

Additional Material for Models of the Hydrogen Atom

Dalton's ideas of the structure of matter

Dalton's atomic theory proposed that all matter was composed of **atoms**, indivisible and indestructible building blocks. While all **atoms** of an element were identical, different elements had **atoms** of differing size and mass.

Thomson's Model of atom

In 1904, Sir J. J. Thomson proposed the first atomic model.

According to this model, atom was assumed to consist of a sphere of uniform distribution of about 10^{-10} m positive charge with electrons embedded in it.

Here number of electrons is equal to the number of positive charges and the atom is electrically neutral.

This model of atom could not explain the results of gold foil scattering experiment carried out by Rutherford.

Rutherford's Scattering Experiment

Rutherford conducted α -ray scattering experiment in 1911 to find out the arrangement of electrons and protons. He bombarded a thin gold foil with a stream of fast moving positively charged alpha α -particles emitted from the radium atom.

Rutherford's Nuclear model of an atom

This model resulted from the conclusions drawn from the scattering of alpha particles on the gold foil. According to him,

(i) Most of the space in the atom is empty, as large number of α -particles passed undeflected through the foil.

(ii) A few positively charged α -particles were deflected. The deflection must be due to enormous repulsive force showing that the positive charge of the atom is not spread throughout the atom as Thomson had thought. The positive charge has to be concentrated in a very small volume. This very small portion of the atom was called nucleus by Rutherford.

(iii) Calculations by Rutherford showed that the volume occupied by the nucleus is negligibly small as compared to the total volume of the atom. The diameter of the atom is about 10^{-10} m, while that of nucleus is 10^{-15} m.

On the basis of above observations and conclusions, Rutherford proposed the nuclear model of atom.

According to this model:

(a) An atom consists of a tiny positively charged nucleus at its centre.

(b) The positive charge of the nucleus is due to protons. The mass of the nucleus, on the other hand, is due to protons and some neutral particles each having mass nearly equal to the mass of proton.

This neutral particle, called neutron, was discovered later on by Chadwick in 1932. Protons and neutrons present in the nucleus are collectively known as nucleons. The total number of nucleons is termed as mass number (A) of the atom.

(c) The nucleus is surrounded by electrons that move around the nucleus with very high speed in circular paths called orbits. Rutherford's model of atom resembles the solar system in which the sun plays the role of the nucleus and the planets that of revolving electrons.

(d) The number of electrons in an atom is equal to the number of protons in it. The total positive charge of the nucleus exactly balances the total negative charge in the atom making it electrically neutral. The number of protons in an atom is its atomic number(Z).

(e) Electrons and nucleons are held together by electrostatic forces of attraction.

Defects of Rutherford's model

According to Rutherford's model, an atom consists of a positive nucleus with the electrons moving around it in circular orbits. However it had been shown by J. C. Maxwell that whenever an electron is subjected to acceleration, it emits radiation and loses energy. As a result of this, its orbit should become smaller and smaller and finally it should spiral into the nucleus. This means that atom would collapse. Rutherford's model failed to explain the stability of atoms.

Another drawback of the Rutherford's model is that it says nothing about how the electrons are distributed around the nucleus and what are the energies of these electrons. This model failed to explain the existence of certain definite lines in the hydrogen spectrum.

Postulates of Bohr's model of an atom

To overcome the above defects of Rutherford's model, Niels Bohr in 1913 gave a modification based on Quantum theory of radiation. The important postulates are:

(1) The electrons revolve round the nucleus only in certain selected circular paths called orbits. These orbits are associated with definite energies or energy levels or quantum levels. These are numbered as 1, 2, 3, 4 etc. (starting from the nucleus) are designated as K, L, M, Netc.

(2) As long as an electron remains in a particular orbit, it does not lose or gain energy. This means that energy of an electron in a particular path remains constant. Therefore, these orbits are also called stationary states.

(3) Only those orbits are permitted in which angular momentum of the electron is a whole number multiply of $\frac{h}{2\pi}$, where h is the planck's constant. An electron moving in a circular orbit has an angular momentum equal to mvr where m is the mass of the electron and v the angular momentum, mvr is a multiply of $\frac{h}{2\pi}$ i.e.,

$$mvr = n = \frac{nh}{2\pi} \text{ where } n = 1, 2, 3, \dots$$

In other words, angular velocity of electrons in an atom is quantised.

(4) If an electron jumps from one stationary state to another, it will absorb or emit radiation of a definite frequency. When an electron jumps back to the lower energy level, it radiates same amount of energy in the form of radiation.

Limitation of Bohr's Theory

- (i) Bohr Theory could not explain about the fine lines of hydrogen spectrum (Fine spectrum).
- (ii) Appearance of the several lines implies that there are several energy levels, which are close together for each quantum number n . This would require the existence of new quantum numbers.
- (iii) Bohr's theory explained the spectra of hydrogen atom and hydrogen like ions (e.g. He^+ , Li^{2+} , Be^{3+} etc.), it could not explain the spectral series for the atoms having a large number of electrons.
- (iv) He could not give any explanation for using the principle of quantisation of angular momentum and it was introduced by him arbitrarily.
$$mvr = \frac{nh}{2\pi}$$
- (v) Bohr could not explain Heisenberg's Uncertainty Principle.
- (vi) Bohr could not explain Zeeman effect (splitting of spectral lines in magnetic field).
- (vii) Bohr could not explain Stark effect (splitting of spectral lines in electric field).

Schrödinger wave equation

For a system (such as an atom or a molecule whose energy does not change with time) the Schrödinger equation is written as $\hat{H}\psi = E\psi$, where \hat{H} is a mathematical operator called Hamiltonian.

Schrödinger gave a recipe of constructing this operator from the expression for the total energy of the system.

The total energy of the system takes into account the kinetic energies of all the sub-atomic particles (electrons, nuclei), attractive potential between the electrons and nuclei and repulsive potential among the electrons and nuclei individually. Solution of this equation gives E and ψ .

Electronic configuration and quantum numbers

Quantum Numbers

The quantum numbers are the details that are required to locate an electron in an atom. In an atom a large number of electron orbitals are permissible. An orbital of smaller size means there is more chance of finding the electron near the nucleus. These orbitals are designated by a set of numbers known as quantum numbers. In order to specify energy, size, shape and orientation of the electron orbital, three quantum numbers are required these are discussed below.

1. The principal quantum number (n)

The electrons inside an atom are arranged in different energy levels called electron shells or orbits. Each shell is characterized by a quantum number called principal quantum number. This is represented by the letter n and n can have values, 1,2,3,4 etc. The first level is also known as K

level. Second as **L** level, third as **M** level, fourth as **N** level and so on. The first or **K** level is the orbit nearest to the nucleus and next one is second or **L** level and so on.

2. The subsidiary or azimuthal quantum number (**l**)

According to Sommerfield, the electron in any particular energy level could have circular path or a variety of elliptical paths about the nucleus. This results in slight differences in orbital shapes with slightly differing energies. This is due to the differences in the attraction exerted by the nucleus on the electron. This concept gave rise to the idea of the existence of sub-energy levels in each of the principal energy levels of the atom. This is denoted by the letter **l** and have values from 0 to $n-1$.

Thus, if

$n=1$, $l=0$ only one value (one level only) s level.

$n=2$, $l=0$ and 1 (2 values or 2 sub- levels) s and p level.

$n=3$, $l=0$, 1 and 2 (3 values or 3 sub-levels) s, p and d level.

$n=4$, $l=0$, 1, 2 and 3 (4 values or 4 sub-levels) s, p ,d and f level.

3. Magnetic quantum number (**m**)

In a strong magnetic field a sub-shell is resolved into different orientations in space. These orientations called orbitals have slight differences in energy. This explains the appearance of additional lines in atomic spectra produced when atoms emit light in magnetic field. Each orbitals is designated by a magnetic quantum number m and its values depends on the value of ' l '. The values are ' $-l$ ' through zero to ' $+l$ ' and thus there are $(2l+1)$ values.

Thus when,

$l=0$, $m= 0$ (only one value or one orbital)

$l=1$, $m= -1, 0, +1$ (3 values or 3 orbitals)

$l=2$, $m= -2, -1, 0, +1, +2$ (5 values or 5 orbitals)

$l=3$, $m= -3,-2, -1, 0, +1, +2, +3$ (7 values or 7 orbitals).

The three quantum numbers labeling an atomic orbital can be used equally well to label electron in the orbital.

However, a fourth quantum number, the spin quantum number, (s) is necessary to describe an electron completely.

4. Spin quantum number (**s**)

The electron in the atom rotates not only around the nucleus but also around its own axis. Two opposite directions of rotation are possible for the spin(clock wise and anticlock wise). Spin quantum number can have only two values $+1/2$ or $-1/2$. For each values of m including zero, there will be two values for s .

To sum up, the four quantum numbers provide the following informations:

1. **n** identifies the shell, determines the size of the orbital and also to a large extent the energy of the orbit.
2. There are n subshells in the n th shell. **l** identifies the subshell and determines the shape of the orbital. There are $(2l+1)$ orbitals of each type in a subshell i.e., one s orbital ($l=0$), three p orbitals ($l=1$), and five d orbitals ($l=2$) per subshell. To some extent l also determines the energy of the orbital in a multi-electron atom.

3. m_l designates the orientation of the orbital. For a given value of l , m_l has $(2l+1)$ values, the same as the number of orbitals per subshell. It means that the number of orbitals is equal to the number of ways in which they are oriented.

4. m_s refers to orientation of the spin of the electron.

Shapes or boundary surfaces of Orbitals

s-orbitals:

For s-orbital $l = 0$ and hence, m can have only one value, i.e., $m = 0$. This means that the probability of finding the electron in s-orbital is the same in all directions at a particular distance. s-orbitals are spherically symmetrical.

The electron cloud picture of 1s-orbital is spherical. However, they are more diffused and have spherical shells within them where probability of finding the electron is zero. These are called nodes. In 2s-orbital there is one spherical node. In the ns orbital, number of nodes are $(n-1)$.

p-orbitals:

For p-orbitals $l = 1$ and hence 'm' can have three possible values +1, 0, -1. There are three possible orientations of electron cloud in a p-sub-shell. The three orbitals of a p-sub-shell are designated as p_x , p_y and p_z respectively along x-axis, y-axis and z-axis respectively. Each p-orbital has two lobes, which are separated by a point of zero probability called node. Each p-orbital is thus dumb bell shaped.

In the absence of magnetic field these three p-orbitals are equivalent in energy and are said to be three-fold degenerate or triply degenerate. In the presence of an external magnetic field, the relative energies of the three p orbitals vary and depend on their orientation or magnetic quantum number. This probably accounts for the splitting of a single spectral line into a number of closely spaced lines in presence of a magnetic field (fine structure).

d-orbitals:

For d-orbitals $l = 2$, $m = 0, \pm 1, \pm 2$ indicating that d- orbitals have five orientations with five d-orbitals which are named as d_{xy} , d_{yz} , d_{zx} , d_z^2 and $d_{x^2-y^2}$. All these five orbitals, in the absence of magnetic field, are equivalent in energy and are five-fold degenerate.

The three orbitals namely d_{xy} , d_{yz} and d_{zx} have their lobes lying symmetrically between the coordinate axes. This set of three orbitals is known as t_{2g} set. $d_{x^2-y^2}$ and d_z^2 orbitals have their lobes along the axes. This set is known as e_g set.

de-Broglie Relation

The wavelength of the wave associated with any material particle was calculated by analogy with photon as follows :-

In case of a photon, if it is assumed to have wave character, its energy is given by

$$E = h\nu \text{ (according to the Planck's quantum theory)} \quad \dots(i)$$

where ν is the frequency of the wave and h is Planck's constant.

If the photon is supposed to have particle character, its energy is given by

$$E = mc^2 \text{ (according to Einstein equation)} \quad \dots(ii)$$

where m is the mass of photon and c is the velocity of light.
From equations (i) and (ii), we get

$$\begin{aligned} & \mathbf{h v = mc^2} \\ \text{But} & \quad \mathbf{v = c / \lambda} \\ \therefore & \quad \mathbf{h . c / \lambda = mc^2} \\ \text{or} & \quad \mathbf{\lambda = h / mc} \end{aligned}$$

de Broglie pointed out that the above equation is applicable to any material particle. The mass of the photon is replaced by the mass of the material particle and the velocity “ c ” of the photon is replaced by the velocity v of the material particle. For any material particle like electron, we may write

$$\lambda = h / mv \text{ or } \lambda = h / p$$

where $mv = p$ is the momentum of the particle.

The above equation is called **de Broglie equation** and λ is called de Broglie wavelength.

Thus the significance of de Broglie equation lies in the fact that it relates the particle character with the wave character of matter.

The de-Broglie’s concept can be applied to electrons and other small particles like neutrons, protons, atoms, molecules etc.

Significance of de-Broglie waves

The wave nature of matter has no significance for objects of ordinary size because wavelength of the wave associated with them is too small to be detected. This can be illustrated by the following examples.

i) Suppose we consider an electron of mass 9.1×10^{-31} kg and moving with a velocity of 10^7ms^{-1} . Its de-Broglie wavelength will be;

$$\lambda = h / mv = 6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1} / 9.1 \times 10^{-31} \text{ kg} \times 10^7 \text{ ms}^{-1}$$

$$\lambda = 0.727 \times 10^{-10} \text{ m} = 7.27 \times 10^{-11} \text{ m}$$

This value of λ can be measured by the method similar to that for the determination of wave length of X-rays.