

ATOMIC STRUCTURES

Describe the Rutherford Atomic model? Write down the weakness of Rutherford atomic model?

Rutherford Atomic Model:

- ① Atom has a tiny dense central core or the nucleus which contains practically the entire mass of the atom, leaving the rest of the atom almost empty.
- ② The entire positive charge of the atom is located on the nucleus, while electrons were distributed in vacant space around it.
- ③ The electrons were moving in orbits or closed circular paths around the nucleus like planets around the sun.

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Weakness of Rutherford Atomic model:

The assumption that electrons were orbiting around the nucleus was unfortunate. According to the classical electromagnetic theory if a charged particle accelerates around an oppositely charged particle, the former will radiate energy. If an electron radiates energy, its speed will decrease and it will go into spiral motion, finally falling into the nucleus. This does not happen as then the atom would be unstable which it is not. This was the chief weakness of Rutherford Atomic Model.

□ What is Atomic number and Mass number?

Atomic number: Atomic number of an element is defined as the number of protons in the nucleus of the atom of that element.

Mass number: The sum of the numbers of neutrons and protons present in the nucleus of an atom is called the mass number (A) of the atom.

$$\text{Mass number } A = P + n, \quad P = \text{proton}, \quad n = \text{neutron}.$$

Fardin

I Describe Bohr's Atomic Model with Limitations.

Bohr's postulates:

- ① Electrons travel around the nucleus in specific permitted circular orbits and in no others.
- ② While in these specific orbits, an electron does not radiate or lose energy.
- ③ An electron can move from one energy level to another by quantum or photon jumps only.
- ④ The angular momentum (mvr) of an electron orbiting around the nucleus is an integral multiple of Planck's constant divided by 2π .

Limitation of the Bohr atom model

- ① The great success of Bohr theory was in its ability to predict lines in the hydrogen atom spectrum. But it was spectacularly unsuccessful for every other atom containing more than one electron.
- ② No explanation of the effect of magnetic field and electric field on the spectra of atoms.
- ③ Bohr had assumed that an electron behaves as a material particle of small mass. But De Broglie suggested that an electron has a dual nature that is material particle and as a wave.

II Calculation the radius of orbits of Atom?

Consider an electron of charge e revolving around a nucleus of charge ze . z is the atomic number, e the charge on a proton.

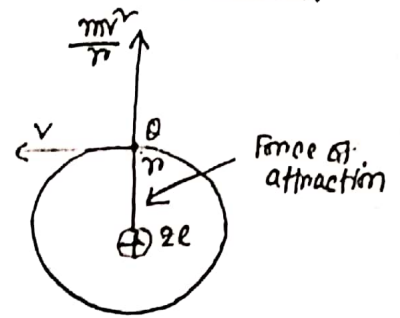
Let, m be the mass of the electron, r be the radius of the orbit and v be the velocity of the revolving electron.

The electrostatic force of attraction between the nucleus and the electron

$$= k \frac{ze \times e}{r^2}$$

The centrifugal force acting on the electron

$$= \frac{mv^2}{r}$$



Bohr assumed that these two opposing forces must be balancing each other exactly to keep the electron in orbit. Thus,

$$\frac{kze^2}{r^2} = \frac{mv^2}{r}$$

for hydrogen $z=1$,

$$\frac{ke^2}{r^2} = \frac{mv^2}{r}$$

$$\frac{ke^2}{r} = mv^2$$

According to Bohr's theory, angular momentum of the revolving electron is

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

$$v = \frac{nh}{2\pi mr}$$

$$v^2 = \frac{n^2 h^2}{4\pi^2 m^2 r^2}$$

$$\therefore \frac{ke^2}{r} = \frac{m n^2 h^2}{4\pi^2 m^2 r^2}$$

$$r = \frac{n^2 h^2}{4\pi^2 m e^2 k}$$

□ Calculation the energy of electron in each orbit.

Let, the energy of the revolving electron 'E', z is the atomic number and e is the charge on a proton.

Now, kinetic energy, $E_k = \frac{1}{2}mv^2$

$$E_k = \frac{1}{2}m \times \frac{ze^2}{mr}$$

$$E_k = \frac{ze^2}{2r} \quad \text{--- (i)}$$

And potential energy $U = E_p = -\frac{ze^2}{r}$ --- (ii)

from equation,

$$E = E_k + E_p$$

$$= \frac{ze^2}{2r} - \frac{ze^2}{r}$$

$$= -\frac{ze^2}{2r}$$

$$= -\frac{ze^2}{2 \times \frac{n^2 h^2}{4\pi^2 m z e^2}}$$

$$E = -\frac{2\pi^2 m z^2 e^4}{n^2 h^2}$$

□ Calculation of frequency of electron

We know,

$$E = -\frac{2\pi^2 m z^2 e^4}{n^2 h^2}$$



for $n=n_1$ we get, $E_1 = -\frac{2\pi^2 m z^2 e^4}{h^2} \times \frac{1}{n_1^2}$ --- (i)

for $n=n_2$ we get, $E_2 = -\frac{2\pi^2 m z^2 e^4}{h^2} \times \frac{1}{n_2^2}$ --- (ii)

from (1) - (1), we get,

$$\Delta E = E_2 - E_1$$

$$h\nu = \frac{2\pi^2 m_2^2 v^4}{h^2 r} \left(\frac{1}{n_1 r} - \frac{1}{n_2 r} \right)$$

$$\nu = \frac{2\pi^2 m_2^2 v^4}{h^3} \left(\frac{1}{n_1 r} - \frac{1}{n_2 r} \right)$$

$$\frac{c}{\lambda} = \frac{2\pi^2 m_2^2 v^4}{h^3} \left(\frac{1}{n_1 r} - \frac{1}{n_2 r} \right)$$

$$\frac{1}{\lambda} = \frac{2\pi^2 m_2^2 v^4}{h^3 c} \left(\frac{1}{n_1 r} - \frac{1}{n_2 r} \right)$$

Wave Mechanics

Q Describe about De Broglie's equation

Ans: De Broglie had arrived at his hypothesis with the help of Planck's Quantum theory and Einstein's Theory of relativity. He derived a relationship between the magnitude of the wavelength associated with the mass 'm' of a moving body and its velocity. According to Planck's The photon energy E is given by the equation,

$$E = h\nu \quad (1)$$

where h is Planck's constant and ν is frequency of radiation. By applying Einstein mass energy relationship, $E = mc^2$ (2), where c is the velocity of radiation,

comparing (1) and (2) $mc^2 = h\nu = h \cdot \frac{c}{\lambda}$

$$mc = \frac{h}{\lambda}$$

$$\lambda = \frac{h}{mv}$$

$$\text{wavelength} = \frac{\text{Planck's constant}}{\text{mass} \times \text{velocity}}$$

□ Write down Schrodinger's wave equation.

The equation of standing wave

$$\psi = A \sin 2\pi \frac{x}{\lambda} \quad \text{--- (1)}$$

where ψ is a mathematical function representing the amplitude of wave, x be the displacement in a given direction and λ be the wavelength and A is a constant.

By differentiating equation (1) with respect to x , we get,

$$\frac{d\psi}{dx} = A \cos \frac{2\pi x}{\lambda} \times \frac{2\pi}{\lambda}$$

again,

$$\frac{d^2\psi}{dx^2} = -A \sin 2\pi \frac{x}{\lambda} \cdot \frac{2\pi}{\lambda} \cdot \frac{2\pi}{\lambda}$$

But,

$$A \sin \frac{2\pi x}{\lambda} = \psi$$

$$\therefore \frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} \psi$$

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{\lambda^2} \psi = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{\left(\frac{h}{mv}\right)^2} \psi = 0 \quad \text{[from De Broglie equation]}$$

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2 \times m^2 v^2}{h^2} \psi = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 \times m \times \frac{1}{2} m v^2}{h^2} \psi = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m (E_k) \psi}{h^2} = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m (E-U) \psi}{h^2} = 0 \quad \text{[} E = E_k + U \text{]}$$

This is Schrodinger's equation in one dimension. It needs to be generalised for a particle whose motion is described by three space co-ordinates x, y and z .

Thus,
$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2m(E-U)}{h^2}\psi = 0$$

This equation is called Schrodinger's wave equation. The first three terms on the LHS are represented by $\Delta^2\psi$.

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

□ Write down the distinction between orbit and orbital.

Orbit

- ① The electrons move around a fixed circular shell. It is called orbit. They have a definite energy and a fixed distance.
- ② It expresses the exact position of an electron in an atom.
- ③ Orbital represents the planar motion of electron.
- ④ Maximum number of electrons in an orbit is $2n^2$, where n is the number of principal shell.

Orbital

- ① An orbital is defined as a three dimensional region within which there is higher probability that an electron having a certain energy will be found.
- ② Orbital does not specify the exact position of an electron in an atom.
- ③ Orbital represents the dimensional motion of electron.
- ④ Maximum number of electrons in an orbital is $2(2l+1)$, where l indicates the sub shell.

Q. What is quantum number? write down the application.

The numbers which indicate both the position and energy of an electron that moving round the nucleus is called Quantum Number.

Application

- (i) To identify the exact position of an electron in an atom.
- (ii) To determine the exact momentum of an electron in an atom.
- (iii) To determine the direction of self rotation of an electron in an atom.

Principal Quantum Number

The quantum number which determines the energy shell in which the electron is revolving round the nucleus is called principal quantum number. It is denoted by symbol n .

Azimuthal quantum number

The quantum number which denotes the shape of the orbital occupied by the electron and the angular momentum of the electron is called azimuthal quantum number. It is denoted by symbol l .

For principal quantum number,

$n=1$, there is only one possible value $l=0$

$n=2$, there are two possible values $l=0, l=1$

$n=1$

$l=0$ (1s)

$n=2$

$l=0$ (2s)

$l=1$ (2p)

$n=3$

$l=0$ (3s)

$l=1$ (3p)

$l=2$ (3d)

s < p < d < f (except for H atom)

Magnetic Quantum number:

This quantum number has been proposed to account for the splitting up of spectral lines. This is also called Orientation quantum number because it gives the orientation or distribution of the electron cloud. The value of m depends upon the value of l . For each value of the azimuthal quantum number l , the magnetic quantum number m , may assume all the integral values between $+l$ to $-l$ through zero. For example, for $l=1$ (p-orbital) the magnetic quantum number m will have three values $+1, 0, -1$.

Spin quantum number:

It determines the direction of a electron which is revolving round the nucleus and moving about its own axis. The electron can spin clockwise (\downarrow) direction or anticlockwise (\uparrow) direction. It is denoted by s . The value of s may be $+\frac{1}{2}$ or $-\frac{1}{2}$.

□ Write down the Hund's rule of maximum multiplicity.

Electrons are distributed among the orbitals of a subshell in such a way as to give the maximum number of unpaired electrons and have the same direction of spin.

According to the rule, electrons are arranged in a sub-shell in such a way that they contain maximum number of unpaired electrons and these unpaired electrons must have same direction of spin.

□ Describe Pauli's exclusion principle

It is stated as "No two electrons in an atom can have the same set of four identical quantum numbers."

According to this principle, if two electrons in an atom have identical values of n , l and m it follows that they differ in their spins. Thus every electron in an atom differs from every other electron in total energy and therefore there can be as many electrons in a shell as there are possible arrangements of different quantum numbers.

n	l	m	s
1	0	0	$+\frac{1}{2}$ (1st electron)
1	0	0	$-\frac{1}{2}$ (2nd electron)

Ground state Electron configuration of elements

For complicated atoms which may contain many electrons and have many energy levels or orbitals, the 'building up' process for the electrons is governed by the following rules:

Rule 1: Each electron shell can hold a maximum of $2n^2$ electrons where n is the shell number.

Rule 2: These electrons are accommodated in s, p, d and f orbitals, the maximum number of each electrons in each type of orbitals being determined by its electron holding capacity (for s=2, p=6, d=10, f=14)

Rule 3: In the ground state of atom, the electrons tend to occupy the available orbitals in the increasing order of energies, the orbitals of lower energy being filled first. This is called "building up principle" or 'Aufbau Principle'.

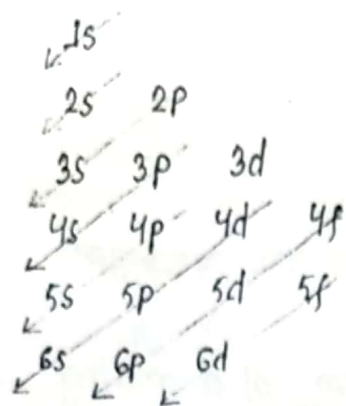


Fig: Aufbau order of orbitals for filling in electrons.

Rule 4: Any orbital may have one or two electrons at the most. Two electrons can occupy the same orbital only if they have opposite spins (Pauli's exclusion principle)

Rule 5: When several orbitals of equal energy are available, electrons prefer to occupy separate orbitals rather than getting paired in the same orbital. (Hund's rule)

Heisenberg's uncertainty principle

This principle is an important feature of wave mechanics and discusses the relationship between a pair of conjugate properties of a substance. According to uncertainty principle, "It is impossible to know simultaneously both the conjugate properties accurately."

For example, the position and momentum of a moving particle are interdependent and thus conjugate properties also. Both the position and momentum of particle can not be determined with absolute exactness. If momentum is measured very accurately, a measurement of position of particle becomes less precise. On the other hand, if position is determined with accuracy, the momentum becomes less accurately. Thus, certainty of determination of one property introduces uncertainty of determination of the other. The uncertainty in measurement of position, Δx and the uncertainty of determination of momentum, Δp (or Δmv) are related by Heisenberg's relationship as

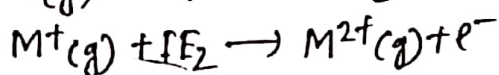
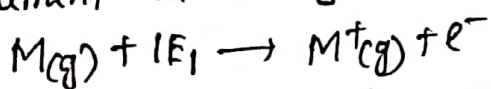
$$\Delta x \times \Delta p \geq \frac{h}{2\pi}$$

$$\Delta x \times m \Delta v \geq \frac{h}{2\pi}$$

where h is Planck's constant.

Ionisation Energy or Ionisation Potentials

The ionisation energy (IE) of an element is defined as the energy needed to remove a single electron from an atom of the element in the gaseous state.

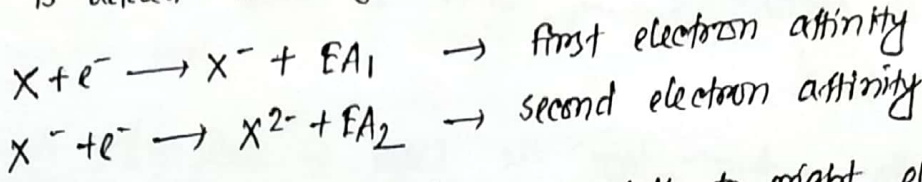


IE_1 First ionisation energy

IE_2 second ionisation energy

Electron Affinity

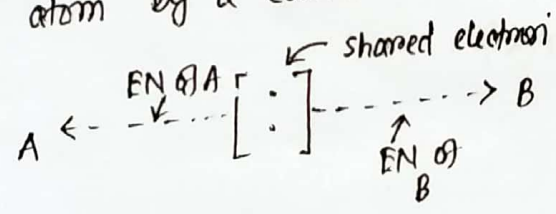
Electron affinity of an element is the amount of energy released when an electron is added to a gaseous atom to form an anion.



In periodic table when we proceed from left to right, electron affinity increases. when we proceed from up to down, electron affinity decreases.

Electronegativity

The attraction exerted by an atom on the electron pairs bonding it to another atom by a covalent bond is called electronegativity.



It is evident that an atom of high electronegativity will attract the shared electron pairs away from one of lower electronegativity. Thus the former atom will acquire a partial negative charge while the other atom will get a partial positive charge.

In periodic table when we proceed from left to right, electronegativity increases, when we proceed from up to down, electronegativity decreases.

Li	Be	B	C	N	O	F
1	1.5	2	2.5	3	3.5	4

→ Increase across a period.

F	Cl	Br	I
4	3	2.8	2.5

→ Decrease across down a group.

□ Importance of electronegativity:

- ① In predicting the polarity of a particular bond.
- ② In predicting the degree of ionic character of a covalent bond.
- ③ In understanding the shape of molecules.
- ④ In predicting the inductive effects in organic chemistry.

□ Alpha particles

It has twice the charge of a proton and about 4 times its mass.



Atomic spectra

A spectrum in which each line represents a specific wavelength of radiation emitted by the atoms is referred to as the Line spectrum or Atomic Emission spectrum.

Atomic spectrum of hydrogen

The atomic spectrum of hydrogen can be obtained by passing electric discharge through the gas contained in a discharge tube at low pressure. The light radiation emitted is then examined with the help of spectroscope.

1884 **Balmer** observed that there were **four** prominent colored lines in the visible hydrogen spectrum.

- (i) a **red** line with a wavelength of **6563 \AA**
- (ii) a **blue green** line with a wavelength **4861 \AA**
- (iii) a **blue** line with a wavelength **4340 \AA**
- (iv) a **violet** line with a wavelength **4102 \AA** .

Math ২ম নম্বর উদ্ভ
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$$\lambda = \frac{h}{mv}$$
$$v = \frac{c}{\lambda}$$
$$\lambda = \frac{c}{v}$$

$$\Delta x \times \Delta p = \frac{h}{4\pi}$$

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