr	38	2	2 6	2 6 10	2 6	2		
Y	39	2	2 6	2 6 10	2 6 1	2		
Zr	40	2	2 6	2 6 10	2 6 2	2		
Nb	41	2	2 6	2 6 10	2 6 4	1		
Mo	42	2	2 6	2 6 10	2 6 5	1		
Te	43	2	2 6	2 6 10	2 6 (5)	(2)		
Ru	44	2	2 6	2 6 10	2 6 7	1		
Rh	45	2	2 6	2 6 10	2 6 8	1		
Pd	46	2	2 6	2 6 10	2 6 10			
Ag	47	2	2 6	2 6 10	2 6 10	1		
Cd	48	2	2 6	2 6 10	2 6 10	2		
In	49	2	2 6	2 6 10	2 6 10	2 1		
Sn	50	2	2 6	2 6 10	2 6 10	2 2		
Sb	51	2	2 6	2 6 10	2 6 10	2 3		
Te	52	2	2 6	2 6 10	2 6 10	2 4		
I	53	2	2 6	2 6 10	2 6 10	2 5		
Xe	54	2	2 6	2 6 10	2 6 10	2 6		
Cs	55	2	2 6	2 6 10	2 6 10	2 6	1	
Ba	56	2	2 6	2 6 10	2 6 10	2 6	2	

Ele- ment	At. No.	1	2	3	4	5	6	7
		s	s p	s p d	s p d f	s p d f	s p d f	S
La	57	2	2 6	2 6 10	2 6 10	2 6 1	2	
Ce	58	2	2 6	2 6 10	2 6 10 (2)	2 6	(2)	
Pr	59	2	2 6	2 6 10	2 6 10 (3)	2 6	(2)	
Nd	60	2	2 6	2 6 10	2 6 10 (4)	2 6	(2)	
Pm	61	2	2 6	2 6 10	2 6 10 (5)	2 6	(2)	
Sm	62	2	2 6	2 6 10	2 6 10 6	2 6	2	
Eu	63	2	2 6	2 6 10	2 6 10 7	2 6	2	
Gd	64	2	2 6	2 6 10	2 6 10 (7)	2 6 (1)	2	
Tb	65	2	2 6	2 6 10	2 6 10 (8)	2 6 (1)	2	
Dy	66	2	2 6	2 6 10	2 6 10(10)	2 6	(2)	
Ho	67	2	2 6	2 6 10	2 6 10(11)	2 6	(2)	
Er	68	2	2 6	2 6 10	2 6 10(12)	2 6	(2)	
Tm	69	2	2 6	2 6 10	2 6 10 13	2 6	2	
Yb	70	2	2 6	2 6 10	2 6 10 14	2 6	2	
Lu	71	2	2 6	2 6 10	2 6 10 14	2 6 1	2	
Hf	72	2	2 6	2 6 10	2 6 10 14	2 6 2	2	
Ta	73	2	2 6	2 6 10	2 6 10 14	2 6 3	2	
W	74	2	2 6	2 6 10	2 6 10 14	2 6 4	2	
Re	75	2	2 6	2 6 10	2 6 10 14	2 6 5	2	
Os	76	2	2 6	2 6 10	2 6 10 14	2 6 6	2	
Ir	77	2	2 6	2 6 10	2 6 10 14	2 6 7	2	
Pt	78	2	2 6	2 6 10	2 6 10 14	2 6 9	2	
Au	79	2	2 6	2 6 10	2 6 10 14	2 6 10	2	
Hg	80	2	2 6	2 6 10	2 6 10 14	2 6 10	2	
Tl	81	2	2 6	2 6 10	2 6 10 14	2 6 10	2 1	
Pb	82	2	2 6	2 6 10	2 6 10 14	2 6 10	2 2	
Bi	83	2	2 6	2 6 10	2 6 10 14	2 6 10	2 3	
Po	84	2	2 6	2 6 10	2 6 10 14	2 6 10	2 4	
At	85	2	2 6	2 6 10	2 6 10 14	2 6 10	2 5	
Rn	86	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	

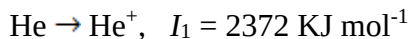
Ele- ment	At. No.	1	2	3	4	5	6	7
		s	s p	s p d	s p d f	s p d f	s p d f	S
Fr	87	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	1
Ra	88	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	2
Ac	89	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 (1)	(2)
Th	90	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 (2)	(2)
Pa	91	2	2 6	2 6 10	2 6 10 14	2 6 10 (2)	2 6 (1)	(2)
U	92	2	2 6	2 6 10	2 6 10 14	2 6 10 (3)	2 6 (1)	(2)
Np	93	2	2 6	2 6 10	2 6 10 14	2 6 10 (5)	2 6	(2)
Pu	94	2	2 6	2 6 10	2 6 10 14	2 6 10 (6)	2 6	(2)
Am	95	2	2 6	2 6 10	2 6 10 14	2 6 10 (7)	2 6	(2)
Cm	96	2	2 6	2 6 10	2 6 10 14	2 6 10 (7)	2 6 (1)	(2)
Bk	97	2	2 6	2 6 10	2 6 10 14	2 6 10 (8)	2 6 (1)	2
Cf	98	2	2 6	2 6 10	2 6 10 14	2 6 10(10)	2 6	2
Es	99	2	2 6	2 6 10	2 6 10 14	2 6 10 11	2 6	2
Fm	100	2	2 6	2 6 10	2 6 10 14	2 6 10 12	2 6	2
Md	101	2	2 6	2 6 10	2 6 10 14	2 6 10 13	2 6	2
No	102	2	2 6	2 6 10	2 6 10 14	2 6 10 14	2 6	2
Lr	103	2	2 6	2 6 10	2 6 10 14	2 6 10 14	2 6 1	2

2. 10. IONIZATION ENERGIES

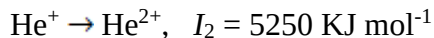
The distribution of electrons in the various orbitals, determined in an empirical way by the operation of exclusion principle, is supported by experimentally by the analysis of atomic spectra and also by the measurement of the so-called ionization potentials or ionization energies. The ionization potential is defined as the energy needed to remove the most easily removable

electron from its equilibrium position in the neutral gaseous atom to infinity. This energy can be determined in kilojoules per mole.

Many-electron atoms have a series of ionization potentials. The first ionization energy is the energy needed to remove one electron from a neutral atom in the gaseous state,



The second ionization energy is defined as the energy needed to remove an electron from a singly charged ion to infinity,



I_2 is greater than I_1 since the negatively charged electron has to be dragged away from an ion with a net positive charge. In other multi-electron atoms there is a third and even a fourth ionization potential, and for the same reason they have a very high energies.

The first ionization energies of the elements in the first two short periods are given in Figure (2.15). We see that the energy needed to remove an electron from a lithium atom is very much less than that needed to remove an electron from helium. The configuration Li, $1s^2 2s^1$, explain this. Ionization of a lithium atom requires the removal of the electron in a 2s orbital, which is effectively screened from the nuclear charge by the inner electrons in the 1s orbital. The electrons in a helium atom, configuration $1s^2$,

are not effectively screened, and so very much more energy to remove one of them.

The next break in the first ionization energy plot comes at beryllium. We see that it takes more energy to remove an electron from this atom than it does to remove one from its neighbors lithium and boron. The configuration $1s^2 2s^2$ is evidently more stable than that for lithium. The electronic configuration of boron is $1s^2 2s^2 2p^1$, and the experimental value for the first ionization energy shows that an electron in a $2p$ orbital is more effectively screened from the nuclear charge by the two paired electrons in the $2s$ orbital.

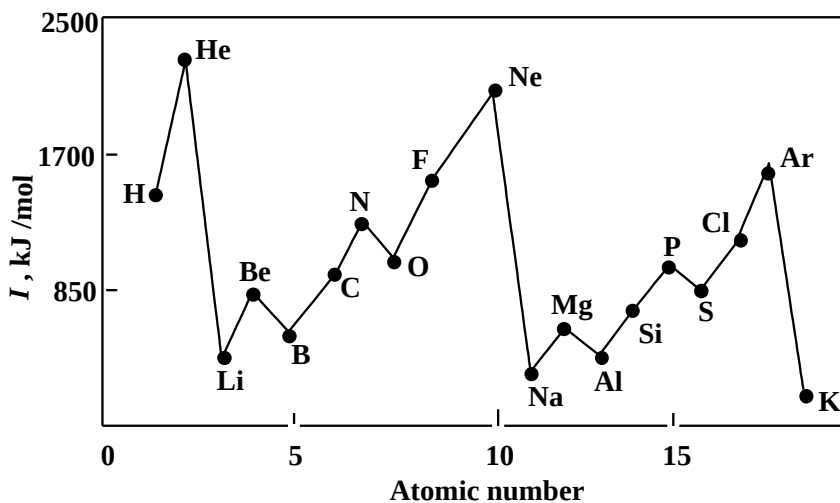


Figure (2.15): The first ionization energies of the elements in the first two short periods.

Figure (2.15), clearly shows that neon (and all the noble elements) configuration represents a particularly stable arrangement from which it is difficult to remove an electron and the very much smaller value for the ionization energy of lithium or sodium (and all the alkali metals) indicates that the electron removed is in an orbital (2s or 3s) well screened from the nuclear charge and stable electronic configurations are obtained for the ions, e.g. Li^+ ($1s^2$), Na^+ ($1s^2 2s^2 2p^6$), etc. the low value for boron reflects the stability of the configuration B^+ , $1s^2 2s^2$, while the low value for oxygen compared with its adjacent elements is perhaps related to the configuration of the O^+ ion, $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$ in which there is one electron in each of the three p orbitals. Similarly, configurations with a half-filled d or f orbitals are more stable than arrangements containing one electron more or less than this number.

2.11- ELECTRON AFFINITY

The energy released when an extra electron is added to a neutral gaseous atom is termed the electron affinity. Usually only one electron is added, forming a negative ion. This repels further electrons and energy is needed to add on a second electron. Hence, the electron affinity of O^{2-} is negative. Electron affinities depends

on the size and effective nuclear charge. They cannot be determined directly, but are obtained indirectly from Born-Harber cycle. Table (2.5) gives the affinities for some elements.

Table (2.4): the electron affinity values for some elements

Process	Affinity, kJ mol^{-1}	Process	Affinity, kJ mol^{-1}
$\text{H} \rightarrow \text{H}^-$	72	$\text{He} \rightarrow \text{He}^-$	-54
$\text{Li} \rightarrow \text{Li}^-$	-66	$\text{Na} \rightarrow \text{Na}^-$	21
$\text{Be} \rightarrow \text{Be}^-$	15	$\text{Mg} \rightarrow \text{Mg}^-$	-67
$\text{C} \rightarrow \text{C}^-$	121	$\text{Al} \rightarrow \text{Al}^-$	26
$\text{N} \rightarrow \text{N}^-$	-31	$\text{Si} \rightarrow \text{Si}^-$	135
$\text{O} \rightarrow \text{O}^-$	142	$\text{P} \rightarrow \text{P}^-$	60
$\text{O} \rightarrow \text{O}^{2-}$	-702	$\text{S} \rightarrow \text{S}^-$	200
$\text{F} \rightarrow \text{F}^-$	333	$\text{S} \rightarrow \text{S}^{2-}$	-332
$\text{Ne} \rightarrow \text{Ne}^-$	-99	$\text{Cl} \rightarrow \text{Cl}^-$	348

The above values show that the halogens all liberate a large amount of energy on forming negative halide ions. It is perhaps not surprising that these ions occur in a large number of compounds. However, there is a substantial absorption of energy when O^{2-} and S^{2-} are formed. Despite this, compounds containing these ions are

known, and it follows that the energy needed to form them must come from other process such as the **lattice energy** when the ions are packed to make a crystalline solid, or from **solvation energy** in solution.

2. 12. Electronegativity

The tendency of an atom to attract electrons to itself when combined in a compound is termed the ***electronegativity*** of the atom. Generally, small atoms attract electrons more than large ones and are therefore more electronegative. Atoms with nearly filled shells of electrons will tend to have higher electronegativities than those with sparsely occupied ones. Ionization energies and electron affinity may be regarded as measures of electronegativity. Table (2.6) summarizes a few electronegativity values of some elements in its most common oxidation states determined by professor Pauling .

Table (2.6): Pauling electronegativity coefficients

												H	2.1
Li	1.0	Be	1.5	B Al	2.0	C	2.5	N	3.0	O	3.5	F	4.0
Na	0.9	Mg	1.2		1.5	Si	1.8	P	2.1	S	2,5	Cl	3.0
K	0.8	Ca	1,0									Br	2.8
Rb	0.8	St	1.0									I	2.5
Cs	0.7	Ba	0.9										

3 – CHEMICAL BONDING

The attractive forces that hold atoms together in compounds are called chemical bonds. There are major classes of bonding.

(i) Ionic bonding results electrostatic interactions among ions, which can take the form of the complete transfer of one or more electrons from one atom or group of atoms to another.

(ii) Covalent bonding results from sharing one or more electron pairs between two atoms.

These two classes represent two extremes; all bonds have at least some degree of both ionic and covalent character. Compounds containing predominately ionic bonding are called ionic compounds. Those containing predominately covalent bonding are called covalent compounds.

3.1- Lewis dot representations of atoms

The number and arrangement of electrons in the outermost shells of atoms determine the chemical and physical properties of the elements as well as the kinds of chemical bonds they form. We write Lewis dot representations (or Lewis dot formulas) as a convenient method for keeping track of these chemically important

electrons. We now introduce this method for atoms of elements; in our discussion of chemical bonding in subsequent sections, we shall frequently use such formulas for atoms, molecules, and ions.

Table (3.1): Lewis electron dot formulas for representative elements

group period	IA	IIA	IIIA	IVA	VA	VIA	VIIA	0
1	H ^x							He ^{xx}
2	Li ^x	Be ^{xx}	B ^{xx x}	C ^{x x}	N ^{x x x}	O ^{xx x}	F ^{xx x}	Ne ^{xx xx}
3	Na ^x	Mg ^{xx}	Al ^{xx x}	Si ^{x x}	P ^{x x}	S ^{xx x}	Cl ^{xx x}	Ar ^{xx xx}
4	K ^x	Ca ^{xx}	Ga ^{xx x}	Ge ^{x x}	As ^{x x}	Se ^{xx x}	Br ^{xx x}	Kr ^{xx xx}
5	Rb ^x	Sr ^{xx}	In ^{xx x}	Sn ^{x x}	Sb ^{x x}	Te ^{xx x}	I ^{xx x}	Xe ^{xx xx}
6	Cs ^x	Ba ^{xx}	Tl ^{xx x}	Pb ^{x x}	Bi ^{x x}	Po ^{xx x}	At ^{xx x}	Rh ^{xx xx}
7	Fr ^x	Ra ^{xx}						

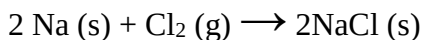
Chemical bonding usually involves only the outermost electrons of atoms, also called valence electrons. In Lewis dot representation, only the electrons in the outermost occupied s and p orbitals are shown as dots (x). Paired and unpaired electrons are also indicated.

Table (3.1) shows Lewis dot formulas for the representative elements. All elements in a given group have the same outer shell configuration.

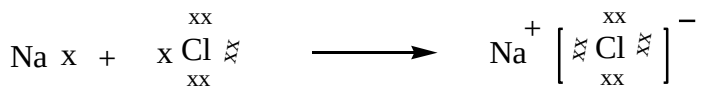
3.2- IONIC BONDING

Ionic bonding results from the transfer (complete transfer) of one or more electrons from one atom or group of atoms to another. Ionic bonding occurs most easily when elements that have low ionization energies (metals) react with elements having high electronegativities and high electron affinities (non-metals). In other words when the electronegativity difference, ΔE_n , between two elements is large enough, the elements are likely to form a compound by ionic bonding (transfer of electrons).

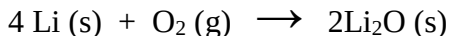
All the group IA metals (Li, Na, K, Rb, Cs) react with the non-metals of group VIIA (F, Cl, Br, I) to form ionic compounds of the general formula, MX. Here the metal atom loses one electron and the non-metal atom accepts that electron and the resulting ions retain the corresponding noble gas configuration. For example, sodium reacts with chlorine to give sodium chloride according to the following reaction;



In this reaction, Na atoms loses one electron each to form Na^+ ions, which contain only ten electrons which is the same as the noble gas neon (we say that is Na^+ isoelectronic with neon). In contrast, chlorine atoms gain one electron each to form chloride ions, Cl^- , which contains 18 electrons, isoelectronic with the noble gas argon. We can use Lewis dot formulas to represent the reaction,

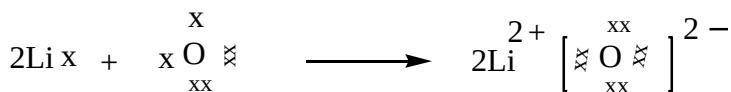


Consider the reaction of lithium with oxygen to form lithium oxide, a solid ionic compound. We may represent the reaction as;

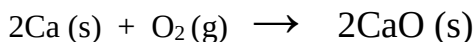


The formula of, Li_2O , indicates that two atoms of lithium combine with one atom of oxygen. Lithium ions, Li^+ , are isoelectronic with helium atoms, while oxide ions, O^{2-} are isoelectronic with neon atoms.

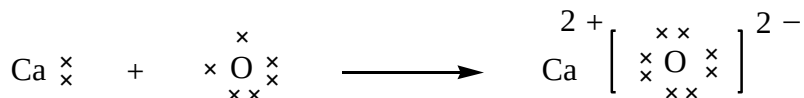
Lewis dot representation for the reaction can be stated as;



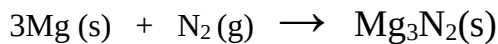
Calcium reacts with oxygen to form calcium oxide a white solid ionic product, according to the following reaction;



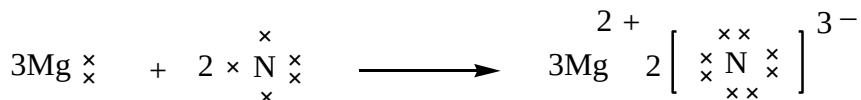
Calcium ions, Ca^{2+} , are isoelectronic with argon (18 electrons) and oxide ions, O^{2-} , are isoelectronic with neon. Lewis dot representation for the reaction is as follows;



A white solid, ionic compound called magnesium nitride; Mg_3N_2 is obtained during the reaction of magnesium and nitrogen at elevated temperature according to the reaction;



Using Lewis dot formulas we may represent the reaction as;



Both Mg^{2+} and N^{3-} ions are isoelectronic with neon (10 electrons)

*State Lewis dot formulas for the following compounds, LiBr , MgCl_2 , GaF_3 , Al_2O_3 , Li_3N , Ca_3P_2 , AlP (all of these compounds are ionic).

Before we leaving the discussion of ionic bonding we must ask the question, why ionic bonding occurs between elements with low ionization potentials and those with high electronegativities. The answer is “there is a general tendency in nature to achieve stability”. One way to do this is by lowering potential energy; lower energies generally represent more stable arrangements. This can be illustrated by studying Born-Haber cycle

3.2.1. Born – Haber cycle

This cycle devised by Born and Haber in 1919 relates the lattice energy of a crystal to other thermochemical data. The energy terms involved in building a crystal lattice such as sodium chloride may be taken in steps. The elements in their standard states are first converted to gaseous atoms, then to ions and finely backed into the crystal lattice, as shown in Figure (3.1).

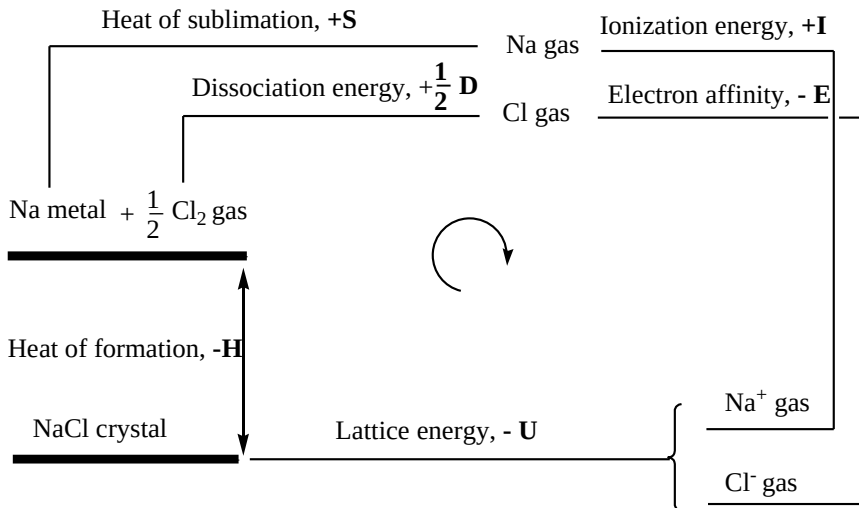


Figure (3.1): Born – Haber cycle

The heats of sublimation, dissociation and ionization energy are positive since energy is supplied to the system. The formation of ions does not explain why the process occurs, but the strong attractive forces between ions of opposite charges into a regular array (crystal) shown in Figure (3.2) for sodium chloride as an example.

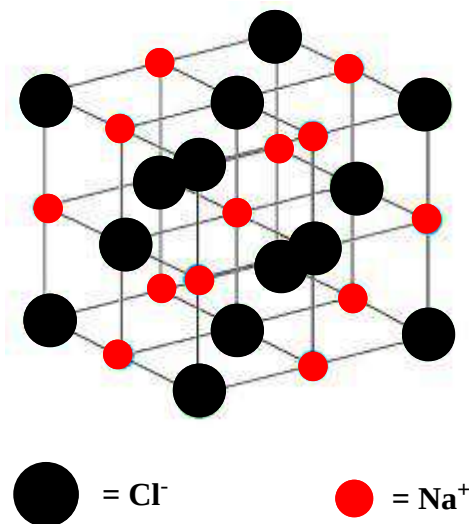


Figure (3.2): NaCl (solid) exists in a regular, extended array of positive and negative ions (crystal)

The energy associated with this process is called **the crystal lattice energy**, U , and it is a negative value because the energy is subtracted from the system. The electron affinity is also negative because of the same reason. According to Hess's law the overall energy change in a process depends only on the energy on the initial and final states and not on the route taken. Thus the heat of formation, H is equal to the sum of the terms going the other way round the cycle.

$$-H = +S + 1/2 D + I - E - U$$

* For the present, we may consider sodium chloride as a typical example, given the values; $S = 109$, $D = 243$, $I = 496$, $E = 356$, and $U = 780$ KJ / mol. The heat of formation, H , is 411 kJ. Thus we see that a major driving force in the formation of ionic compounds is the large electrostatic stabilization due to the attraction of the ionic charges.

Distinct molecules of solid ionic substances do not exist, so we must refer to formula units instead of molecules. The sum of all the forces that hold all the particles in an ionic solid is quite large. This explains why such substances have quite high melting and boiling points.

3.3. Covalent bonding

A covalent bond is formed when two atoms share one or more pairs of electrons, and occurs when the electronegativity difference, ΔE_n , between the elements is zero or relatively small. The result of this sharing is that each atom attains a more stable electron configuration, frequently the same as that of the nearest noble gas configuration. In covalent compounds, the bonds between atoms within a molecule (intramolecular bonds) are relatively strong, but the forces of attraction between molecules (intermolecular forces) are relatively weak. As a result, covalent

compounds have lower melting and boiling points than ionic compounds.

3.3.1. Formation of covalent bonds

The formation of covalent bond can be understood if we considered the simple case, the formation of a hydrogen molecule from two hydrogen atoms. An isolated hydrogen atom has the ground state electronic configuration $1s^1$, with the probability density for this one electron spherically distributed about the hydrogen nucleus. As the two hydrogen atoms approach one another, the electron of each hydrogen atom is attracted by the nucleus of the other hydrogen atom as well as by its own nucleus. If these two electrons have opposite spins so they can occupy the same region (orbital) between the two nuclei. This process is called ***orbital overlapping***. The pair of electrons is now shared between the two hydrogen atoms and a single covalent bond is formed. Each hydrogen atom now has the helium configuration, $1s^2$.

The bonded atoms are at lower energy than the separated atoms. This is shown in the plot of potential energy versus the internuclear distance, Figure (3.3), a minimum energy, - 435 kJ/mol is reached when the two hydrogen nuclei are separated by a

distance of $0.74 \text{ \AA}$. At greater or smaller distances the potential energy increases.

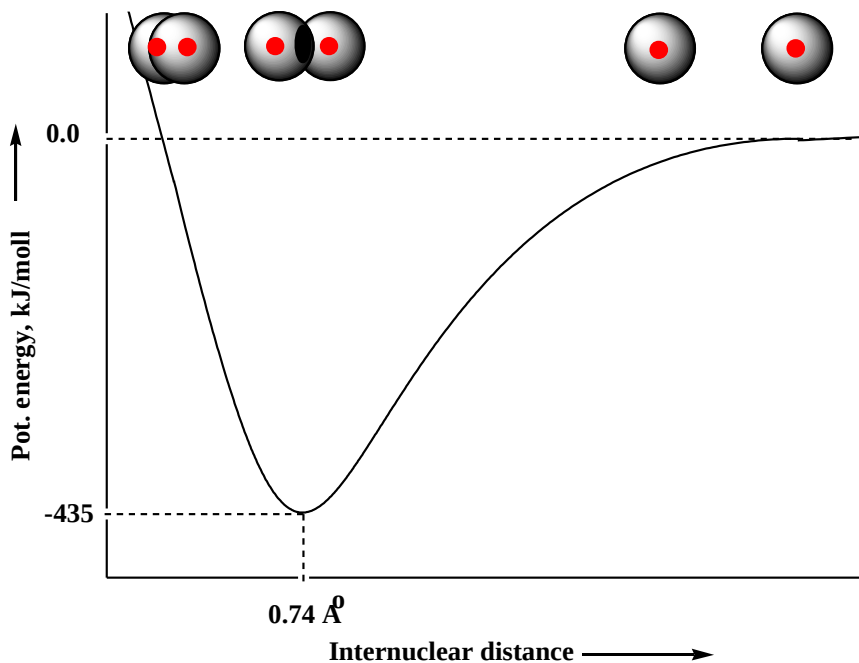
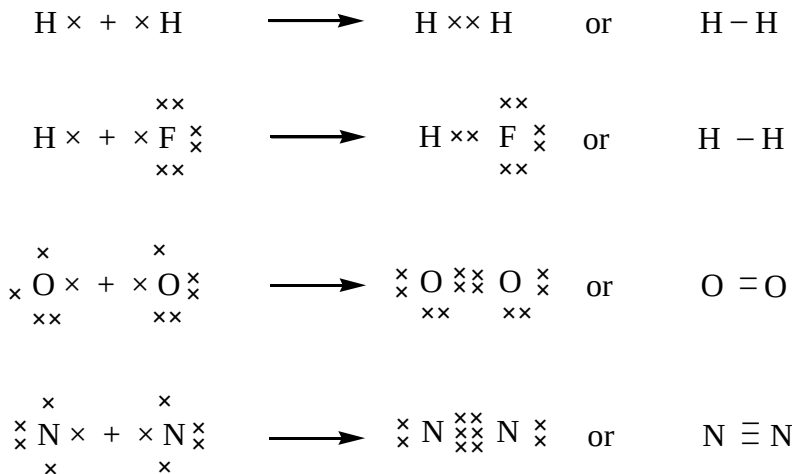


Figure (3.3): *The potential energy of H_2 molecule as a function of distance between the two nuclei.*

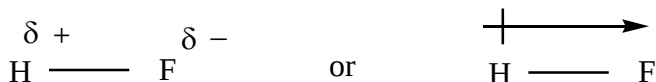
We can represent the formation of single (one pair of electron), double (two pairs), and triple (three pairs) bonds as shown in the following examples;



3.3.2. Polarity of covalent bonds

The bonding electrons in H_2 , Cl_2 , N_2 , O_2 , and other symmetric diatomic molecules (**homodiatomc molecules**) are shared equally between the bonded atoms. These molecules are electrically symmetric as well as neutral and they are called **nonpolar molecules**. On the other hand, the hydrogen and fluorine atoms do not share equally the electron pair that bonds them. A molecule of HF is electrically neutral, but is not electrically symmetrical. The fluorine end of the molecule is negatively charged because it has more than half a share in the bonding electron pair, and the hydrogen end of the molecule is positively charged because it has more than half a share in the bonding electron pair. In short, the bonding pair is pulled closer to the

fluorine atom than to the hydrogen (fluorine is more electronegative than hydrogen). Hence, the bond between hydrogen and fluorine is **polar**, and the HF molecule is said to have a **dipole moment**. The dipole moment, μ , is a measure of asymmetry of a molecule and equal to $q \times d$, (q = charge and d = the distance separating the two oppositely charges). The polarity of the bond and hence, the dipole moment of the molecule increase as the electronegativity, ΔE_n , increases. The polar HF bond can be represented as



where δ^+ and δ^- indicate partial positive and partial negative charges respectively. Table (3.2) lists dipole moments in Debyes unite for some diatomic molecules and the corresponding electronegativity differences.

Table (3.2) : Dipole moments for some diatomic

molecule	Dipole moment, μ	ΔE_n
H-F	1.91 D	1.9
H-Cl	1.03 D	0.9
H-Br	0.97 D	0.7
H-I	0.38 D	0.4
H-H	0.00 D	0.0

3.4. Polarizing power and polarizability

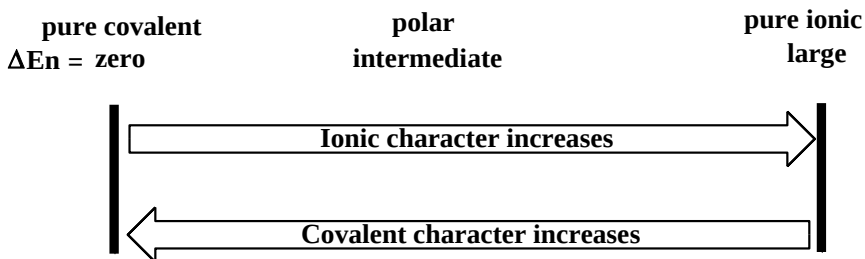
If two ions A^{n+} and B^{n-} are brought together to their equilibrium distance, the type of bond between them depends on the effect of one ion on the other. The positive ion attracts the electrons on the negative ion and repels the nucleus, thus distorting or polarizing the negative ion. If the polarization is quite small, then an ionic bond results. If the degree of polarization is large, electrons are drawn from the negative ion to the positive ion and appreciable covalent character results.

The extent of ion distortion depends on both the power of an ion to distort the other, i.e. its polarizing power, and the susceptibility of an ion to distortion, i.e. its polarizability. Generally, the polarizing power increases as the ions become smaller and more highly charged. The polarizability of a negative ion is greater than that of a positive ion since the electrons are less firmly bound because of the difference in effective nuclear charge. Large negative ions are more polarizable than small ones. These trends are summarized in Fajans' rules which stated that the covalent bonding is favoured by:

1. Small positive ion,
2. large negative ion,
3. large charges on either ions.

3.4.1. The continuous range of bonding types

Before we leave this discussion, it is desirable to have an answer to this question: At what point does a covalent bond become so polar that we consider it to be ionic? Nonpolar covalent bonding occurring when $\Delta E_n = \text{zero}$ is one extreme. Ionic bonding involving a complete transfer of electrons represents the other extreme, and occurs when the ΔE_n is large. Polar covalent bonds may be understood as an intermediate case between pure (nonpolar) covalent and pure ionic bonds, as shown in the following scheme;



On the other hand, we have shown that ionic bonding may attain some degree of covalent character, depending on the nature of cation and anion involved.

Lastly, we may conclude that almost all bonds have both ionic and covalent character and a given type of bond can be identified as being closer to one or other extreme type.

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Appendix 1

According to the Bohr assumption that the angular momentum of the electron is an integral multiple of the quantity $\hbar / 2\pi$, i.e.,

$$mvr = nh / 2\pi \dots\dots\dots 1$$

thus $r = nh / 2\pi mv \dots\dots\dots 2$

the force of attraction between the electron and the nucleus **F**

$$= e^2 / r^2 \dots\dots\dots 3$$

where **e** is the charge of the electron. Substituting for the value of **r**,
thus

$$F = 4 \pi^2 m^2 v^2 e^2 / n^2 h^2$$

Assuming that the electron remains in its orbit due to the equilibrium between the force of attraction **F** and the centripetal force mv^2 / r , i.e.,

$$e^2 / r^2 = mv^2 / r \dots\dots\dots 4$$

$$4 \pi^2 m^2 v^2 e^2 / n^2 h^2 = mv^2 / r$$

$$r = n^2 h^2 / 4 \pi^2 m e^2$$

For the orbit nearest to the nucleus, i.e., for **n = 1**

$$r = 0.529 \times 10^{-8} \text{ cm}^{-1}$$

Appendix 2

Assuming that the potential energy, E_p , of the electron at infinity is equal to zero, we obtain E_p for the electron move in an orbit of radius r

$$E_p = - e^2 / r = - 4 \pi^2 m e^4 / n^2 h^2$$

and for the kinetic energy, $E_k = mv^2 / 2$. From equation 4

$$E_k = mv^2 / 2 = e^2 / 2r$$

Substitution for the value of r

$$E_k = 2 \pi^2 m e^4 / n^2 h^2$$

The total energy $E = E_p + E_k$, thus

$$E = - 2 \pi^2 m e^4 / n^2 h^2$$

Appendix 3

The energy change when an electron transfer from an orbit of $n = 2$ to an orbit of $n = 1$ (emission spectra)

$$\Delta E = - 2 \pi^2 m e^4 / n_2^2 h^2 + 2 \pi^2 m e^4 / n_1^2 h^2$$

$$= 2 \pi^2 m e^4 / h^2 (1/n_1^2 - 1/n_2^2)$$

$$\tilde{\nu} = E / h C$$

$$= 2 \pi^2 m e^4 / h^3 C (1/n_1^2 - 1/n_2^2)$$

where the constant $2\pi^2 m e^4 / h^3 C$ is the same as the Rydberg constant

