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DEPARTMENT OF CHEMISTRY
CHM 101 (GENERAL CHEMISTRY 1)

Modern electronic theory of atoms ---- Prof. A. A. Adeniyi

A. The salient features of modern atomic theory

1. An atom is no longer indivisible.
2. Atoms of the same element can have different atomic masses (Isotopes).
3. Atoms of different elements may have same atomic masses/mass numbers, e.g. $^{40}_{18}$Ar, $^{40}_{19}$K, $^{40}_{20}$Ca, (Isobars).
4. Atoms of one element can be transmuted into atoms of other elements (Radioactivity). One of the notable outcomes of radioactivity is the synthesis of the so-called trans-uranium elements (that is elements after uranium, atomic number 92). The first two of these elements, neptunium (element 93) and plutonium (element 94) were made in the USA in the 1940s using mini-nuclear reactors in the laboratory. By 1971, the number grew to 11 (Np - Lr). The discovery of most of these elements were spearheaded by G.T. Seaborg in his California laboratories. It is believed that 20 or more additional new elements have been synthesized after lawrencium, awaiting full certification by IUPAC (international union of pure and applied chemistry and IUPAP (international union of pure and applied physics).

Notes:

i. **Mass numbers also called atomic mass** is the total number of protons and neutrons.

$^{A}_{Z}X$ A= mass number (no. of protons + neutrons); Z = atomic number (no. of protons); X = element of interest.

ii. **Isotopes** are atoms that have the same atomic number but different mass numbers. It occurs because some elements have different numbers of neutrons. [carbon -12 (6 protons + 6 neutrons); carbon-13 (6 protons + 7 neutrons); carbon -14 (6 protons + 8 neutrons)].

iii. **Isobars** are atoms having the same mass number but different atomic number. For example, the atomic numbers of C and N are 6 and 7 respectively. Carbon-14 an isotope of carbon has mass number of 14 which is the same as that of nitrogen and hence ^{14}C and ^{14}N are isobars

iv. Radioactivity, the natural process by which some atoms spontaneously disintegrate emitting both particles and energy.

B. **Notable scientists involved in our present understanding of the atomic structure**

1. John Dalton (1803) - Atoms are indivisible
2. Henri Becquerel (1896) – Discovered radioactivity
3. Max Planck (1900) – Quantum theory
4. J. J. Thomson (1904) - Discovered electrons
5. Ernest Rutherford (1911) - Identified the presence of atomic nucleus
6. Niels Bohr (1913) - Planetary model of the atom
7. Louis de Broglie (1924) - Wave properties of electrons
8. Werner Heisenberg (1925) - Uncertainty principle
9. Erwin Schrodinger (1927) - Wave equation

C. Major subatomic particles

Particle	Symbol	Mass/u	Mass number	Charge/e	Spin
Electron	e^-	5.486 x 10	0	-1	½

		$^{-4}$			
Proton	p^+	1.0073	1	+1	½
Neutron	n^0	1.0087	1	0	½

Notes: i. Masses are expressed in atomic mass units, u, with 1 u = 1.6605 x 10^{-27} kg; ii. The elementary charge e is 1.602 x 10^{-19} C (C, coulomb)

D. Planck's theory: Different atoms and molecules can emit or absorb energy in discrete quantities. The smallest amount of energy that can be emitted or absorbed in the form of electromagnetic radiation is known as quantum.

E. **Bohr model**: Niels Bohr, 1913 conceived the atomic theory that earned him the Nobel prize for physics in 1922. His idea was that the nucleus was surrounded by electrons moving in orbits like planets round the sun. Several problems arise from this concept: - i. The electrons might be expected to slow down gradually. ii. Why should electrons move in an orbit round the nucleus? iii. Since the nucleus and electrons have opposite charges, they should attract each other. Thus, one would expect the electrons to spiral inwards until eventually they collide with the nucleus. To explain these problems, Bohr postulated: - i. An electron did not radiate energy if it stayed in one orbit, and therefore should not slow down. ii. When an electron moved from one orbit to another, it either radiated or absorbed energy. If it moved towards the nucleus energy was radiated, and if moved away from the nucleus energy was absorbed. iii. For an electron to remain in its orbit, the electrostatic attraction between the electron and the nucleus, which tends to pull the electron towards the nucleus must be equal to the centrifugal force which tends to pull the electron out of its orbit. For an electron of mass, m, moving with a velocity v in an orbit of radius r,

Centrifugal force = mv^2/r

If the charge on the electron is e, the number of charges on the nucleus, Z, and the permittivity of a vacuum, ϵ_o. Coulombic attractive force = $Ze^2/4\pi\epsilon_o r^2$

$\therefore \quad mv^2/r = Ze^2/4\pi\epsilon_o r^2$ -------- (1)

Hence, $v^2 = Ze^2/4\pi\epsilon_o mr$ ------(2)

According to Planck's quantum theory, energy is not continuous, but is discrete. This means that energy occurs in "packets" called quanta, of magnitude $h/2\pi$, where h is Planck's constant. The energy of an electron in an orbit, that is, its angular momentum mvr, must be equal to a whole number, n of quanta

$mvr = nh/2\pi$

$v = nh/2\pi mr$

$v^2 = n^2h^2/4\pi^2m^2r^2$ -------- (3)

Combining equation (3) with equation (2), we have

$Ze^2/4\pi\epsilon_o mr = n^2h^2/4\pi^2m^2r^2$

Hence, $r = \epsilon_o n^2h^2/\pi me^2Z$ -------- (4)

For hydrogen, the charge on the nucleus, Z = 1

n = 1 this gives a value $r = 1^2$ x 0.0529 nm

n = 2 this gives a value $r = 2^2$ x 0.0529 nm

n = 3 this gives a value $r = 3^2$ x 0.0529 nm

This gives the picture of the hydrogen atom, where an electron moves in circular orbits or radius proportional to 1^2, 2^2, 3^2 ------.

Defining n, that is the energy of orbitals, which is now referred to as the principal quantum number is the only enduring aspect of the Bohr's theory.

F. Wave-particle duality

The ability of matter to show both wave and particle behaviour is called wave-particle duality.

de Broglie's equation: $m\nu = h/\lambda$

m = mass of an electron
ν = velocity
h = Planck's constant
λ = wave length

This equation connected the particle like property of momentum, $m\nu$, with the wave- like property of wave- length, λ (lambda).

If we accept de Broglie's theory and represent the electron as a wave, this wave must exactly fit into the circumference of the circle. This can only happen if a whole number of wavelengths will fit on the circumference. In symbols, this means that $n\lambda = 2\pi r$. The whole number, n, turns out to be the principal quantum number that Bohr introduced.

G. Heisenberg uncertainty principle

Calculations on the Bohr model of an atom require precise information about the position of an electron and its velocity. It is difficult to measure both quantities accurately at the same time. An electron is too small to see and may only be observed if perturbed. For example, we could hit the electron with another particle such as a photon or an electron, or we could apply an electric or magnetic force to the electron. This will intensely change the position of the electron or its velocity and direction.

Heisenberg stated that the more precisely we can define the position of an electron, the less certainly we are able to define its velocity, and vice versa.

If Δx is the uncertainty in defining the position and $\Delta\nu$ the uncertainty in the velocity, the uncertainty principle may be expressed mathematically as: $\Delta x.\Delta \nu \geq h/4\pi$; where h= Planck's constant= 6.0262×10^{-34} Js

This implies that it is impossible to know both the position and the velocity, exactly.

The concept of an electron following a definite orbit, where its position and velocity are known exactly, must therefore be replaced by the probability of finding an electron in a particular position, or in a particular volume of space (**orbital**).

The Schrodinger wave equation

The Schrodinger wave equation provides a satisfactory description of an atom in the terms described by Heisenberg. Solutions to the wave equation are called wave functions and given the symbol ψ (psi). The probability of finding an electron at a point in space whose coordinates are x, y and z is ψ^2 (x, y, z). The wave equation is shown in the box below:

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

∇^2 = Del symbol (or nabla) indicates the three differentials of electrons movement in x, y, z directions; ψ = Schrodinger wave function; E = energy; V = potential energy; m = mass; h = Planck's constant

Like Bohr, Schrodinger tackled the atom problem. Using a totally different method to Bohr's, he derived the same formula for the energy levels. The principal quantum number, n, had the same set of values as in the Bohr's formula. However, this was not the only quantum number that came out of the Schrodinger's calculations. In fact, two more appeared. These were called azimuthal/subsidiary quantum number (l), and the magnetic quantum number, m.

It turned out that all three quantum numbers were needed to explain many of the more peculiar properties of the hydrogen atom and other atoms.

The quantum numbers n, l and m

Symbol	**Name**	**Information**
n	Principal	Governs the orbital energy

l	Azimuthal/ subsidiary	Governs the orbital shape
m	Magnetic	Governs the number of orbitals for each value of l

Acceptable solutions to the wave equation, that is, solutions which are physically possible, must have certain properties:

1. ψ must be continuous
2. ψ must be finite
3. ψ must be single valued
4. The probability of finding the electron over all the space from plus infinity to minus infinity must be equal to one.

The probability of finding an electron at a point x, y, z is ψ^2, so

$$\int_{-\infty}^{+\infty} \psi^2 dxdydz = 1$$

Several wave functions called ψ_1, ψ_2, ψ_3 … will satisfy these conditions to the wave equation, and each of these has a corresponding energy E_1, E_2, E_3 …. Each of these wave functions ψ_1, ψ_2, etc. is called an orbital, by analogy with the orbits on the Bohr theory.

For a given type of atom, there are a number of solutions to the wave equation which are acceptable, and each orbital may be described uniquely by a set of three quantum numbers, n, l and m (these are the same quantum numbers- principal, subsidiary and magnetic- as were used in the Bohr theory).

The subsidiary quantum number l describes the shape of the orbital occupied by the electron; l may have values 0, 1, 2 or 3. When l = 0, the orbital is spherical and is called an s orbital; when l = 1, the orbital is dumb-bell shaped and is called a p orbital; when l = 2 the orbital is

double dumb- bell shaped and is called a d orbital; and when l = 3 a more complicated f orbital is formed.

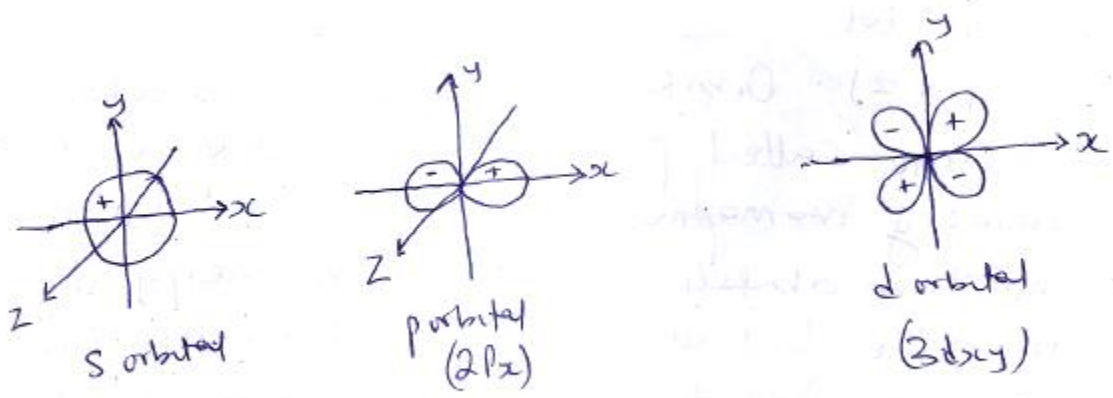

Figure 1, showing s, $2p_x$ and $3d_{xy}$ orbitals

The letters s, p, d and f come from the spectroscopic terms sharp, principal, diffuse and fundamental, which were used to describe the lines in the atomic spectra.

Examination of a list of all the allowed solutions to the wave equation shows that the orbitals fall into groups as follows.

a. In the first group of solutions the value of the wave function ψ, and, hence the probability of distance r from the nucleus, and is the same in all the directions. $\psi = f(r)$

   This leads to a spherical orbital and occurs when the subsidiary quantum number l = 0. These are called s orbitals. When l = 0, m = 0 (m= -1 to +1). Consequently, there is only one such orbital for each value of n.

b. In the second group of solutions to the wave equation, ψ depends both on the distance from the nucleus, and on the direction in space (x, y, or z). Orbitals of this kind occur when l = 1 and are called p orbitals, with three possible values of magnetic quantum number (m= -l, 0, +1). The three orbitals are identical in energy, shape and

size but differ only in their direction in space. These three solutions to the wave equation may be written as

$\psi_x = f(r).\ f(x)$

$\psi_y = f(r).\ f(y)$

$\psi_z = f(r).\ f(z)$

Orbitals that are identical in energy are termed degenerate, thus three degenerate p orbitals occur for n = 2, 3, 4 etc.

c. The third group of solutions to the wave equation depends on the distance from the nucleus and also two directions in space, for example; $\psi = f(r).\ f(x).\ f(y)$

This group of orbitals has l = 2, and are called d orbitals. There are five solutions corresponding to m= -2, -1, 0, +1, +2 and are degenerate for each of the values of n= 3, 4, 5….

c. Another set of solutions occurs when l = 3 and are called f orbitals. There are seven values of m: -3, -2, -1, 0, +1, +2, +3, seven degenerate f orbitals when n = 4, 5, 6…

Summary of the atomic orbitals

n	l	m (-1 to +1)	Symbol	
1	0	0	1s (one orbital)	one orbital
2	0	0	2s (one orbital)	four orbitals
2	1	-1, 0, +1	2p (three orbitals)	
3	0	0	3s (one orbital)	nine orbitals
3	1	-1, 0, +1	3p (three orbitals)	
3	2	-2, -1, 0, +1, +2	3d (five orbitals)	
4	0	0	4s (one orbital)	sixteen orbitals
4	1	-1, 0, +1	4p (three orbitals)	
4	2	-2, -1, 0, +1, +2	4d (five orbitals)	
4	3	-3, -2, -1, 0, +1, +2	4f (seven orbitals)	