Scope: This paper explains the evolution of matter from electron to molecules, different properties of atoms and molecules, structure of molecuels, radioactivity etc.

Objectives: To make the students understant the basics of atoms and molecules, molecular structure, different types energy transfer in molecules etc.

UNIT I Discharge of electricity through gases – Cathode rays, positive rays, x-rays – Discovery of electron – Determination of e/m by Thomson''s method – Determination of charge of electron – Thomson''s experiment - Electron theory and applications – electrical conductivity in metals – Thermal conductivity – Thermo-electric effect – Langevin''s theory of diamagnetism and paramagnetism – Thermionic emission – photoelectric emission – applications

UNIT II The Thomson atom model – Rutherford atom model – Bohr atom model – Applications of Bohr"s theory – excitation and ionization of atoms – X-ray spectra – Continuous and Characteristic x-ray spectra – The Sommerfeld relativistic atom model – Vector atom model – Electronic structure in atoms – Fine structure of spectral lines

UNIT III Radioactivity – origin of radiation from natural radioelements – alpha disintegration – wave mechanical theory – Beta disintegration – internal conversion of gamma rays – gamma ray emission – origin of gamma rays

UNIT IV Molecular Structure – General classification of molecules – Electronic structure in molecules – linkage between atoms – electrovalent and covalent atomic molecules – wave mechanical theory of covalent linkage – Van der Waals type of binding – metallic binding – electric moments of molecules – size and shape of molecules – heat of disassociation – photo-chemical disassociation – Frank Condon principle

UNIT V Molecular spectra – experimental study – theoretical explanation – pure rotation spectra – rotation-vibration spectra – Fortrat diagram – Peculiarities of certain band spectra – Isotopic effect in molecular spectra.

Text Book:

- 1. Murugeshan. R, 17th edition 2014, Modern Physics, S. Chand & Company, New Delhi.
- 2. Arutherbeiser ; 1st edition 1969 Mcgraw hill ; Prespective of morden physics.

- 1. J.B.Rajam, "Atomic Physics", S.Chand& Co., New Delhi, 7th edition 2009.
- 2. White H.E., "Introduction to Atomic Spectra", McGraw Hill Book Co., New York, 1934.
- 3. Banwell, "Fundamentals of Molecular Spectroscopy", Tata McGraw Hill Education, 1994.

LECTURE PLAN UNIT - I

S.No	Lecture	Topics to be covered	Support material
	Duration		
	(Hr)		
1	1	Discharge of electricity through gases –	R1 (6-20)
2		Cathode rays, positive rays, x-rays	R1 (6-20)
3	1	Discovery of electron – Determination of e/m by	R1 (33)
		Thomson"s method	
4	1	Determination of charge of electron – Thomson"s	R1 (38)
		experiment	
5	1	Electron theory and applications	R1 (54)
6	1	Electrical conductivity in metals	R1 (54)
7	1	Thermal conductivity – Thermo-electric effect	R1 (54-57)
8	1	Langevin"s theory of diamagnetism	R1 (61-67)
9	1	Langevin"s theory of paramagnetism	R1 (65-68)
10	1	Thermionic emission-photoelectric emission – applications	R1 (104-121)
11	1	Revision	-
12	1	Possible big mark questions discussion	-
13	1	Possible multiple choice questions discussion	-
14	1	Unit test	-
15	1	Semester question discussion on particular unit	-
		Total no.of Hours planned for unit –I	15 hrs

Text Book:

- 1. Murugeshan. R, 17th edition 2014, Modern Physics, S. Chand & Company, New Delhi.
- 2. Arutherbeiser ; 1st edition 1969 Mcgraw hill ; Prespective of morden physics.

- 1. J.B.Rajam, "Atomic Physics", S.Chand& Co., New Delhi, 7th edition 2009.
- 2. Banwell, "Fundamentals of Molecular Spectroscopy", Tata McGraw Hill Education, 1994

LECTURE PLAN UNIT - II

S.No	Lecture	Topics to be covered	Support material
	Duration		
	(Hr)		
1	1	The Thomson atom model	R1 (554)
2	1	Rutherford atom model	R1 (554-556)
3	1	Bohr atom model	R1 (565-583)
4		Applications of Bohr"s theory	
5	1	Excitation and ionization of atoms – X-ray spectra	R1 (583-595)
6	1	Continuous and Characteristic x-ray spectra	R1 (595-597)
7	1	The Sommerfeld relativistic atom model	R1 (615-623)
8	1	Vector atom model	R1 (624-636)
9	1	Electronic structure in atoms	R1 (636-655)
10	1	Fine structure of spectral lines	R1 (656-662)
11	1	Revision	-
12	1	Possible big mark questions discussion	-
13	1	Possible multiple choice questions discussion	-
14	1	Unit test	-
15		Semester question discussion on particular unit	-
		Total no.of Hours planned for unit -II	15 hrs

Text Book:

- 1. Murugeshan. R, 17th edition 2014, Modern Physics, S. Chand & Company, New Delhi.
- 2. Arutherbeiser ; 1st edition 1969 Mcgraw hill ; Prespective of morden physics.

- 1. J.B.Rajam, "Atomic Physics", S.Chand& Co., New Delhi, 7th edition 2009.
- 2. Banwell, "Fundamentals of Molecular Spectroscopy", Tata McGraw Hill Education, 1994

LECTURE PLAN UNIT - III

S.No	Lecture	Topics to be covered	Support material
	Duration		
	(Hr)		
1	1	Radioactivity	R1 (823)
2	1	Origin of radiation from natural radioelements	R1 (823)
3	1	Alpha disintegration	R1 (824-825)
4	1	Wave mechanical theory	R1 (825-828)
5	1	– Beta disintegration	R1 (825-828)
			D1 (000, 000)
6	1	Internal conversion of gamma rays	RI (828-829)
7	1	Commo nou omiosio n	D1 (920, 920)
/	1	Gamma ray emission	KI (829-830)
8	1	Continuation of gamma rays	R1 (829-830)
0	1	Origin of gamma rave	P1 (820 833)
2	1	Origin of gamma rays	KI (050-055)
10	1	Continuation of origin of gamma rays	R1 (830-833)
11	1	Revision	-
12	1	Possible big mark questions discussion	-
13	1	Possible multiple choice questions discussion	-
14	1	Unit test	-
15	1	Semester question discussion on particular unit	-
		Total no.of Hours planned for unit -III	8 hrs

Text Book:

- 1. Murugeshan. R, 17th edition 2014, Modern Physics, S. Chand & Company, New Delhi.
- 2. Arutherbeiser ; 1st edition 1969 Mcgraw hill ; Prespective of morden physics.

- 1. J.B.Rajam, "Atomic Physics", S.Chand& Co., New Delhi, 7th edition 2009.
- 2. Banwell, "Fundamentals of Molecular Spectroscopy", Tata McGraw Hill Education, 1994

LECTURE PLAN UNIT - IV

S.No	Lecture Duration (Hr)	Topics to be covered	Support material
1	1	Molecular Structure – General classification of molecules	R1 (746-747)
2	1	Electronic structure in molecules	R1 (748)
3	1	Linkage between atoms	R1 (748-751)
4		Electrovalent and covalent atomic molecules	
5	1	Wave mechanical theory of covalent linkage	R1 (751-754)
6	1	Van der Waals type of binding	R1 (755-756)
7	1	metallic binding - electric moments of molecules	R1 (756-758)
8	1	size and shape of molecules	R1 (756-758)
9	1	Heat of disassociation – photo-chemical disassociation	R1 (759-760)
10	1	Frank Condon principle	R1 (761-763)
11	1	Revision	-
12	1	Possible big mark questions discussion	-
13	1	Possible multiple choice questions discussion	-
14	1	Unit test	-
15	1	Semester question discussion on particular unit	-
		Total no.of Hours planned for unit -IV	15 hrs

Text Book:

- 1. Murugeshan. R, 17th edition 2014, Modern Physics, S. Chand & Company, New Delhi.
- 2. Arutherbeiser ; 1st edition 1969 Mcgraw hill ; Prespective of morden physics.

- 1. J.B.Rajam, "Atomic Physics", S.Chand& Co., New Delhi, 7th edition 2009.
- 2. Banwell, "Fundamentals of Molecular Spectroscopy", Tata McGraw Hill Education, 1994

LECTURE PLAN UNIT - V

S.No	Lecture	Topics to be covered	Support material
	Duration		
	(Hr)		
1	1	Molecular spectra	R1 (764-765)
2	1	Experimental study	
3	1	Theoretical explanation	R1 (765-766)
4	1	pure rotation spectra	R1 (767-769)
5	1	rotation-vibration spectra	R1 (771-772)
6	1	Enders & d'annual a	D1(77(770))
0	1	Fortrat diagram	RI (776-778)
7	1	Desuliarities of contain hand one stre	D1(792,794)
/	1	Pecunarities of certain band spectra	RI (785-784)
0	1	Icotonic offect in melecular spectre	D1 (794 795)
0	1	isotopic effect in molecular spectra	KI (704-703)
0	1	Povicion	
9	1	Revision Describle hig mark questions discussion	-
10	1	Possible of ginark questions discussion	-
11	1	Possible multiple choice questions discussion	-
12	1	Unit test	-
13	1	Semester question discussion on particular unit	-
14	1	Previous year question paper discussion	-
15	1	Previous year question paper discussion	-
		Total no.of Hours planned for unit -V	15 hrs

Text Book:

1. Murugeshan. R, 17th edition 2014, Modern Physics, S. Chand & Company, New Delhi.

2. Arutherbeiser ; 1st edition 1969 McGraw hill ; Prespective of morden physics.

- 1. J.B.Rajam, Atomic Physics, S.Chand& Co., New Delhi, 7th edition 2009.
- 2. Banwell, Fundamentals of Molecular Spectroscopy, Tata McGraw Hill Education, 1994

Unit I: Discharge of electricity through gases – Cathode rays, positive rays, x-rays – Discovery of electron – Determination of e/m by Thomson''s method – Determination of charge of electron – Thomson''s experiment - Electron theory and applications – electrical conductivity in metals – Thermal conductivity – Thermo-electric effect – Langevin''s theory of diamagnetism and paramagnetism – Thermionic emission – photoelectric emission – applications

Discharge of electricity through gases

Electric discharge in gases occurs when electric current flows through a gaseous medium due to ionization of the gas. Depending on several factors, the discharge may radiate visible light. The properties of electric discharges in gases are studied in connection with design of lighting sources and in the design of high voltage electrical equipment.

I: Townsend discharge, below the breakdown voltage. At low voltages, the only current is that due to the generation of charge carriers in the gas by cosmic rays or other sources of ionizing radiation. As the applied voltage is increased, the free electrons carrying the current gain enough energy to cause further ionization, causing an electron avalanche. In this regime, the current increases from femtoamperes to microamperes, i.e. by nine orders of magnitude, for very little further increase in voltage. The voltage-current characteristics begin tapering off near the breakdown voltage and the glow becomes visible.

II: glow discharge, which occurs once the breakdown voltage is reached. The voltage across the electrodes suddenly drops and the current increases to milliampere range. At lower currents, the voltage across the tube is almost current-independent; this is used in glow discharge voltage stabilizers. At lower currents, the area of the electrodes covered by the glow discharge is proportional to the current. At higher currents the normal glow turns into abnormal glow, the voltage across the tube gradually increases, and the glow discharge covers more and more of the surface of the electrodes. Low-power switching (glow-discharge thyratrons), voltage stabilization, and lighting applications (e.g. Nixie tubes, decatrons, neon lamps) operate in this region.

III: arc discharge, which occurs in the ampere range of the current; the voltage across the tube drops with increasing current. High-current switching tubes, e.g. triggered spark gap, ignitron, thyratron and krytron (and its vacuum tube derivate, sprytron, using vacuum arc), high-power mercury-arc valves and high-power light sources, e.g. mercury-vapor lamps and metal halide lamps, operate in this range.

Glow discharge is facilitated by electrons striking the gas atoms and ionizing them. For formation of glow discharge, the mean free path of the electrons has to be reasonably long but shorter than the distance between the electrodes; glow discharges therefore do not readily occur at both too low and too high gas pressures.

The breakdown voltage for the glow discharge depends nonlinearly on the product of gas pressure and electrode distance according to Paschen's law. For a certain pressure \times distance value, there is a lowest breakdown voltage. The increase of strike voltage for shorter electrode distances is related to too long mean free path of the electrons in comparison with the electrode distance.

A small amount of a radioactive element may be added into the tube, either as a separate piece of material (e.g. nickel-63 in krytrons) or as addition to the alloy of the electrodes (e.g. thorium), to pre ionize the gas and increase the reliability of electrical breakdown and glow or arc discharge ignition. A gaseous radioactive isotope, e.g. krypton-85, can also be used. Ignition electrodes and keep alive discharge electrodes can also be employed.

The E/N ratio between the electric field E and the concentration of neutral particles N is often used, because the mean energy of electrons (and therefore many other properties of discharge) is a function of E/N. Increasing the electric intensity E by some factor q has the same consequences as lowering gas density N by factor q.

Its SI unit is $V \cdot cm^2$, but the Townsend unit (Td) is frequently used.

Cathode rays and positive rays

Cathode rays are streams of fast moving electrons. Properties: (i) Cathode rays are emitted normally from the cathode surface. Their direction is independent of the position of the anode.

(ii) Cathode rays travel in straight lines. (Cast shadows of objects placed in their path).

(iii) Cathode rays exert mechanical force on the objects they strike.

(iv) Cathode rays produce heat when they strike a material surface.

(v) Cathode rays produce fluorescence when they strike a number of crystals, minerals and slats.

(vi) When cathode ray strikes a solid object, specially a metal, X-rays are emitted from the object. (It is not safe to use Geissler tube at potential differences above about 5-6 kV because of this X-ray emission, generated by striking of cathode rays of metal anode).

(vii) Cathode rays are deflected by an electric field and also by a magnetic field. The direction of deflection is the same as that of a stream of negatively charged particles.

(viii) Cathode rays ionize the gas through which they are passed.

(ix) Cathode rays can penetrate thin foils of metal.

(x) Cathode rays affect photographic plates.

(xi) Cathode rays are found to have velocity upto one tenth of the velocity of light. The e/m of electrons was measured by J.J. Thomson (so credit of discovering electron is given to Thomson).

The e of electron was measured by R.A./Millikan e/m = 1.759×10^{11} c/kg e = 1.602×10^{-19} C m = 9.09×10^{-31} kg

The e/m of an electron is called the specific charge of an electron.

If one includes the relativistic variation of mass with speed then specific charge of an electron decreases with the increase in the velocity of the electron.

Positive Rays :

Positive rays are sometimes known as the canal rays. These were discovered in 1896 by Goldstein. If the cathode of a discharge tube has holes in it and the pressure of the gas is around 1 mm of mercury than faint luminous glow come out from each hole on the backside of the cathode.

This shows that something is coming out of the holes. These are called canal rays or positive rays.



Origin of positive rays :

When potential difference is applied across the electrodes, electrons (cathode rays) are emitted from the cathode. As they move towards anode, they gain energy.

These energetic electrons which collide with the atoms of the gas in the discharge tube, they ionize the atoms. The positive ions formed at various places between cathode and anode, travel towards the cathode. Since during their motion, the positive ions when reach the cathode, some pass through the holes in the cathode. These stream of positive ions are the positive rays or canal rays.

If the discharge tube is totally evacuated then no positive rays are produced. Thus positive rays are positive ions of the gas in the tube. Properties of positive rays were studied by Thomson. The q/m of the hydrogen was found to be $\sim 10^8$ C/kg much less then the e/m of electron $\sim 10^{11}$ C/kg indicating that mass of positive rays is much greater than that of electrons.

Properties of Positive Rays :

(i) These are positive ions having same mass if the experimental gas does not have isotopes. However if the gas has isotopes then positive rays are group of positive ions having different masses.

(ii) They travel in straight lines and cast shadows of objects placed in their path. But the speed of the positive rays is much smaller than that of cathode rays.

(iii) They are deflected by electric and magnetic fields but the deflections are small as compared to that of cathode rays.

(iv) They show a spectrum of velocities. Different positive ions move with different velocities.

(v) q/m ratio of these rays depends on the nature of the gas in the tube (while in case of the cathode rays q/m is constant and does not depend on the gas in the tube).

(vi) They carry energy and momentum.

(vii) They cause ionization (which is much more than that produced by cathode rays).

- (viii) They cause fluorescence (in ZnS or CdS screen) and affect photographic plates.
- (ix) They have a little penetration power (but much less in comparison to cathode rays)

X-Rays

W. C. Rontgen conducted various experi-ments to study the discharge of electricity through gases and accidently discovered X-rays. He used a glass tube fitted with two electrodes cathode and anode. An exhaust pump was connected through a side tube and a high electric potential of about 25 kV was applied across the electrodes. Rontgen made the following important observations:



(a) When air inside the tube was at atmospheric pressure there was no discharge of electricity through it.

(b) When pressure inside the tube was reduced to few cm of mercury, a feeble discharge of electricity occurred between the electrodes. At the same time air inside the tube started giving visible light.

(c) When air pressure was reduced to 10^{-3} mm of mercury, air lumininescence gets disappeared but the glass walls of the tubes starts glowing. Rontgen concluded that this glow was due to some invisible penetrating radiations from anode that were falling on the glass and

producing fluorescence. Rontgen did not know much about the nature of these rays and therefore, he called them X-rays.

(B) Explanations: Rontgen explained the production of these X-rays due to the bombardment of high velocity electrons on anode. Due to low pressure (10^{-3} mm) inside the tube, the air gets ionised producing a few electrons and the positive ions.

The positive ions are highly accelerated towards the cathode, these ions knock out electrons from the cathode. The released electrons move with tremendous speed towards highly positive anode. They strike the anode surface and produce X-rays. On his experimental basis, Rontgen observed that in order to produce X-rays, the following three things are required.

(a) The source of electron

(b) Means of accelerating these electrons to high speeds.

(c) Anode or target on which these high speed electrons should strike to produce X-rays.

Origin of X-ray:

X-rays are produced by bombarding high speed electrons on some heavy elements (e.g. tungsten) known as target.



A big fraction of the kinetic energy of the majority of striking electrons is spent in undergoing collisions with the atoms of the target and consequently the temperature of target material is considerably increased. It is found that nearly 99% of the incident energy of electron is used up in heating the target. However, some fraction of the K.E. of the bombarding electrons is used up to produce X-rays in the following two ways :

CONTINUOUS X-RAYS OR BRAKING X-RAYS :

The bombarding electrons may be slowed down by the nucleus as they pass close to it, thus releasing the loss of energy in the form of X-rays. The high speed electrons go into the interior of the atoms of the target material and are attracted by the positive charge on their Nuclei. As an electron passes lose to the positive nucleus of an atom in the target the electron is deflected from its path as shown in fig. This result in deceleration of the electron. The loss in energy of the electron during deceleration is emitted in the form of X-rays. X-rays produced in this way are called Braking or Bremsst Rahluung X-rays as they are produced due to the braking or slowing down of the bombarding electrons by the atoms of the target.

Properties Of X-ray:

X-rays are produced when fast moving electrons (or cathode rays) strike any heavy element and have the following properties.

(1) X-rays are electromagnetic waves of very short wave length (0.03 A° to 30 A°). Hence they carry high energy. It is to be noted here that wave length of light rays ranges from 4000 to 7500 A° . This is the only difference between X-rays and light rays.

(2) X-rays travel in straight lines like light.

(3) X-rays travel with speed of light.

(4) Just like light rays, X-rays also show the phenomenon of reflection, referaction, interference, diffraction and polarisation.

(5) X-rays are not deflected by magnetic or electric fields. Hence they are not charged particles.

(6) X-rays produce flourescence (i.e., give out light) when they fall on certain materials like zinc sulphide, glass, rock salt etc.

(7) X-rays produce continuous spectrum just like light rays.

(8) X-rays penetrate through different substant e.g. thin metal sheets, flesh etc. depending upon their frequency or energy. They do not pass through heavy metals and bones. If such objects are placed in their path, they cast their shadow.

(9) X-rays blacken the photography plate when they fall in it.

(10) X-ray ionise the gases they pass through.

(11) X-rays produce photo electric and compton effects when they fall on matter.

DETERMINATION OF e/m OF AN ELECTRON

Introduction

J.J Thomson was the first scientist who measured charge to mass ratio (e/m) of an electron.

Principle

When a narrow beam of charged particles are projected at constant speed (v) across a magnetic field in a direction perpendicular to the field, the beam of particles experiences a force, which makes them move in a circular path.

Apparatus

It consists of a highly evacuated glass tube, fitted with electrodes. Electrons are produced by heating a tungsten filament electrically. Electrons are made to accelerate and form a beam by passing through discs A and B. They are passed through electric and magnetic field. Finally they fall on zinc sulphide screen.



Theory

Actually electrons moving side ways are also directed towards the screen by applying a –ve potential on a hollow cylinder (c) open on both sides surrounding the filament. Electrons are accelerated by applying a potential difference of above 1000 V between the filament and disc A. A further potential difference of 500 V is applied between the discs A and B. The arrangement focuses the beam to the hole of the disc B from where it is further proceeds to a straight line. When beam of electrons enters a magnetic field it moves in a circular track. The force experienced by the electron is

$$\mathbf{F}_{\mathbf{m}} = \mathbf{evB} - \cdots - (1)$$

This magnetic field provides necessary centripetal force to electron so that it follows a circular path.

i.e. $F_m = F_c$ $evB = mv^2/r$ eB = mv/re/m = v/Br -----(2)

By knowing the values of v, B and r, value of e/m can be determined.

Radius of curvature of the path

If r is the radius of curvature of circular path, 'a' is the distance b/w 'O' and 'O'', and 'b' is the distance b/w electron gun and screen then by using the property of chord:



Since 'a' is very small as compared to '2r', so we neglect 'a²'. $2ra = b^2$

 $r = b^2/2a$

Determination of the velocity (First Method)

The electrons are first accelerated by applying a potential (V) b/w discs A and B before entering the magnetic field.

BSc Physics 2017-2018-ODD	Unit –I Discharge of Electricity	Atomic and Molecular Physic 15PHU50
	K.E = V.e	
	Or	
	1/2 mv ² = Ve	
	$v = (2Ve/m)^{1/2}$	
Putting the value of v in eq. (2)		
	e/m = v/Br	
	$e/m = (2Ve/m)^{1/2}/Br$	
Squaring on both sides		
	$e^2/m^2 = 2Ve/m/B^2r^2$	
	or	
	$e/m = 2Ve/B^2r^2$	
Particle Selector Method		

is passed through crossed electric and magnetic field. The electric field is so adjusted that the light spot comes back to 'O' from 'O''. i.e. electron beam passes and straight without deflection.

Force on electron by electric field

$$\mathbf{F}_{\mathbf{e}} = \mathbf{E}\mathbf{e}$$

Force on electron by magnetic field

$$\mathbf{F}_{\mathbf{m}} = \mathbf{B}\mathbf{e}\mathbf{v}$$

Since both forces balance each other

BSc Physics 2017-2018-ODD	Unit –I Discharge of Electricity	Atomic and Molecular Physics 15PHU501
	$\mathbf{F_m} = \mathbf{F_e}$	
	Bev = Ee	
	$\mathbf{V} = \mathbf{E}/\mathbf{B}$	
Putting the value in eq. (2)		
	e/m = v/Br	
	e/m = E/B/Br	

After substituting the values we get

$$e/m = 1.75888 \times 10^{11} C/Kg$$

 $e/m = E/B^2r$

Conductivity

Introduction In an ionic solid, the atom forming a cation gives up its valence electron that is captured by the atom forming an anion. Here the electrons are strictly localized. However in metals, the core electrons are localized at the atoms but the valence electrons are delocalized and belong to the entire solid. The behaviour and energy states of these delocalized electrons determine many properties of these solids. We shall try to understand the behavious of these electrons and see how they influence the property of the solid. The simplest approach is the classical free electron model that was successful in explaining some of the properties of metals. This was succeeded by the more sophisticated band theory of solids.

The general characteristics of electrical conductors are:

- (i) The current density in the steady state is proportional to the electric field strength (Ohm's law).
- (ii) (ii) For pure specimens, the electrical conductivity (σ) and the thermal conductivity (k) vary with temperature as follows: $\sigma \propto T-1$ and k = constant (for $T > \theta D$) so that σT KT is a constant independent of temperature (Wiedemann-Franz law); $\sigma \propto T-5$ and K $\propto T-2$ (for T < θD) where θD is the

characteristic Debye temperature. The relation ρ α T5 is known as Bloch Gruneisen T^5 law.

- (iii) For metals that exhibit the phenomenon of superconductivity, their resistivity disappears at temperature above 0 K and below the critical temperature (Tc) for the superconducting phase transition (Tc = 4.15 k) for mercury.
- (iv) For metals containing small amounts of impurities, the electrical resistivity (ρ) may be written as $\rho = \rho 0 = \rho p$ (T) where $\rho 0$ is a constant that increases with increasing unpurity content and ρ (T) is the temperature dependent part of the resistivity. This is known as Matthiessen's rule. (v) For most metals the electrical resistivity decreases with increase of pressure. (vi) The resistivity of alloys that exhibit order-disorder transitions shows pronounced minimum corresponding to the ordered phase.

Thermal conductivity

Thermal conductivity (often denoted k, λ , or κ) is the property of a material to conduct heat. It is evaluated primarily in terms of Fourier's Law for heat conduction.

Heat transfer occurs at a lower rate across materials of low thermal conductivity than across materials of high thermal conductivity. Correspondingly, materials of high thermal conductivity are widely used in heat sink applications and materials of low thermal conductivity are used as thermal insulation. The thermal conductivity of a material may depend on temperature. The reciprocal of thermal conductivity is called thermal resistivity.

$$Q/t = kA\Delta T/d$$

The letter Q represents the amount of heat transferred in a time t, k is the thermal conductivity constant for the material, A is the cross sectional area of the material transferring heat, ΔT is the difference in temperature between one side of the material and the other, and d is the thickness of the material.

The thermoelectric effect

The **thermoelectric effect** is the direct conversion of temperature differences to electric voltage and vice versa. A thermoelectric device creates voltage when there is a different temperature on each side. Conversely, when a voltage is applied to it, it creates a temperature difference. At the atomic scale, an applied temperature gradient causes charge carriers in the material to diffuse from the hot side to the cold side.

This effect can be used to generate electricity, measure temperature or change the temperature of objects. Because the direction of heating and cooling is determined by the polarity of the applied voltage, thermoelectric devices can be used as temperature controllers.

The term "thermoelectric effect" encompasses three separately identified effects: the **Seebeck effect**, **Peltier effect**, and **Thomson effect**. The Seebeck and Peltier effects are different manifestations of the same physical process; textbooks may refer to this process as the **Peltier–Seebeck effect** (the separation derives from the independent discoveries of French physicist Jean Charles Athanase Peltier and Baltic German physicist Thomas Johann Seebeck). The Thomson effect is an extension of the Peltier–Seebeck model and is credited to Lord Kelvin.

Langevin theory of dia-magnetism and paramagnetism

Langevin gave a satisfactory explanation of diamagnetism on the basis of electron theory the basic principle of which ia Lenz's law in electromagnetic induction which states that when a magnetic flux linked with electric current due to revolving electrons is changed, an induced current is set up in such a direction as to oppose the change in flux. It is manifested by the very small and negative value of magnetic susceptibility.

If ω_o be the frequency of electron in the absence of applied field and r is the radius of the loop then:

$$F_o = m\omega_o^2 r = Ze^2/4\pi\epsilon_o r^2$$

Lorentz force acting on the electron moving with velocity v is given by

$$F_L = -Bev = -Be\omega r$$

 $\omega = \pm \omega_o - eB/2m$

BSc Physics	Unit –I	Atomic and Molecular Physics
2017-2018-ODD	Discharge of Electricity	15PHU501

The -ve sigm indicates that these electrons whise orbital magnetic moments are parallel to the magnetic field are slowed downand those with moments antiparallel are speeded by an amount eB/2m : LARMOR THEOREM.

The additional current produced due to change in frequency of the electron is given by $\mathbf{I} = -\mathbf{e}^2 \mathbf{B}/4\pi \mathbf{m}$ and the change in magnetic moment is given by $\Delta \mathbf{M} \mathbf{a} = -\mathbf{e}^2 \mathbf{r}^2 \mathbf{B}/4\mathbf{m}$

$$<\!\!r^2\!\!> = <\!\!x^2\!\!> +<\!\!y^2\!\!> \text{ and } <\!\!r_0^2\!\!> = <\!\!x^2\!\!> +<\!\!y^2\!\!> +<\!\!z^2\!\!>$$

$$<\!\!r^2\!\!> = 2/3 <\!\!r_0^2\!\!>$$

$$M = -e^2 Z \mu_0 HN <\!\!r_0^2\!\!> /\!6m$$

$$\chi = M/H$$

$$= -e^2 Z \mu_0 N <\!\!r_0^2\!\!> /\!6m$$

Since χ is independent of temperature so the diamagnetic behavior of the material does not change into temperature.

According to quantum theory, the magnetic moments are quantized, so they can orient only in specific direction with respect to the magnetic field.

$$\mu = -g \mu_B J$$
 μ_B is called Bohr magneton

g = 1+(J(J+1)+S(S+1)-L(L+1))/2J(J+1)

Using Maxwell Boltzmann statistics, magnetization is given as

 $M{=}~N\sum m_J~g~\mu_B~e^{mJ~g~\mu B/k\beta~T}{\!\!\!/}~e^{~mJ~g~\mu B/k\beta~T}$

CASE I At ordinary temperatures $\mathbf{Bm}_{J} \mathbf{g} \mu_{B} / \mathbf{k}_{\beta} \mathbf{T} \ll 1$ Using the exponential series and $\sum \mathbf{m}_{J}^{2} = (1/3)(J+1)(2J+1)$

$$\begin{split} M &= Ng^2 \mu_B{}^2 \mu_0 \ H \ J(J+1)/3k_\beta T \\ \chi &= M/H \qquad \qquad \chi_{para} = Ng^2 \mu_B{}^2 \mu_0 \ P_{eff}{}^2 \qquad \qquad Peff = g \sqrt{J(J+1)} \end{split}$$

CASE II At low temperature and strong magnetic field $Bm_J g \mu_B / k_\beta T$ is not less than unity

Let $x = B g \mu_B / k_\beta T$ $M = \sum Bm_J g \mu_B emJx$

As $\sum mJ x$ is a geometric progression with (2J+1) terms

Magnetization,

Susceptibility,

$$\begin{split} M &= Ng\mu_B \ d/dx \ (ln(\ e^{Jx} \ (1\mbox{-}e^{-(2J+1)x}/(1\mbox{-}e^{-x}))) \\ &= NgJ\mu_B \ B_J(a) \\ BJ(a) &= (2J\mbox{+}1)/2J \ coth \ (2J\mbox{+}1)a/2J \ - 1/2J \ coth \ (a/2J), \\ Brillouin \ function \ a &= Jg\mu B/k_\beta T \end{split}$$

In the limit J tends to ∞ Brillouin function approaches the Langevin function i.e., infinite number of possible orientations are allowed.

Thermionic emission

Thermionic emission definition

The process by which free electrons are emitted from the surface of a metal when external heat energy is applied is called thermionic emission.

Thermionic emission occurs in metals that are heated to a very high temperature. In other words, thermionic emission occurs, when large amount of external <u>energy</u> in the form of heat is supplied to the free electrons in the metals.

Metals under normal temperature

When a small amount of heat energy is applied to the metal, the <u>valence electrons</u> gain enough energy and break the bonding with the parent <u>atom</u>. The valence electron, which breaks the bonding with the parent atom, becomes free. This electron, which breaks the bonding with the parent atom, is called as the free electron.

The free electrons in the metal have some <u>kinetic energy</u>. However, they do not have enough energy to escape from the metal. The attractive force of the atomic nuclei opposes the free electrons, which try to escape from the metal.

Free electrons in the metal have less energy compared to the free electrons in vacuum. Hence, free electrons require extra energy from the outside source in order to jump into the vacuum.

Metals under high temperature

When heat energy applied to the metal is increased to a higher value, the free electrons gain enough energy and overcome the attractive force of the atomic nucleus, which holds the free electrons in the metal. The free electrons, which overcome the attractive force of the nuclei, break the bonding with the metal and jumps into the vacuum.



The free electrons, which are escaped from the surface of a metal when heat energy is supplied, are called thermions. Thermionic emission process plays a major role in the operation of electronic devices.

Thermionic emission depends on heat applied to the metal and work function of the metal

The number of free electrons escaped from the metal is depends on the amount of heat applied to the metal and the work function of the metal.

Heat applied to the metal:

If large amount of heat is applied to the metal, large number of free electrons gains enough energy and breaks the bonding with the metal. The free electron, which breaks the bonding with the metal, jumps into the vacuum.

On the other hand, if less amount of heat is applied to the metal, less number of free electrons gains enough energy and breaks the bonding with the metal. The free electron, which breaks the bonding with the metal will jumps into the vacuum.

Hence, the number of free electrons emitted from the metal increases with increase in heat. Thus, the free electrons emitted from the surface of metals are directly proportional to the temperature of the metals.

The minimum temperature at which the metal starts emitting the free electrons is called threshold temperature.

If the temperature of the metal is below the threshold temperature, the metal does not emit the free electrons. On the other hand, if the temperature of the metal is equal to the threshold temperature or greater than the threshold temperature, the metal emits the free electrons.

Work function of the metal:

The amount of external heat energy required to remove the free electron from the metal is called work function or threshold energy. The work function of metals is measured

Metals that have low work function will require less amount of heat energy to cause the free electrons to escape from the metal. Hence, the metals with low work function emit large number of free electrons at high temperature.

On the other hand, metals that have high work function will require more amount of heat energy to cause the free electrons to escape from the metal. Hence, the metals with high work function emit less number of free electrons at high temperature. Thus, the emission of free electrons from the metal is inversely proportional to the work function of a metal.

Applications of thermionic emission

The components, which are made by the process of thermionic emission are used in the electronic devices such as cathode ray tube, radio etc.

Photoelectric emission

The process by which free electrons are emitted from the metal surface by the application of light is called photoelectric emission.

It is also defined as, the process by which free electrons are released from the metal when it absorbs light energy. Photoelectric emission is also called as photoemission or photoelectron emission or photoelectric effect.

In this method, light or photons is used to remove the free electrons from the solid metal. Hence, the free electrons emitted from the solid metal are called photoelectrons and current produced due to this process is called photoelectric current.

Metals without light energy

When the light energy is not applied to the metals, the free electrons cannot escape from the metals. However, some of the valence electrons become free from the atoms.

At normal temperature, some valence electrons get enough energy from the heat source. The valence electrons, which gets sufficient energy will breaks the bonding with the parent atom and becomes free.

The free electrons, which breaks the bonding the parent atom, have some kinetic energy. So, they move freely from one point to another point. However, they do not have enough energy to become free from the metal. The strong attractive force of the nuclei prevents the free electrons, which try to escape from the metal.

To overcome the attractive force of the nuclei, the free electrons need sufficient energy from the light. The free electrons, which break the bonding with metal, will moves into the vacuum.

Photons and its effect on metals

Photons are the smallest particles of light. Unlike electrons and protons, photons have no mass. However, photons have energy.

Visible light and all other forms of light such as radio waves, microwaves, infrared light, ultraviolet light, X-rays, and gamma rays are made up of photons. However, the energy of photons is not same for all these lights. For example, gamma rays (photons) have more energy than the infrared light (photons). The energy of photons is depends on its frequency, whereas the intensity of light is depends on the number of photons.

When the light energy is applied to the metal, the free electrons gains energy. In other words, when the light particles (photons) hits free electrons in the metal, they transfer their energy to the free electrons. The free electrons, which gains extra energy from the light, will try to the overcome the attractive force of the nuclei.



If the light energy applied to the metal is further increased to a higher value, the free electrons in the metals gain sufficient energy and overcome the strong attractive force of the nuclei. The free electrons, which overcome the attractive force of the nuclei, will jumps into the vacuum.

Photoelectric emission depends on the frequency of light and does not depends the intensity of light

Frequency of light

The energy of photons is depends on its frequency. Photons with low frequency have low energy whereas photons with high frequency have high energy. High-energy photons or high When the high-energy photons are applied to the metals, free electrons are escaped from the metal surface. photons required to remove the free electrons from the metals is called threshold frequency or threshold energy of photons. This threshold frequency is not same for all metals. It is different for different metals. If the light energy applied to a metal reaches or exceeds the threshold frequency, it starts emitting the free electrons. On the other hand, if the light energy applied to a metal is below the threshold frequency, it does not emit the free electrons.

Intensity of light

The number of photons strikes the free electrons in the metal depends on the intensity of

light. Low intensity light has less number of photons. Hence, if low intensity light is applied to the metal, less number of photons strikes the free electrons in the metal.

On the other hand, high intensity light has more number of photons. Hence, if high intensity light is applied to the metal, more number of photons strikes the free electrons in the metal.

High frequency and low intensity light

If high frequency and low intensity light is applied to the metal, less number of photons hits the free electrons in the metals. However, each individual photon, which hit the free electron, has energy or frequency greater than the threshold frequency or threshold energy.

Hence, each individual photon provides enough energy to the free electron to escape from the metal. Thus the free electrons emitted from the metal surface is depends on the frequency of light.

Low frequency and high intensity light

If low frequency and high intensity light is applied to the metal, more number of photons hits the free electrons in the metals. However, each individual photon, which hits the free electron, has energy or frequency less than the threshold frequency or threshold energy.

Hence, each individual photon does not provide enough energy to the free electron to escape from the metal. A single electron absorbs energy from a single photon. They cannot absorb energy from more than one photon to escape from the metal. Thus, the free electrons emitted from the metals do not depend on the intensity of light

Possible Questions (Part B- 8 marks)

- 1. Discuss in detail about cathode rays, positive rays, x-rays.
- 2. Drive the susceptibility equation in Langevin's theory of diamagnetism
- 3. Determine the value of e/m by Thomson's method.
- 4. Describe the Langevin's theory of paramagnetism
- 5. Describe in detail about electrical conductivity and thermal conductivity of metals.
- 6. Explain in detail about electron theory and applications.
- 7. write a brief note on Thermionic emission and photoelectric emission
- 8. Explain the process of discharge of electricity through gases

KARPAGAM UNIVERSITY, COIMBATORE-21

DEPARTMENT OF PHYSICS CLASS:III BSC PHYSICS Atomic and Molecular Physics (15PHU501) Batch 2015 MULIPLE CHOICE QUESTIONS

QUESTIONS	opt1	opt2	opt3	opt4	answer
Unit - I					
Photoelectric effect can be explained by	Is a form of transverse	Is a form of	Can be polarised	Consists of quanta	Consists of quanta
assuming that light	wave	longitudinal wave		Consists of quanta	Consists of quanta
The Photoelectric effect is based on the law of	Energy	Linear mass	Linear momentum	Angular momentum	Energy
conservation of	Energy			ingular momontum	Energy
In the Photoelectric effect the velocity of the	The frequency of the	The intensity of the	The time for which the	The polarisation of the	The frequency of the
ejected electrons depends upon the nature of the target and	incident light	incident light	light has been incident	incident light	incident light
In order to increase the kinetic energy of	The intensity of	The wavelength of	The frequency of	Both wavelength and	The frequency of
ejected photoelectrons:	radiation should be	radiation should be	radiation should be	intensity of radiation	radiation should be
	increased	increased	increased	should be increased	increased
	Newton's corpuscular	Huvgens wave theory	Maxwell's		
Photoelectric effect supports	nature of light	of light	electromagnetic theory of light	Quantum theory of light	Quantum theory of light
The photoelectrons emitted from a metal		They all have the same	Their energy varies	Their energy varies	Their energy varies
surface are such that	They are all at rest	energy	from 0 to ∞	from 0 to a finite	from 0 to a finite
		energy	110111 0 10	maximum value	maximum value
	Ultraviolet light only	Gamma rays but not by X-rays	Visible light but not by X-rays	Visible light,	Visible light,
Photoelectric effect can be caused by:				Ultraviolet rays, X-rays	Ultraviolet rays, X-rays
				and Gamma rays also	and Gamma rays also
incident light has more than a certain	frequency	wavelength	speed	energy	frequency
The time required in emitting photoelectrons	10^-8 sec	10^-4 sec	1 sec	zero	10^-8 sec
The phenomenon of photoelectric effect is	adiabatic process	instantaneous process	isothermal process	spontaneous process	instantaneous process
	Wave-like behaviour of	Particle-like behaviour	Both Wave-like and	Neither Wave-like nor	Particle-like behaviour
Photoelectric effect shows	light	of light	Particle-like behaviour	Particle-like behaviour	of light
	ingitt	or ingit	of light	of light	oringin
Photovoltaic solar energy conversion system makes use of	fuel cell	solar cell	solar pond	none of the above.	solar cell
In photo electric effect, emission of electrons is	electric field	thermal energy	electromagnetic	applied potential	electromagnetic
due to		ulennai energy	radiation	difference	radiation
Photo electric emission confirms	dual nature of radiation	corpuscular nature of	wave nature of	electromagnetic nature	corpuscular nature of
		radiation	radiation	of radiation	radiation

			electrons come out of a	electrons come out of a	electrons come out of a
		photons come out of a	metal with a constant	metal with different	metal with different
Photoelectric effect is the phenomenon in	photons come out of a	nucleus of an atom	velocity which depends	velocity which depends	velocity which depends
which .	metal when it is hit by a	under the action of an	upon the frequency and	upon the frequency and	upon the frequency and
	beam of electrons	electric field	intensity of the incident	not on the intensity of	not on the intensity of
		ciccure nera	wave	the incident wave	the incident wave
The photoelectric effect is described as the			wave		the merdent wave
ejection of electrons from the surface of a	It is heated to a high	electrons of suitable	Light of suitable	It is placed in a strong	Light of suitable
metal when:	temperature	velocity impinge on it	wavelength falls on it	magnetic field	wavelength falls on it
Photoelectrons are being obtained by					
irradiating zinc by a radiation of 3100 Å. In	The intensity of	The wavelength of	The wavelength of	Both wavelength and	The wavelength of
order to increase the kinetic energy of ejected	radiation should be	radiation should be	radiation should be	intensity of radiation	radiation should be
nhotoelectrons	increased	increased	decreased	should be increased	decreased
The mass of electron as determined by J J					
Thomson is	9.1 X 10 -10gm	9.1 X 10 -15gm	9.1 X 10 -25gm	9.1 X 10 -31gm	9.1 X 10 -31gm
The nature of cathode rays were identified		These		II: time ff	Thomas
by?To	william crook	I nomson	perrin	Hluroll	I nomson
Neutrons were discovered by?	Faraday	Thomson	Dalton	Chadwick	Chadwick
Cathoda rays are deflected by?	Both electric and	alactric field	magnetic field	none of the above	electric and magnetic
Calloue lays are deflected by?	magnetic field		magnetic neiu	none of the above.	field
The nature of positive rays depends on?	The nature of discharge	The nature of electrode	The nature of residual	All of above	The nature of residual
The nature of positive rays depends on?	tube.	The nature of electrode	gas	All of above.	gas
Cathode rays are deflected	both electrodes	none of the electrodes	nositive electrode	negative electrode	nositive electrode
towards	both ciccuodes	none of the electrodes	positive electrode		positive electiode
	radiate electromagnetic	absorb particular	radiate electromagnetic		radiate electromagnetic
When we excite some atoms by heat collision	energy with a	wavelengths when	energy of discrete	emit either invisible or	energy of discrete
or electrical discharge they will	continuous distribution	white light is incident	characteristic	visible light	characteristic
	of wavelength	on them	wavelength		wavelength
The radiations emitted form hydrogen filled	hand spectrum	line spectrum	continuous spectrum	absorption spectrum	line spectrum
discharge tube show	band spectrum	nne spectrum	continuous spectrum	absorption spectrum	nne spectrum
Bracket series is obtained when all transition of	Ath orbit	5th arbit	ard orbit	2nd orbit	Ath orbit
electron terminate on	4111 01 011	5111 01011	510 01010	2110 01011	4111 01011
Reverse process of photoelectric effect is	pair production	Compton effect	annihilation of matter	X-rays production	X-rays production
The penetrating power of X-rays depends on	applied voltage	fraguanov	source	all of the above	fraguancy
their	applied voltage	nequency	source	an of the above	nequency
Quality of X-rays depends upon					
A-filament current B-accelerating voltage C-	A&B	B&C	A&C	A B & C	B&C
material of the target					

n an X-ray tube electrons each of charge e are accelerated through V potential difference allowed to hit a metal target. The wavelength of the X-rays emitted is	he/ev	he/Vc	eV/h	impossible to predict	he/ev
The minimum wavelength of X-rays can further be reduced by	Reducing the pressure or cooling the target.	Increasing the temperature of the filament.	Using a target element of higher atomic number.	Increasing the potential difference between the cathode and the target.	Increasing the potential difference between the cathode and the target.
The minimum wavelength of X-rays produced by the bombardment of electrons on the screen of a television set where the accelerating potential is 2.0K V will be	6.2 x 10-10m	9.1 x 10-18m	3.11 x 10-10m	4 x 10-10m	6.2 x 10-10m
Maximum frequency in the spectrum from X- ray tube is directly proportional to the	Number of incident electron i.e. filament current	The kinetic energy of the incident electron i.e. the potential difference through which they are accelerated.	The soft target which can easily emit electrons.	all of above are correct.	The kinetic energy of the incident electron i.e. the potential difference through which they are accelerated.
Tick the right statement	no photo electronic emission takes place if the frequency of radiation however intense it may be is less than a certain critical value called threshold frequency	threshold frequency depends upon the nature of the metal surface	maximum energy of a photoelectron is a function of frequency rather than intensity of radiation	all of the above	all of the above
A device based on photoelectric effect is called	photo sensitive detection	photo diode	photosynthesis	photo cell	photo cell
When we excite some atoms by heat collision or electrical discharge they will	radiate electromagnetic energy with a continuous distribution of wavelength	absorb particular wavelengths when white light is incident on them	radiate electromagnetic energy of discrete characteristic wavelength	emit either invisible or visible light	radiate electromagnetic energy of discrete characteristic wavelength
Tick the correct statement	an atom has limited number of ionization potentials but a large number of excitation potentials	there are as many excitation potentials as there are excited states	the difference between the energy of the ground sate and any one of the excited states is the measure of excitation energy	all of above	all of above

			the frequency of		the frequency of
Stopping potential for a metal surface in case	the threshold frequency	the intensity of incident	incident light and work	all of the above	incident light and work
of photoelectric emission depends on	for the metal surface	light	function of the metal		function of the metal
			surface		surface
In a photoelectric effect monochromatic light is incident on a metal surface. If the incident light of twice the intensity but of same wavelength the kinetic energy of the emitted electron	Becomes double	Remains same	Becomes half	First increases then decreases because curvilinear graph	Remains same
	The maximum kinetic	The minimum kinetic	The minimum kinetic	The average kinetic	The average kinetic
If the wavelength of incident radiation is	energy of the	energy of the	energy of the	energy of the	energy of the
increased in photoemission then	photoelectrons	photoelectrons	photoelectrons	photoelectrons	photoelectrons
	increases.	decreases.	increases	decreases	decreases
Charge on an electron was determine by	Ampere	Maxwell	Millikan	Thomson	Millikan
Electrons contineoulsy radiate energy during theri motion was given by	J J Thomson	Rutherford	Neils Bohr	none of above	Rutherford
when a photo emissive surface is exposed to light of some suitable frequnecy	photoelectrons are emitted	protons are emitted	photograph can be taken	photons are emitted	photoelectrons are emitted
According to Einstein's photoelectric equation, the graph of K.E. of the photoelectron emitted from the metal versus the frequency of the incident radiation gives a straight line graph, whose slop	is same for all metals and independent of the intensity of the incident radiation.	(B) depends on the nature of the metal.	(C) depends on the intensity of the incident radiation.	(D) depends on the nature of the metal and also on the intensity of incident radiation.	is same for all metals and independent of the intensity of the incident radiation.
The ratio of minimum wavelengths of Lyman and Balmer series will be	1.25	0.25	0.5	1	0.25

Unit:II The Thomson atom model – Rutherford atom model – Bohr atom model – Applications of Bohr"s theory – excitation and ionization of atoms – X-ray spectra – Continuous and Characteristic x-ray spectra – The Sommerfeld relativistic atom model – Vector atom model – Electronic structure in atoms – Fine structure of spectral lines

Thomson model: Introduction

In 1897, J.J.Thomson discovered a negatively charged particle known as an electron. Thomson discovered electron by cathode ray tube experiment. Cathode ray tube is a vacuum tube. Thomson assumed that an electron is two thousand times lighter than a proton and believed that an atom is made up of thousands of electrons having the negative charge. In this atomic structure model, he considered atoms to have a cloud of negative charge and the positive charges. He along with Rutherford was also the first to demonstrate the ionization of air by X-rays. Thomson's model of an atom is similar to plum pudding model or a watermelon.



Thomson's Model

of Atom

Postulates of Thomson's atomic model

- An atom consists of a positively charged sphere with electrons filled into it. The negative and positive charge present inside an atom are equal and as a whole, an atom is electrically neutral.
- Thomson's model of the atom was compared to plum pudding and watermelon. He compared the red edible part of the watermelon to positively charged sphere whereas the seeds of watermelon to negatively charged particles.

Limitations of Thomson's atomic model

- This model of atom failed to explain how a positive charge holds the negatively charged electrons in an atom. Therefore, it failed to explain the stability of an atom.
- This theory also failed to account for the position of the nucleus in an atom.
- Thomson's model failed to explain the scattering of alpha particles.

Although Thomson's model was not an accurate model to account for the atomic structure, it proved to be the base for the development of other atomic structure models

Drawbacks

(i) According electromagnetic vibrating electron to theory, the should frequency radiate energy and the of the emitted spectral line should the be the as electron. In the case of hydrogen atom, same Thomson's model gives only one spectral line of about 1300 Å. But the experimental observations hydrogen consists of reveal that spectrum different with se veral lines five series in each series. (ii) It could account for scattering of α -particles through not the large angles.

Rutherford atomic model

Also called **nuclear atom** or **planetary model of the atom**, description of the structure of atoms proposed (1911) by the New Zealand-born physicist Ernest Rutherford. The model described the atom as a tiny, dense, positively charged core called a nucleus, in which nearly all the mass is concentrated, around which the light, negative constituents, called electrons, circulate at some distance, much like planets revolving around the Sun.



Diagram of the Rutherford atomic model

Unit –II Atom Models

The nucleus was postulated as small and dense to account for the scattering of alpha particles from thin gold foil, as observed in a series of experiments performed by undergraduate Ernest Marsden under the direction of Rutherford and German physicist Hans Geiger in 1909. A radioactive source capable of emitting alpha particles (i.e., positively charged particles, identical to the nucleus of the helium atom and 7,000 times more massive than electrons) was enclosed within a protective lead shield. The radiation was focused into a narrow beam after passing through a slit in a lead screen. A thin section of gold foil was placed in front of the slit, and a screen coated with zinc sulfide to render it fluorescentserved as a counter to detect alpha particles. As each alpha particle struck the fluorescent screen, it would produce a burst of light called a scintillation, which was visible through a viewing microscope attached to the back of the screen. The screen itself was movable, allowing Rutherford and his associates to determine whether or not any alpha particles were being deflected by the gold foil.

Problems with the Rutherford Model

In the years after Rutherford discovered the nucleus, chemists and particle physicists discovered that electron behavior was much more complicated than depicted in the Rutherford model. Electrons did not travel in set paths, their speeds were inconsistent, and their location around the nucleus could change based on how much energy they had. It was no longer accurate to depict electrons as traveling in straight paths. Instead, physicists began to represent them by an electron cloud that could suggest where electrons might be at any given time. The electron cloud model is the current model of the atom.

The Bohr Model has an atom consisting of a small, positively-charged nucleus orbited by negatively-charged electrons. Here's a closer look at the Bohr Model, which is sometimes called the Rutherford-Bohr Model.

OVERVIEW OF THE BOHR MODEL

Niels Bohr proposed the Bohr Model of the Atom in 1915. Because the Bohr Model is a modification of the earlier Rutherford Model, some people call Bohr's Model the Rutherford-Bohr Model.

The modern model of the atom is based on quantum mechanics. The Bohr Model contains some errors, but it is important because it describes most of the accepted features of atomic theory without all of the high-level math of the modern version. Unlike earlier models, the Bohr Model explains the Rydberg formula for the spectral emission lines of atomic hydrogen. The Bohr Model is a planetary model in which the negatively-charged electrons orbit a small, positively-charged nucleus similar to the planets orbiting the Sun (except that the orbits are not planar). The gravitational force of the solar system is mathematically akin to the Coulomb (electrical) force between the positively-charged nucleus and the negatively-charged electrons.

MAIN POINTS OF THE BOHR MODEL

- Electrons orbit the nucleus in orbits that have a set size and energy.
- The energy of the orbit is related to its size. The lowest energy is found in the smallest orbit.
- Radiation is absorbed or emitted when an electron moves from one orbit to another
- •

BOHR MODEL OF HYDROGEN

The simplest example of the Bohr Model is for the hydrogen atom (Z = 1) or for a hydrogenlike ion (Z > 1), in which a negatively-charged electron orbits a small positively-charged nucleus. Electromagnetic energy will be absorbed or emitted if an electron moves from one orbit to another.

Only certain electron orbits are permitted. The radius of the possible orbits increases as n^2 , where n is the principal quantum number. The $3 \rightarrow 2$ transition produces the first line of the Balmer series. For hydrogen (Z = 1) this produces a photon having wavelength 656 nm (red light).

PROBLEMS WITH THE BOHR MODEL

- It violates the Heisenberg Uncertainty Principle because it considers electrons to have both a known radius and orbit.
- The Bohr Model provides an incorrect value for the ground state orbital angular momentum.
- It makes poor predictions regarding the spectra of larger atoms.
- It does not predict the relative intensities of spectral lines.
- The Bohr Model does not explain fine structure and hyperfine structure in spectral lines.
- It does not explain the Zeeman Effect.
- •

Excitation and ionization of an atom

According to Bohr's theory, there are certain discrete orbits permitted for the motion of the electron. Electron can revolve in these orbits without radiating energy. An atom is said to be in the ground state, when its energy is least. Before an atom can emit spectral radiation, the electron in it has to be raised to a higher orbit. This process is known as the excitation of the atom. The energy required to raise an atom from its normal state into an excited state is called *excitation potential energy* of the atom. For example, the energy required to transfer the electron in hydrogen atom from the ground state to the first excited state = (13.6-3.4) = 10.2eV. The energy required to raise it to the second excited state = (13.6 - 1.51) = 12.09 eV. The potentials corresponding to these energies are called as the excitation potentials.

The ionisation potential is that accelerating potential which makes the impinging electron acquire sufficient energy to knock out an electron from the atom and thereby ionise the atom. For hydrogen atom, the energy required to remove an electron from first orbit to its outermost orbit($n=\infty$) 13.6-0=13.6eV. This energy is known as the ionization potential energy for hydrogen atom. 13.6 V is the ionisation potential of hydrogen atom.

The excitation potential and ionization potential are called as the critical potentials of the atom. The *critical potential* of an atom, is defined as the minimum potential required to excite a free neutral atom from its ground state to higher state.

X-ray spectra - continuous and characteristic X-ray spectra.

The spectrum from an X-ray tube contains two distinct parts :

(i) Continuous X-ray spectra

It consists of radiations of all possible wavelengths, from a certain lower limit to higher values continuously, as in the case of visible light.

Origin - Continuous X-ray spectra

X-rays are produced, when high velocity electrons strike the target material of high atomic number. It has also been mentioned in the production of X-rays, that most of the energy of the electrons goes into the heating of the target material.



A few fast moving electrons penetrate deep into the interior of the atoms of the target material and are attracted towards the nuclei by the attractive forces of their nuclei. Due to these forces, the electrons get deflected from their original path. As a result of this, the electrons are decelerated, and hence energy of the electron decreases continuously. This loss of energy during retardation is given off in the form of X-rays of continuously varying wavelength. The X - rays consist of continuous range of frequencies upto a maximum frequency λ_{max} or minimum wave length λ_{min} . This is called as continuous X - rays. The minimum wave length depends on the anode voltage. If V is the potential difference between the anode and the cathode

$$eV = hv_{max} = hc / \lambda_{min}$$

The minimum wavelength of the given radiation is,

$$\lambda_{\min} = hc / eV$$

where h is Planck's constant, c is the velocity of light and e, the charge of the electron. Substituting the known values in the above equation.

$$\lambda_{min} = 12400/V \; A^0$$

For the given operating voltage, the minimum wave length is same for all metals.

(ii) Characteristic X-ray spectra

It consists of definite, well defined wavelengths superimposed on the continuous spectrum. These spectral lines generally occur in the form of small groups and are characteristic of the material of the target.



Origin - Characteristic X-ray spectra

Few of the fast moving electrons having velocity of about $(1/10)^{\text{th}}$ of the velocity of light may penetrate the surface atoms of the target materials and knock out the tightly bound electrons even from the inner most shells (like K, L shells) of the atom. Fig shows the case, when the fast moving electrons knock off one electron from K-Shell and the vacancy is filled by the nearby electron from the L shell. During this transition, the energy difference is radiated in the form of X-rays of very small wave length. This corresponds to K_{α} - line of the series. The frequency v_1 of this line is given by the relation ($E_K - E_L$) = h v_1 . Suppose, the electron from M shell jumps to the K shell, it gives out K_{β} line and so on. If an electron jumps from the M-Shell to the vacant state in L-Shell, it contributes L_{β} and so on. The frequency of radiation depends upon the target material. The X-ray spectra consists of sharp lines and is the characteristic of target material. Hence this spectra is known as characteristic spectra.

Sommerfeld atom model and its Drawbacks



In order to explain the observed fine structure of spectral lines, Sommerfeld introduced two main modifications in Bohr's theory.

Sommerfeld atom model

In order to explain the observed fine structure of spectral lines, Sommerfeld introduced two main modifications in Bohr's theory.

(i) According to Sommerfeld, the path of an electron around the nucleus, in general, is an ellipse with the nucleus at one of its foci.

(ii) The velocity of the electron moving in an elliptical orbit varies at different parts of the orbit. This causes the relativistic variation in the mass of the moving electron.

Now, when elliptical orbits are permitted, one has to deal with two variable quantities.

(i) The varying distance of the electron from the nucleus (r).

(ii) The varying angular position of the electron with respect to the nucleus i.e the azimuthal



angle ϕ (Fig).

To deal with these two variables, two quantum numbers are introduced

(i) The principal quantum number n of Bohr's theory, which determines the energy of the electrons, and

(ii) a new quantum number called orbital (or azimuthal) quantum number (l) which has been introduced to characterize the angular momentum in an orbit i.e., it determines the orbital angular momentum of the electron. Its values vary from zero to (n-1) in steps of unity. This orbital quantum number (l) is useful in finding the possible elliptical orbits. The possible elliptical orbits are such that

b/a = l+1/n

where a and b are semi-major and semi-minor axes respectively of the ellipse.

According to Sommerfeld's model, for any principal quantum number n, there are n possible orbits of varying eccentricities called sub-orbits or sub-shells. Out of n subshells, one is circular and the remaining (i.e., n-1) are elliptical in shape.

These possible sub-orbits possess slightly different energies because of the relativistic variation of the electron mass.

Consider the first energy level (n=1). When n = 1, l = 0 i.e., in this energy level, there is only one orbit or sub-shell for the electron. Also, when a = b, the two axes of the ellipse are equal. As a result of this, the orbit corresponding to n=1 is circular. This subshell is designated as *s* sub-shell. Since, this sub-shell belongs to n=1, it is designated as 1s (Fig a).



Similarly, for the second energy level n=2, there are two permissible sub-shells for the electrons. For n=2, l can take two values, 0 and 1.

When n = 2, l = 0.

b/a= 0+1/2 =1/2

or

b=a/2

This subshell corresponding to l = 0 is elliptical in shape and is designated as 2s.

when n = 2, l = 1.

b/a= 1+1/2 =2/2 =1

or

b=a

This sub-shell corresponding to l = 1 is circular in shape and is designated as 2p (Fig b).

For n = 3, *l* has three values 0, 1 and 2, i.e. there are three permissible sub-shells for the electrons.

when n = 3, l = 0. b/a = (0+1)/3 = 1/3 = 1 or b = a/3when n = 3, l = 1. b/a = (1+1)/3 = 2/3 = 1 or b = 2a/3and when n = 3, l = 2. b/a = (2+1)/3 = 3/3 = 1 or b = aThe sub-shells corresponding to l = 0, 1 and

The sub-shells corresponding to l = 0, 1 and 2 are designated as 3s, 3p and 3d respectively. The circular shell is designated as 3d and the other two are elliptical in shape (Fig c).

It is common practice to assign letters to *l*-values as given below:

Orbital quantum number 1	:	0	1	2	3	4
electron state :		S	р	d	f	g

Hence, electrons in the l = 0, 1, 2, 3 states are said to be in the s, p, d, f states.

Fine structure of spectral line

Based on Sommerfeld atom model, the total energy of an electron in the elliptical orbit can be shown as,

 $En = (-me^4Z^2) / (8\epsilon_0^2h^2n^2)$

This expression is the same as that obtained by Bohr. Thus the introduction of elliptical orbits gives no new energy levels and hence no new transition. In this way, the attempt of Sommerfeld to explain the fine structure of spectral lines failed. But soon, on the basis of variation of mass of electron with velocity, Sommerfeld could find the solution for the problem of the fine structure of the spectral lines.

According to Sommerfeld, the velocity of the electron is maximum when the electron is nearest to the nucleus and minimum when it is farthest from the nucleus, since the orbit of the electron is elliptical. This implies that the effective mass of the electron will be different at different parts of its orbit. Taking into account the relativistic variation of the mass of the electron, Sommerfeld modified his theory and showed that the path of electron is not a simple ellipse but a precessing ellipse called a rosette (Fig).



Based on this idea, Sommerfeld successfully explained the fine structure of spectral lines of hydrogen atom.

Drawbacks

- (i) Though Sommerfeld's modification gave a theoretical background of the fine structure of spectral lines of hydrogen, it could not predict the correct number of observed fine structure of these lines.
- (ii) It could not explain the distribution and arrangement of electrons in atoms.
- (iii) Sommerfeld's model was unable to explain the spectra of alkali metals such as sodium, potassium etc.
- (iv) It could not explain Zeeman and Stark effect.
- (v) This model does not give any explanation for the intensities of the spectral lines.

The vector atom model

The vector atom model basically deals with the *total angular momentum* of an atom, which is results of the combination of orbital and spin angular momenta. The two fundamental features of the vector atom model are (i) space quantization of orbits and (ii) spinning electron hypothesis.

Space Quantization

The angular momentum is a vector quantity, hence its direction must be specified to describe it completely. To specify the orientation or direction of an orbit, a reference is required. The direction of the magnetic field applied to the atom is chosen as the reference line.

Unit –II

Atom Models

The rotating electron about the nucleus forms a current loop which has a magnetic moment $\mu = IA$, where I is the current in the loop and A is the area vector. The energy of loop-field system is given by $U = -\mu B = -|\mu| |B| \cos\theta$, where θ is the angle between the magnetic moment θ and magnetic field B. As such classically any energy value between $-\mu B$ to $+\mu B$ is possible for the loop.

An electron orbiting around the nucleus in an atom possess angular momentum L which interacts with external applied magnetic field B. According to quantum theory, there are fixed directions of magnetic moment 1.1. of magnetic dipole (formed by closed loop motion of electron about nucleus) with respect to the magnetic field B. The magnetic moment μ and angular momentum L can be related as

$$\mu = \left(\frac{e}{2m_e}\right)L$$

This relationship is true from both classical and quantum mechanical point of view. Since discrete directions of μ are allowed, as such the direction of L will also be quantized in space. Here, the quantization refers the projection of L along the Z-direction (L₂) which can have discrete values only. The orbital magnetic quantum number m_l gives the direction of L and tells the possible components of L in the Z-direction (the field direction). The phenomenon of quantization of L in the direction of magnetic field B is commonly known as **space quantization.** The direction of B is along the Z axis. As such the component of L along Z-direction is given as $L_Z = m_l$, h, the m_l can table the values from -l to +l including zero.

The above discussed space quantization of orbits and possible components of L can be understood with the following example.

Let us calculate the allowed projections of L for 1 = 2. The L can be visualized as a vector lying on the surface of a cone (see Figure a).



The possible values of m_l for l = 2 can be -2, -1, 0, 1, 2 hence $L_Z = m_l h = -2h - h$, 0, h, 2h. Figure (b) and (c) show space quantization of L for l=2.

Spin Quantization

Goudsmit and Uhlenbeck in 1925 proposed that electron 'spins' about an axis through its centre of mass and further it has both angular momentum and a magnetic moment. The spin of electron is analogous to the planetary motion about the Sun in our solar system. Quantum mechanical treatment has demonstrated that the spin of electron should be quantized. As such a new quantum number 5 has been introduced. The spin angular momentum S is related with spin quantum number s as

$$s = \sqrt{s(s+1)h} \qquad \dots (1)$$

The spin can be either clockwise or anticlockwise as such s can have two values *i.e.*, $\pm \frac{1}{2}$

$$S = \sqrt{\frac{1}{2}(\frac{1}{2}+1)} h = \frac{\sqrt{3}}{2} h$$

Component of S along the direction of magnetic field is governed by quantum, number m_s as

$$S_z = m_s h$$
 ... (2)

where m_s is the spin magnetic quantum number. The m_s can take (2s + 1) values.

```
as such m_s can be 2 \times \frac{1}{2} + 1 = 2 values m_s = \pm \frac{1}{2}
Hence S_z = \pm \frac{1}{2}h
```

We have seen that the orbital and spin motions of an electron are quantized in magnitude as well as in direction. These motions are represented by quantized vectors, as such the atomic model is termed as *vector atom model*.

Unit –II

Atom Models

The Quantum Numbers and Spectroscopic Notations

The Bohr-Sommerfeld atomic theory uses four quantum numbers which are (i) Principal quantum number (n) (*ii*) Orbital quantum number (1) (*iii*) Spin quantum number (s) and (iv). Total angular momentum quantum number (j). In addition to these, three other quantum numbers have been introduced in vector atom model which are (i) Magnetic orbital quantum number (m_i) , (*ii*) Magnetic spin quantum number (m_s) and (*iii*) Magnetic total an momentum quantum number (m_j) . The general description and possible values of these quantum numbers is given below.

Principal Quantum Number (n): This quantum number represents the serial number of the atomic shells starting from the innermost. The 'n' can have only positive integral values excluding zero.

n = 1,2,3,4

Orbital Quantum Number (I): The Orbital quantum number l' can have the values from a to (n - 1), where n' is the principal quantum number.

For example, if n = 3, then l = 0, 1, 2. Conventionally we call 1 = 0 s electron l = 1 p electron l = 2 d electron

l = 3 f electron

I

Spin Quantum Number (s): Spin quantum number s has only one value

i.e. $\frac{1}{2} \Rightarrow s = \frac{1}{2}$

Total Angular Momentum Quantum Number (j): The total angular momentum quantum number *j* is the sum of orbital angular momentum 'l' and spin quantum number's'. As such *j* can have $l \pm s$ or $l \pm \frac{1}{2}$ values.

Magnetic Orbital Quantum Number ' m_l **'**: As discussed previously in article 10.3.1, the magnetic orbital quantum number m_l can have 2l + 1 values. For example, I = 2, m_l can have -2, -1, 0, 1, 2 *i.e.*, total 5 values.

Magnetic Spin Quantum Number 'm_s': The magnetic spin quantum number take (2s + 1) values. We know that $s = \frac{1}{2}$ and hence m_s , can take $(2 \times \frac{1}{2} + 1) = 2$ in total. The values of m_s ' therefore are -s and +s or $-\frac{1}{2}$ and $+\frac{1}{2}$.

Magnetic Total Angular Momentum Quantum Number m_j : The total momentum J of an atom is a vector quantity and is the vector sum of orbital momentum L and spin angular momentum S *i.e.*, J = L + S. We define quantum number m_j which is known as the magnetic total angular mom quantum number and specify the orientation of J in space with respect to Z-axis.

According to quantum mechanics

$$J = \sqrt{J(J+1)} h$$
 ... (1)
and $J_s = m_j h$

The possible values of m_j are 2j + 1 *i.e.*, m_j can take values from -j to +j including zero in integral steps.

Now $J_z = L_z \pm S_z$

which implies that $m_j = m_l \pm m_s$. Now m_l is an integer and m_s is $\pm \frac{1}{2}$ as such m_j will have the half integral values only. The m_j , m_l and m_s can have the maximum value j, l and s respectively.

Fine structure of spectral lines

Recall that the energy levels of a hydrogen atom are given by

 $E_n = -13.6/n^2$

This will give rise to a series of spectral lines at a set of allowed transition frequencies when the electron in the atom is excited.

Unit –II

Atom Models

W_{ni} - $W_{nf} = E_{ni}$ - E_{nf}/h

Here, ni and nf represent the initial energy level to which the electron is excited and represents the final level to which it decays. In the decay process, electromagnetic radiation is emitted which can be detected in a spectrometer.

If one examines, the Lyman spectrum, for example, which corresponds to nf = 1 and produces spectral lines in the ultraviolet part of the electromagnetic spectrum, one finds that the individual lines are actually several lines of nearly identical frequency. For example, the 2p to 1s transition is actually a doublet, with the two components being separated by ~10⁻⁴ eV which is also on the order of a few tens of wavenumbers, which is about 10⁵ times smaller than the splitting predicted from the formula, i.e., 10.2 eV. Clearly, the simple theory based on the above formulae is not sufficient to explain the multiplicity of lines actually observed.

- o Fine structure of H-atom is due to spin-orbit interaction:
- o If *L* is parallel to S => J is a maximum => high energy configuration.
- o Angular momenta are described in terms of quantum numbers, s, l and j:

Possible questions (Part B- 8 marks)

- 1. Describe in detail about Thomson atom model and Rutherford atom model.
- 2. Explain in detail about Sommerfeld relativistic atom model and drawback of it.
- 3. Describe the vector model of the atom and explain the different quantum numbers associated with it.
- 4. Prove that the energy of an electron for hydrogen atom in the n^{th} is $E_n = -me^4/8\epsilon_0^2 n^2 h^2$
- 5. How the excitation and ionization of atoms occurs according to Bohr's theory.
- 6. Explain the electronic structure of atoms and fine structure of spectral lines
- 7. Describe the origin of continuous and characteristic x –ray.
- 8. What are the drawbacks of sommerfeld atom model and how the vector atom model emerges?
- 9. Derive the equation for the radius of orbit and energy of orbit from Bohr's theory.

KARPAGAM UNIVERSITY, COIMBATORE-21 DEPARTMENT OF PHYSICS CLASS:III BSC PHYSICS Atomic and Molecular Physics (15PHU501) MULTER CHOICE OUESTIONS

ACADEMY OF HIGHER

EDUCATION

Batch 2015

MULIPLE CHOICE QUESTIONS					
QUESTIONS	opt1	opt2	opt3	opt4	answer
unit II					
The concept of spinning of electron was introduced by Uhlenbeck and	J.J Thomson	Sommerfeld	Gouldsmit	Bohr	Gouldsmit
The vector atom model is an extension of the	Rutherford model	Bohr model	Sommerfeld atom model	Rutherford-Bohr Sommerfeld atom model	Rutherford-Bohr Sommerfeld atom model
The features that characterise the vector atom model are the	spatial quantisation	spinning electron	both a and b	none of the above	both a and b
The magnetic moment of the atom will be the resultant of	orbital magnetic moment	spin magnetic moment	both a and b	none of these	both a and b
An orbital quantum number l, may take any integral value	0	n	between 0 to (n-1)	none of the above	between 0 to (n-1)
A total quantum number n, can take	even values	odd values	any integral values 1,2,3,etc.		any integral values 1,2,3,etc.
The magnitude of a spin quantum number s, is	always 1/2	1	0	-1	always 1/2
The different vectors of the electrons may combine to give the vectors representing the	electrons	atoms	molecules	compounds	atoms
Pauli's Exclusion principle states that every completely defined quantum state in an atom can be occupied by	only one electron	two electrons	no electrons	infinite electrons	only one electron
A system is most stable when its energy is	minimum	maximum	minimum or maximum	not minimum	minimum
Hyperfine structure occurs as a result of interaction	nuclear spin and electron	nuclear spin and unpaired	electron spin and paired	nuclear spin and nuclear	nuclear spin and unpaired
between	spin	electron	electron	spin	electron
Complete removal of an electron from an atom is	Ionisation	Dissociation	Predissociation	All the above	Ionisation
How many possible orientations do spin 1/2 nuclei have	1				
when they are located in an applied magnetic field	1	2	. J	, 4	F 1
The physical and chemical properties of elements are determined by	the number of electrons	arrangement of the electrons in the outermost shell	both a and b	none of these	both a and b
Which is called normal coupling	J-J coupling	L-S coupling	J-S coupling	none of the above	L-S coupling
For an atom containing four electron system S is	1/2	3/2 or 1/2	2,1,0	0,1,2,3	2,1,0
For an atom containing two electron system S is	1/2	3/2 or 1/2	2,1,0	1 or 0	1 or 0
For an atom containing a single electron system S is	1/2	3/2 or 1/2	2,1,0	0,1,2,3	1/2
If L=0, J can have	two values	two values	three values	zero	two values
In the one electron system, the state of the atom as a whole is identical with the state of the	electron	positron	neutron	molecule	electron
The Pauli's exclusion principle finds its chief use in the	elucidation of electronic structure	atomic spectra	both a and b	elucidation of molecular structure	both a and b
The number of electrons in the normal					
atomas one passes from light to heavy	increases steadily	decreases steadily	constant	increases or decreases	increases steadily
The table of elements withhorizontal rows called periods	seven	eight	nine	none of these	seven
The table of elements withvertical columns called groups	seven	eight	nine	none of these	eight

The maximum number of electrons in a sub-shell with orbital quantum number 1 is (21 + 1) (21 - 1) 2(21 + 1) 2(21 - 1) 2(21 + 1) The total energy of an electron in an atom zero less than zero more than zero infinity less than zero The number of spectral lines from a single atom of zero one two four one	+ 1) han zero 14
orbital quantum number l is $(2l+1)$ $(2l-1)$ $2(2l+1)$ $2(2l-1)$ $2(2l+1)$ The total energy of an electron in an atomzeroless than zeromore than zeroinfinityless thaThe number of spectral lines from a single atom ofzeroonetwofourone	+ 1) han zero 14
The total energy of an electron in an atom zero less than zero more than zero infinity less than The number of spectral lines from a single atom of zero one two four one	han zero 14
The number of spectral lines from a single atom of zero one two four one	14
I I I I I I I I I I I I I I I I I I I	14
hydrogen is	14
The fourth sub-shell of an atom can have a maximum of 2 10 6 14	at caries
Series that lies in infrared region of electromagnetic spectrum is bracket series bracket series both a and b bracket	let series
For an electron to be confined to a nucleus its speed relative equal less greater equal to infinity greater	er
Atomic spectra band spectra both a and b line spectra	spectra
According to bohr's atomic model angular momentum of	poola
electron in n^{th} orbit is equal to an integral multiple of $h/2\pi$ $h/2\pi$ $h/2\pi$	τ
Electron in atom are held in atom due to coulombs force nuclear force atomic force both a and b coulomb	ombs force
Velocity of electron in second bohr orbit as compared to	11105 10100
equal one half 2 times one fourth one half	ıalf
Bohr's atomic model is based upon Einstein's relativistic theory classical theory planks quantum theory both b and c both b a	b and c
With increasing quantum number energy difference	
between adjacent levels in atoms accreases increases remain constant zero decreases	ases
Spin angular momentum of nucleus varies from nucleus to nucleus nucleus varies from nu	s from nucleus to
The vaue of Bohr Magneton is 9.253×10^{-24} 9.253×10^{-14} 9.253×10^{-20} 0.9253×10^{-20}	3×10 ⁻²⁴
The spectral terms corresponding to L=1 and S=1/2 are $^{2}P_{1/2}$ and $^{2}P_{3/2}$ $^{2}P_{1/2}$ and $^{1}P_{3/2}$ $^{1}P_{1/2}$ and $^{2}P_{3/2}$ none of these $^{2}P_{1/2}$ and $^{2}P_{3/2}$	and ² P _{3/2}
Spectral lines arise due to transitions of thefrom electron atom molecule nucleus atom	
Un the stems belonging to the one electron system all the	
states except the ground one are triplets singlet doublets doublets doublets doublets	lets
Electronic configuration of the normal magnesium atom is represented by $1s^22s^22p^63s^2$ $1s^22s^22p^6$ $1s^22s^22p^3$ $1s^22s^22p^3$ $1s^22s^22p^3$	$s^2 2p^6 3s^2$
Electronic configuration of the normal sodium atom is represented by $1s^22s^22p^63s$ $1s^22s^22p^6$ $1s^22s^22p$ $1s^22s^22p^3$ $1s^22s^22p^3$	s ² 2p ⁶ 3s
The symbolic representation of aluminium atom is $1s^22s^22p^63s^2$ $1s^22s^22p^6$ $1s^22s^22p$ $1s^22s^22p$ $1s^22s^22p^63s^23p$ $1s^22s^22p^63s^23p^2$	$s^{2}2p^{6}3s^{2}3p$
magnetic moment due to electron spin is one Bohr Magneton two Bohr Magneton orbital magnetic moment none of these one Boh	30hr Magneton
short radio waves and visible light and ultraviolet gamma rays and ultraviolet short radio waves and long gamma	na rays and ultraviolet
visible light region rays radiowaves rays	
To produce hard X-rays in Coolidge tube we should current in filament potential difference across potential differ	itial difference across
increase : the filament the filament cathode and anticathode cathode cathode	de and anticathode
The maximum frequency of X-rays is determined by : current in filament current from high tension cathode current from high tension current from	itial difference across ode and anticathode
The characteristic of the target element that determines the	amia numbar
frequency of characteristic X-rays is Instantiation Instan	Jine number
Moseley's law relates the frequencies of X-rays with the following characteristic of the target element: its density its atomic weight its atomic number its atomic number its atomic planes its atomic planes	omic number
Ionisation in a gas cannot be produced by : heat X-rays radioactive emanations gold leaf electroscope gold lea	leaf electroscope

In obtaining an X-ray photograph of our hand we use the principle of :	shadow photography	image formation by an optical system	photoelectric effect	ionisation	shadow photography
X-rays passing through a strong uniform magnetic field	get deflected in the direction of the field	get deflected in the direction opposite to that of the field	get deflected in the direction perpendicular to that of the field	do not get deflected at all	do not get deflected at all
A metal block is exposed to beams of X-rays of different wavelengths, X-rays of which wavelength penetrate most:	1Å	2Å	4Å	3Å	1Å
The X-ray beam coming from an X-ray tube will be:	monochromatic	having all wavelengths smaller than a certain maximum wavelength	having all wavelengths larger than a certain minimum wavelength	having all wavelengths lying between a minimum and a maximum wavelength	having all wavelengths larger than a certain minimum wavelength
The minimum wavelength of the continuous X-ray radiation is :	Ve/h	ch/Ve	Ve/hc	ec/Vh	ch/Ve
X-rays are produced :	during electric discharge at low pressure	during nuclear explosions	when cathode rays are reflected from the target	when electrons from higher energy state come back to lower energy state	when electrons from higher energy state come back to lower energy state
In an X-ray tube, the intensity of the emitted X-ray beam is increased by :	increasing the filament current	decreasing the filament current	increasing the target potential	decreasing the target potential	increasing the filament current
The Compton effect in X-rays proves that	X-rays have corpuscular (particle) nature	X-rays have wave nature	X-rays have quantum nature	electrons have wave nature	X-rays have quantum nature
In Compton effect the electron that takes part is	free	bound	may be free or bound	emitted from nucleus by decay of neutron	bound
when high speed electron hit a target of high atomic number, the efficiency for the production of X-rays is :	100%	99%	50%	even less than 1%	even less than 1%
X-ray is:	phenomenon of conversion of K.E. into radiant energy	conservation of momentum	conversion of mass into energy	principle of conservation of charge	phenomenon of conversion of K.E. into radiant energy
Which of them are atomic models? i. Thomson's plum puddling model ii. Rutherford's nuclear model iii. Bohr's model iv. Sommerfeld's model	i & ii	i, ii & iii	a. ii, iii & iv	All of these	All of these
The maximum number of. electrons that can be	14	6	2	8	6
Principle Quantum number describes?	Shape of orbital	Size of orbital	Orientation of an orbital	Spin of orbital	Size of orbital
Quantum number value for 2p sub shell are?	n = 1 L = 1	n = 2 I = 1	n = 1 I = 0	n = 2 I = 0	n = 2 I = 1
The orbits having same energy are called	Degenerated orbitals	Hybrid orbitals	P-Orbitals	Valence orbitals	Degenerated orbitals
According to Bohr's Model, the radius of the second orbit is	2A°	2.11 X 10-11m	2.11 X 10-12 m	2.1 A°	2.1 A°
The shape of an orbital is governed by	Principle quantum number	Spin quantum number	Magnetic quantum number	Azimuthal quantum number	Azimuthal quantum number
The radius of second Bohr orbit is	0.529 X 2 nm	0.53 X 20 nm	0.53/4 nm	0.053 nm	0.529 X 2 nm
Balmer series lie in the region of spectrum	Ultraviolet	Visible	Infar-infrared	Infrared	Visible
The value of Bohr radius for first orbit of H-atom is	0.529 X 10-12 cm	0.529 X 10-6 cm	0.529 X 10-8 cm	0.529 x 10-10 cm	0.529 X 10-8 cm
Lyman series of spectral lines appear in the portion of spectrum.	Ultraviolet	Visible	Infar-infrared	Infrared	Ultraviolet
When the azimuthal quantum number (L) is 3, than m can have	1	2	7	3	7
The size of the shell Is determined by quantum number	Magnetic quantum number	Principle quantum number	Spin quantum number.	Azimuthal quantum number	Principle quantum number

	the spectrum of hydrogen	the spectrum o hydrogen		spectrum of an atom or ion	spectrum of an atom or ion
Bohr model can explain:	atom only	molecule	the solar spectrum	containing one electron	containing one electron
Which of the following statements does not form part of Bohr's model of the hydrogen atom	Electrons revolve in different orbits around the nucleus	Energy of the electrons in the orbit is quantized	The electron in the orbit nearest the nucleus has the lowest energy	The position and velocity of the electrons in the orbit cannot be determined simultaneously	The position and velocity of the electrons in the orbit cannot be determined simultaneously
Energy of orbit	Increases as we move away from nucleus	Decreases as we move away from nucleus	Remains same as we move away from nucleus	None of these	Increases as we move away from nucleus
In hydrogen spectrum which one of the following series lies in the ultraviolet region?	Balmer series	Balmer series	Bracket series	Lymann series	Lymann series
Which one of following postulate is in accordance with the	continuous spectra for		either continuous nor		continuous spectra for
Rutherfords model?	atoms	discrete spectra for atoms	discrete	no spectrum	atoms
Total number of series in hydrogen spectrum is	three	four	five	six	five
The characteristic X-rays spectrum is due to	The illumination of the			The absorption of ?	
	target metal by ultra-violet	The bombardment of the	The bombardment of target	radiation by the target	The bombardment of target
	radiation	target by protons.	by electrons.	metal.	by electrons.
X-rays are diffracted by a crystal but not by a diffraction grating because	The ions in a crystal are well arranged	The lines in a diffraction grating cannot reflect X- rays	The penetration power of X- rays is high in a diffraction grating.	The wavelengths of X-rays are of the same order of magnitude as the separation between atoms in a crystal	The wavelengths of X-rays are of the same order of magnitude as the separation between atoms in a crystal
According to which one of following law the density of		5	5 6	all of above laws contradict	
atom is uniform	J.J.Thomson model	Rutherfords model	Bohrs model	the statement	J.J.Thomson model
Bohr's model based on	potential of high energy	line spectra	target element	infrared region	potential of high energy
The energy required to completely remove an electron from the first Bohr orbit is	ionization energy	potential energy	kinetic energy	infrared energy	ionization energy
X rays consist of series of specific wavelength or frequencies are called	grating	contineous x ray	characteristic x ray	high energy x ray	characteristic x ray
Bohr angular momentum of an electron in one of its allowed orbit is given by	Mv=nh/2pi	M=nh/2pi	Mv=nh/2	Mvr=nh/2pi	Mvr=nh/2pi
one or more electron is completely removed from atom then the atom is called	ionized	radiated	excited	stabilized	ionized
The energy of characteristic x ray depends on	target material	anode	cathode	none of above	target material
The magnetude of ionization energy of hydrogen atom is	13ev	(-13.6ev)	15ev	19ev	(-13.6ev)
The essential features of the vector atom model are	spatial quantisation	spinning	both are correct	D _{3/2} ->P _{1/2}	D _{3/2} ->P _{1/2}

Unit: III Radioactivity – origin of radiation from natural radioelements – alpha disintegration – wave mechanical theory – Beta disintegration – internal conversion of gamma rays – gamma ray emission – origin of gamma rays

Radioactivity and origin of radiation from radioactive elements

In 1896 Henri Becquerel was using naturally fluorescent minerals to study the properties of x-rays, which had been discovered in 1895 by Wilhelm Roentgen. He exposed potassium uranyl sulfate to sunlight and then placed it on photographic plates wrapped in black paper, believing that the uranium absorbed the sun's energy and then emitted it as x-rays. This hypothesis was disproved on the 26th-27th of February, when his experiment "failed" because it was overcast in Paris. For some reason, Becquerel decided to develop his photographic plates anyway. To his surprise, the images were strong and clear, proving that the uranium emitted radiation without an external source of energy such as the sun. Becquerel had discovered radioactivity.

Becquerel used an apparatus similar to that displayed below to show that the radiation he discovered could not be x-rays. X-rays are neutral and cannot be bent in a magnetic field. The new radiation was bent by the magnetic field so that the radiation must be charged and different than x-rays. When different radioactive substances were put in the magnetic field, they deflected in different directions or not at all, showing that there were three classes of radioactivity: negative, positive, and electrically neutral.



The term radioactivity was actually coined by Marie Curie, who together with her husband Pierre, began investigating the phenomenon recently discovered by Becquerel. The Curies extracted uranium from ore and to their surprise, found that the leftover ore showed more activity than the pure uranium. They concluded that the ore contained other radioactive elements. This led to the discoveries of the elements polonium and radium. It took four more years of processing tons of ore to isolate enough of each element to determine their chemical properties.

Ernest Rutherford, who did many experiments studying the properties of radioactive decay, named these alpha, beta, and gamma particles, and classified them by their ability to penetrate matter. Rutherford used an apparatus similar to that depicted in Fig. 3-7. When the air from the chamber was removed, the alpha source made a spot on the photographic plate. When air was added, the spot disappeared. Thus, only a few centimeters of air were enough to stop the alpha radiation.

Because alpha particles carry more electric charge, are more massive, and move slowly compared to beta and gamma particles, they interact much more easily with matter. Beta particles are much less massive and move faster, but are still electrically charged. A sheet of aluminum one millimeter thick or several meters of air will stop these electrons and positrons. Because gamma rays carry no electric charge, they can penetrate large distances through materials before interacting-several centimeters of lead or a meter of concrete is needed to stop most gamma rays.

Alpha disintegration

Alpha decay or α -decay is a type of radioactive decay in which an atomic nucleus emits an alpha particle (helium nucleus) and thereby transforms or 'decays' into an atom with a mass number that is reduced by four and an atomic number that is reduced by two. An alpha particle is identical to the nucleus of a helium-4 atom, which consists of two protons and two neutrons. It has a charge of +2e and a mass of 4u. For example, uranium-238 decays to form thorium-234. Alpha particles have a charge +2, but as a nuclear equation describes a nuclear reaction without considering the electrons -aconvention that does not imply that the nuclei necessarily occur in neutral atoms – the charge is not usually shown.

Alpha decay typically occurs in the heaviest nuclides. Theoretically, it can occur only in nuclei somewhat heavier than nickel (element 28), where the overall binding energy per nucleon is no longer a minimum and the nuclides are therefore unstable toward spontaneous fission-type processes. In practice, this mode of decay has only been observed in nuclides considerably heavier than nickel, with the lightest known alpha emitters being the lightest isotopes (mass numbers 106–110) of tellurium (element 52). Exceptionally, however, beryllium-8 decays to two alpha particles.

Alpha decay is by far the most common form of cluster decay, where the parent atom ejects a defined daughter collection of nucleons, leaving another defined product behind. It is the most common form because of the combined extremely high binding energy and relatively small mass of the alpha particle. Like other cluster decays, alpha decay is fundamentally a quantum tunneling process. Unlike beta decay, it is governed by the interplay between both the nuclear force and the electromagnetic force.

Alpha particles have a typical kinetic energy of 5 MeV (or $\approx 0.13\%$ of their total energy, 110 TJ/kg) and have a speed of about 15,000,000 m/s, or 5% of the speed of light. There is surprisingly small variation around this energy, due to the heavy dependence of the half-life of this process on the energy produced (see equations in the Geiger-Nuttall law). Because of their relatively large mass, +2 electric charge and relatively low velocity, alpha particles are very likely to interact with other atoms and lose their energy, and their forward motion can be stopped by a few centimeters of air. Approximately 99% of the helium produced on Earth is the result of alpha decay of underground the deposits of minerals containing uranium or thorium. The helium is brought to the surface as a byproduct of natural gas production.

Alpha particles were first described in the investigations of radioactivity by Ernest Rutherford in 1899, and by 1907 they were identified as He^{2+} ions.

By 1928, George Gamow had solved the theory of alpha decay via tunneling. The alpha particle is trapped in a potential well by the nucleus. Classically, it is forbidden to escape, but according to the (then) newly discovered principles of quantum mechanics, it has a tiny (but non-zero) probability of "tunneling" through the barrier and appearing on the other side to escape the nucleus. Gamow solved a model potential for the nucleus and derived, from first principles, a relationship between the half-life of the decay, and the energy of the emission, which had been previously discovered empirically, and was known as the Geiger–Nuttall law.

The nuclear force holding an atomic nucleus together is very strong, in general much stronger than the repulsive electromagnetic forcesbetween the protons. However, the nuclear force is also short range, dropping quickly in strength beyond about 1 femtometre, while the electromagnetic force has unlimited range. The strength of the attractive nuclear force keeping a nucleus together is thus proportional to the number of nucleons, but the total disruptive electromagnetic force trying to break the nucleus apart is roughly proportional to the square of its atomic number. A nucleus with 210 or more nucleons is so large that the strong nuclear force holding it together can just barely counterbalance the electromagnetic repulsion between the protons it contains. Alpha decay occurs in such nuclei as a means of increasing stability by reducing size.

One curiosity is why alpha particles, helium nuclei, should be preferentially emitted as opposed to other particles like a single proton or neutron or other atomic nuclei.^[note 1] Part of the answer comes from conservation of wave function symmetry, which prevents a particle from spontaneously changing from exhibiting Bose–Einstein statistics (if it had an even number of nucleons) to Fermi–Dirac statistics (if it had an odd number of nucleons) or vice versa. Single proton emission or the emission of any particle with an odd number of nucleons would violate this conservation law. The rest of the answer comes from the very high binding energy of the alpha particle. Computing the total disintegration energy given by the equation:

Where is the initial mass of the nucleus, is the mass of the nucleus after particle emission, and is the mass of the emitted particle, shows that alpha particle emission will usually be possible just with energy from the nucleus itself, while other decay modes will require additional energy. For example, performing the calculation for uranium-232 shows that alpha particle emission would need only 5.4 MeV, while a single proton emission would require 6.1 MeV. Most of this disintegration energy becomes the kinetic energy of the alpha particle itself, although to preserve conservation of momentum part of this energy becomes the recoil of the nucleus itself. However, since the mass numbers of most alpha emitting radioisotopes exceed 210, far greater than the mass number of the alpha particle (4) the part of the energy going to the recoil of the nucleus is generally quite small.



These disintegration energies however are substantially smaller than the potential barrier provided by the nuclear force, which prevents the alpha particle from escaping. The energy needed is generally in the range of about 25 MeV, the amount of work that must be done against electromagnetic repulsion to bring an alpha particle from infinity to a point near the nucleus just outside the range of the nuclear force's influence. An alpha particle can be thought of as being inside a potential barrier whose walls are 25 MeV. However, decay alpha particles only have kinetic energies of 4 MeV to about 9 MeV, far less than the energy needed to escape.

Quantum mechanics, however, provides a ready explanation, via the mechanism of quantum tunnelling. The quantum tunnelling theory of alpha decay, independently developed by George Gamow^[3] and Ronald Wilfred Gurney and Edward Condon in 1928,^[4] was hailed as a very striking confirmation of quantum theory. Essentially, the alpha particle escapes from the nucleus by quantum tunnelling its way out. Gurney and Condon made the following observation in their paper on it:

It has hitherto been necessary to postulate some special arbitrary 'instability' of the nucleus; but in the following note it is pointed out that disintegration is a natural consequence of the laws of quantum mechanics without any special hypothesis... Much has been written of the explosive violence with which the α -particle is hurled from its place in the nucleus. But from the process pictured above, one would rather say that the α -particle almost slips away unnoticed.^[4]

The theory makes the assumptions that the alpha particle can be considered an independent particle within a nucleus that is in constant motion, but held within the nucleus by nuclear forces. There is, in addition, a very small but decidedly non-zero probability that it will tunnel its way out. An alpha particle with a speed of 1.5×10^7 m/s within a nuclear diameter of approximately 10^{-14} m will thus collide against the potential barrier of the nuclear force more

than 10^{21} times per second, and yet for some radioisotopes it will need to keep doing this for as long as 13 billion years before managing to escape, so the probability of escape is extremely low.

Working out the details of the theory leads to an equation relating the half-life of a radioisotope to the decay energy of its alpha particles, a theoretical derivation of the empirical Geiger–Nuttall law.

a decay : wave mechanical theory: Particle and wave: an effect of quantum mechanics

The great age of uranium and thorium nuclei that reach billions of years shows that the alpha decay occurs with difficulty, although they release millions of electron volts of energy.

These nuclei would be perfectly stable without a laborious process that overcomes the nuclear forces and triggers decay. The attractive effect of the nuclear force stops abruptly out of the nucleus. If four nucleons, grouped into one alpha particle, are not anymore in touch with the other nucleons, this group feels only the repulsion due to the electric charge of the rest of the nucleus. Then it moves away faster and faster to acquire the kinetic energy of a few million electron volts which was discussed. The thing is to get to lose that contact.



A potential well

The alpha decay of polonium-212 is the one that releases the most important quantity of energy, 8.95 MeV. This decay is forbidden by classical mechanics. It is impossible for an

alpha particle to go from inside the nucleus in A to outside in B. It finds itself trapped at the bottom of a "well" as shown by the curve (gray) that represents the potential energy of interaction between the particle and the rest of the nucleus. To get from A to B, the particle must pass through a restricted area where its kinetic energy would be negative. The permitted areas are the well where nuclear attraction dominates, and outside the well where the repulsion due to the nuclear charge prevails.

We owe to a Russian-born American physicist George Gamow, the first explanation of alpha decay, a decay that is not authorized by the laws of classical physics.

The mechanism proposed by Gamow was called "**quantum tunneling**". The quantum tunneling or "**tunnel effect**" describes the fact that a particle behaves as both a particle and a wave in the infinitesimally small world where quantum mechanics replaces classical mechanics.

The Tunnel Effect

The wave associated with an alpha particle trapped inside a nucleus has been superimposed to the previous figure. We see that the wave extends slightly outside the nucleus, where the oscillation amplitude has been amplified to make them visible. The square of the amplitude of the oscillations is, in quantum mechanics, the probability of observing the particle at a given position. So there is a probability of observing the alpha particle outside the nucleus, that is to say a decay.

The alpha particle is found in the situation of a mountain climber, trapped in a crater, which has no more strength to join the mountaintop, passes on the other side and slide down toward the valley. The barrier to cross reflect the competition between the attractive nuclear force and the electrostatic repulsion. The alpha particle can not cross the barrier because it does not have the necessary energy: it is either inside or outside the nucleus. At least for classical mechanics.

In quantum mechanics, the situation is less obvious. The wave, which represent an alpha particle in the nucleus, is not strictly localized and slightly overlaps the other side of the

fence. There is a probability of observing the particle outside the nucleus, where the nuclear force is no longer felt. This probability is extremely small, but it enables the decay. Again with the image of the climber, the trick at his disposal to win the other side of the mountain and find freedom is to dig a tunnel through it.

An empirical law says that higher is the potential barrier, larger is the thickness to cross and greater is the nucleus lifetime. This explains some particularly long lifetimes.

Beta disintegration

Beta decay, any of three processes of radioactive disintegration by which some unstable atomic nuclei spontaneously dissipate excess energy and undergo a change of one unit of positive charge without any change in mass number. The three processes are electron emission, positron (positive electron) emission, and electron capture. Beta decay was named (1899) by Ernest Rutherford when he observed that radioactivity was not a simple phenomenon. He called the less penetrating rays alpha and the more penetrating rays beta. Most beta particles are ejected at speeds approaching that of light.

All atoms heavier than ordinary hydrogen have a nucleus consisting of neutrons and protons (neutral and positively charged particles, respectively), surrounded by negative electrons; these orbital electrons are not involved in the electron emission associated with beta decay. In electron emission, also called negative beta decay (symbolized β^- -decay), an unstable nucleus emits an energetic electron (of relatively small mass) and an antineutrino (with little or possibly no rest mass), and a neutron in the nucleus becomes a proton that remains in the product nucleus. Thus, negative beta decay results in a daughter nucleus, the proton number (atomic number) of which is one more than its parent but the mass number (total number of neutrons and protons) of which is the same. For example, hydrogen-3(atomic number 1, mass number 3) decays to helium-3 (atomic number 2, mass number 3). The energy lost by the nucleus is shared by the electron and the antineutrino, so that beta particles (the electrons) have energy ranging from zero to a distinct maximum that is characteristic of the unstable parent.

In positron emission, also called positive beta decay (β^+ -decay), a proton in the parent nucleus decays into a neutron that remains in the daughter nucleus, and the nucleus emits a neutrino and a positron, which is a positive particle like an ordinary electron in mass but of opposite charge. Thus, positive beta decay produces a daughter nucleus, the atomic number of which is one less than its parent and the mass number of which is the same. Positron emission was first observed by Irène and Frédéric Joliot-Curie in 1934.



In electron capture, an electron orbiting around the nucleus combines with a nuclear proton to produce a neutron, which remains in the nucleus, and a neutrino, which is emitted. Most commonly the electron is captured from the innermost, or K, shell of electrons around the atom; for this reason, the process often is called K-capture. As in positron emission, the nuclear positive charge and hence the atomic number decreases by one unit, and the mass number remains the same.

Each chemical element consists of a set of isotopes the nuclei of which have the same number of protons but differ in the number of neutrons. Within each set the isotopes of intermediate mass are stable or at least more stable than the rest. For each element, the lighter isotopes, those deficient in neutrons, generally tend toward stability by positron emission or electron capture, whereas the heavier isotopes, those rich in neutrons, usually approach stability by electron emission.

In comparison with other forms of radioactivity, such as gamma or alpha decay, beta decay is a relatively slow process. Half-lives for beta decay are never shorter than a few milliseconds.

Gamma emission and Internal Conversion

Gamma emission is not a primary decay process but usually accompanies alpha and beta decay. Typically this type of radiation arises when the daughter product resulting from alpha or beta decay is formed in an excited state. This excited state returns to the ground state through the emission of a gamma photon. Instead of having a well-defined range like alpha and beta particles, gamma rays loose characteristically a certain fraction of their energy per unit distance through matter. Gamma rays are highly penetrating and can result in considerable organic damage. Gamma emitting sources require heavy shielding and remote handling.

Alternatively, the excited nucleus may return to the ground state by ejecting an orbital electron. This is known as internal conversion and results in an energetic electron and X-rays due to electrons cascading to lower energy levels. The ratio of internal conversion electrons to gamma emission photons is known as the internal conversion coefficient. Conversion electrons are monoenergetic. Consider the case of the internal conversion of ¹³⁷Cs. This nuclide is transformed by β- emission to the excired state ^{123m}Ba. This daughter nuclide then emits a 0.661 MeV photon which undergoes internal conversion in 11% of the transitions. These conversion electrons are seen in the beta spectrum of ¹³⁷Cs. Following the internal conversion, outer orbital electrons fill the deeper energy levels and result in characteristic X-ray emission. These X-rays can in turn lead to the ejection of outer electrons through an internal photoelectric effect. These low energy ejected electrons are known as Auger electrons.

Origin of gamma rays

Solution Gamma rays are produced in the disintegration of radioactive atomic nuclei and in the decay of certain subatomic particles. The commonly accepted definitions of the gamma-ray and X-ray regions of the electromagnetic spectrum include some wavelength overlap, with gamma-ray radiation having wavelengths that are generally shorter than a few tenths of an angstrom (10^{-10} metre) and gamma-ray photons having energies that are greater than tens of thousands of electron volts (eV). There is no theoretical upper limit to the energies of gamma-ray photons and no lower limit to gamma-ray wavelengths; observed energies

presently extend up to a few trillion electron volts—these extremely high-energy photons are produced in astronomical sources through currently unidentified mechanisms.

Unit –III

The term gamma ray was coined by British physicist Ernest Rutherford in 1903 \geq following early studies of the emissions of radioactive nuclei. Just as atoms have discrete energy levels associated with different configurations of the orbiting electrons, atomic nuclei configurations have energy level structures determined by the of the protons and neutrons that constitute the nuclei. While energy differences between atomic energy levels are typically in the 1- to 10-eV range, energy differences in nuclei usually fall in the 1-keV (thousand electron volts) to 10-MeV (million electron volts) range. When a nucleus makes a transition from a high-energy level to a lower-energy level, a photon is emitted to carry off the excess energy; nuclear energy-level differences correspond to photon wavelengths in the gamma-ray region.

 \geq When an unstable atomic nucleus decays into a more stable nucleus (see radioactivity), the "daughter" nucleus is sometimes produced in an excited state. The subsequent relaxation of the daughter nucleus to a lower-energy state results in the emission of a gamma-ray photon. Gamma-ray spectroscopy, involving the precise measurement of gamma-ray photon energies emitted by different nuclei, can establish nuclear energy-level structures and allows for the identification of trace radioactive elements through their gamma-ray emissions. Gamma rays are also produced in the important process of pair annihilation, in which an electron and its antiparticle, a positron, vanish and two photons are created. The photons are emitted in opposite directions and must each carry 511 keV of energy—the rest mass energy (see relativistic mass) of the electron and positron. Gamma rays can also be generated in the decay of some unstable subatomic particles, such as the neutral pion.

Gamma-ray photons, like their X-ray counterparts, are a form of ionizing radiation; \triangleright when they pass through matter, they usually deposit their energy by liberating electrons from atoms and molecules. At the lower energy ranges, a gamma-ray photon is often completely absorbed by an atom and the gamma ray's energy transferred to a single ejected electron (see photoelectric effect). Higher-energy gamma rays are more likely to scatter from the atomic electrons, depositing a fraction of their energy in each scattering event (see Compton effect). Standard methods for the detection of gamma rays are based on the effects of the liberated atomic electrons in gases, crystals, and semiconductors (*see* radiation measurement and scintillation counter).

Solution Gamma rays can also interact with atomic nuclei. In the process of pair production, a gamma-ray photon with an energy exceeding twice the rest mass energy of the electron (greater than 1.02 MeV), when passing close to a nucleus, is directly converted into an electron-positron pair (*see* photograph). At even higher energies (greater than 10 MeV), a gamma ray can be directly absorbed by a nucleus, causing the ejection of nuclear particles (*see* photodisintegration) or the splitting of the nucleus in a process known as photofission.

Possible questions (part B- 8 marks)

- 1. What is gamma ray and explain in detail about the origin of gamma rays.
- 2. Explain in detail how the radiation originates from radioactive elements
- 3. Describe in detail about the internal conversion of gamma rays
- 4. Discuss in detail about beta disintegration
- 5. What are radioactive elements? Explain the origin of radiation from radio elements
- 6. Discuss in detail about alpha disintegration

KARPAGAM ACA	DEMY OF HIC	HER EDUCAT	TION				
DEPARTMENT OF PHYSICS							
CLAS	SS:III BSC PHY	'SICS					
Atomic and Molecular Physics (15PHU501)			Batch 2015				
MULIPLE CHOICE QUESTIONS							
QUESTIONS	opt1	opt2	opt3	opt4	answer		
Process of emission of natural radiation from some elements is called	radioactivity	degeneracy	transmutation	radiotransmuta tion	radioactivity		
Gamma (γ) radiation are fast moving	electrons	protons	photons	neutrons	photons		
Radiation that does not change it's direction inside magnetic field is	alpha	beta	gamma	x-ray	gamma		
When unstable nuclei undergo radioactive decay, they emit three types of radioactivity. Which is not one of them?	alpha	beta	gamma	delta	delta		
Which type of radioactive decay doesn't change the atomic number?	alpha	beta	gamma	delta	gamma		
Electromagnetic radiations produced from nuclear reactions are?	alpha rays	gamma rays	beta rays	x rays	beta rays		
Most penetrating radiation of radioactive element is:	alpha rays	gamma rays	beta rays	x rays	gamma rays		
Alpha-particles are fast moving	Protons	Helium nuclei	Electrons	Hydrogen atoms	Helium nuclei		
Radioactivity is confined almost entirely to the elements to in the periodic table	60, 92	83, 106	92, 118	None of the above	83, 106		
As per radioactive decay law, the small amount of disintegration of the isotope in a small period is equal to	–λΝ	λΝ	-2λΝ	2λΝ	$-\lambda N$		
The International system of units (SI) of radioactivity activity is	Becquerel	Curie	Fermi	Moles	Becquerel		
The half life of radioactive nuclei is	0.693 / λ	0.793 / λ	c. 0.693λ	0.793λ	0.693 / λ		
Radioactivity is a (A) Spontaneous activity (B) Chemical property c) unstable	A & B	B & C	C & A	A B & C	C & A		
Radioactive decay obeys which one of the following law?	N=N0e-t	N=N0et	N=N0e-t/2	N0=N(1+et)	N=N0e-t		

	3.74 x 109	3.70 x 1010	3.55 x 1010	3.60 x 1010	3.70 x 1010
The unit of radioactivity curie is equal to	disintegration	disintegration	disintegration	disintegration	disintegration
	per sec	per sec	per sec	per sec	per sec
Radioactive materials can be identified by measuring their	hardness	density	mass	half life	half life
Gamma radiation	has no charge	is photon	has no mass	all are true	all are true
Rate of decay is actually described by	half life	mean life	total life	decay constant	decay constant
When a neutron is disintegrated to give a b-particle	a proton alone is emitted.	a proton and an antineutrino are emitted.	a neutrino alone is emitted.	a proton and neutrino are emitted.	a proton and an antineutrino are emitted.
1 curie represents	1 disintegration per second	10 ⁶ disintegra tions per second	3.7 ′ 10 ¹⁰ disi ntegrations per second	$3.7 \cdot 10^7$ disin tegrations per second	3.7 ' 10 ⁷ disint egrations per second
α particles are	positively charged	doubly positively charged	negatively charged	doubly negatively charged	doubly positively charged
unit IV					
Dipole-induced dipole interactions are present in which of the	H2O and	C12 and CC14	HCl and He	SiF4 and He	HCl and He
following pairs	alcoho	CI2 and CCI4	atoms	atoms	atoms
Which of the following is a polar molecule?	BF3	SF4	SiF4	XeF4	SF4
The molecule having smallest bond angle is:	NC13	AsCl3	SbC13	PC13	SbCl3
Elements in group III are likely to form	ionic bonds	covalent bonds	metallic bonds	diatic bonds	covalent bonds
Simple molecules or giant macromolecules are examples of	ionic bonds	covalent bonds	metallic bonds	diatic bonds	covalent bonds
Molecules having Van der Waals' forces have	higher stability	have high melting points	have low melting points	have high boiling points	have low melting points
Bonding structure refers to the	elements forming it	arrangement of electrons	arrangement of resulting particles	water of crystallization	arrangement of resulting particles

Which sequence of Group 18 elements demonstrates a gradual decrease in the strength of the Van der Waals forces? All the choices are elements in the liquid state.	Xe, Kr, Ar, Ne	Ne, Ar, Kr, Xe	Kr, Xe, Ar, Ne	Ar, Kr, Ne, Xe	Xe, Kr, Ar, Ne
A molecule with a single covalent bond is _	C12	Co2	N2	Со	C12
Which of the following diatomic molecules is joined by a double covalent bond?	N2	O2	He2	Cl2	O2
Which of the following elements can form diatomic molecules held together by triple covalent bonds?	fluorine	carbon	nitrogen	oxygen	nitrogen
The model for metallic bonding is known as	the quantum model	the electron cloud model	the rutherford model	the electron sea model	the electron sea model
Who discovered the interval rule	Pauli	Bhor	Rutherford	Lande	Lande
The selection rule for J is	ΔJ=+ or - 1	ΔJ=0	$\Delta J = + \text{ or } - 1$ or 0	ΔJ=- 1	$\Delta J = + \text{ or } - 1$ or 0
The selection rule for L is	ΔL =+ or - 1	$\Delta L=0$	$\Delta L=+1$	ΔL=- 1	ΔL =+ or - 1
The selection rule for L is	$\Delta S = + \text{ or } - 1$	$\Delta S=0$	$\Delta S = +1$	$\Delta S=-1$	$\Delta S=0$
Molecular structure of SF_6 is	linear	tetrahedral	hexagonal	octahedral	octahedral
Van der Waal's forces are directly proportional to the	temperature	pressure	electronegativi ty	boiling point	boiling point
Van der Waal's forces increase with increase in	number of electrons	number of protons	number of contact points	All of Above	All of Above
Metals conduct electricity when they are	solid	molten	aqueous	both A and B	aqueous
strength of metallic bonding also increases with increase in	positive charge	mobile electrons	negative charge	both A and B	both A and B
Metal atoms	lose their outer electrons	become positively charged	become negatively charged	both A and B	both A and B

In creation of Van der Waal's forces, series of actions that happens first is	A temporary dipole is set up	Temporary dipoles are formed, because electron clouds are always moving	More of charge cloud gathers on one side of molecule/atom	Temporary dipole induces a dipole in neighboring atom/molecule	More of charge cloud gathers on one side of molecule/atom
Molecular structure of an ammonia molecule is	tetrahedral	linear	triangular pyramidal	trigonal	triangular pyramidal
Word for three angles is	octahedra	tetrahedral	trigonal	trigonal planar	trigonal
Metallic bonding is very strong because of	lattice	volatility	electrostatic attraction	All of Above	electrostatic attraction
Degree of polarity of a molecule is measured as	dipole moment	dipole-dipole interaction	dipole reaction	All of Above	dipole moment
When metals combine with non-metals,	hydrogen gas is given off	electrons of outer shells are shared	electrons in outer shells of metals are transferred to non-metals atoms	electrons in outer shells of non-metals are transferred to metals atoms	electrons in outer shells of metals are transferred to non-metals atoms
Molecules which have permanent dipole are known as	polar	non-polar	dipolar	tripolar	polar
The infrared spectrum of a diatomic molecule exhibit transitions at 2144, 4262 and 6354 cm	2157	2170	2183	2196	2170
corresponding to excitation from the ground state to the first, second and third vibration states respectively.					
The different types of energies associated with a molecule are	Electronic energy	b) Vibrational energy	c) Rotational energy	All of the mentioned	All of the mentioned
During the motion, if the centre of gravity of molecule	Electronic	b) Rotational	Translational	Vibrational	Translational
changes, the molecule possess	energy	energy	energy	energy	energy

The increase in bond order results in	increase in bond length and bond energy	decrease in bond length and bond energy both	decrease in bond length and increase in bond energy	none of the above	decrease in bond length and increase in bond energy
Which of the following is the weakest bond?	Metallic	Covalent	Ionic	Н	Н
Higher the bond order greater is	bond energy	bond angle	bond length	paramagnetis m	bond length
Ionic solids are characterised by	good conductivity in solid state	solubility in polar solvent	high vapour pressure	low melting point	solubility in polar solvent
Which of the following is a triatomic molecule?	Ammonia	Sulphurous anhydride	Sulphuric anhydride	Phosphine	Sulphurous anhydride
With the rise of temperature conductivity of metals	increases	decreases	may increase or decrease	remains constant	increases

Unit:IV Molecular Structure – General classification of molecules – Electronic structure in molecules – linkage between atoms – electrovalent and covalent atomic molecules – wave mechanical theory of covalent linkage – Van der Waals type of binding – metallic binding – electric moments of molecules – size and shape of molecules – heat of disassociation – photochemical disassociation – Frank Condon principle

General classification of molecules

Classification of molecules based on inertia moments

The principal axes are ordered such that associated inertia moments decrease, that is, the A-axis has the smallest moment of inertia and other axes are such that $I_A \leq I_B \leq I_C$. Depending on the relative size of the inertia moments, rotors can be divided into four classes.

Linear rotors

For a linear molecule $I_A \ll I_B = I_C$. For most purposes I_A can taken to be zero. For a linear molecule the separation of lines in the rotational spectrum can be related directly to the moment of inertia of the molecule. Since the moment of inertia is quadratic in the bond lengths, the microwave spectrum yields the bond lengths directly, provided the atomic masses are known.

Examples of linear molecules are obviously the diatomics such as oxygen (O=O), carbon monoxide (C=O), and nitrogen (N=N). But also many triatoms are linear: carbon dioxide (O=C=O), hydrogen cyanide (HC=N), and carbonyl sulfide (O=C=S). Examples of larger linear molecules are chloroethyne (HC=CCl), and acetylene (HC=CH).

Symmetric tops

A symmetric top is a rotor in which two moments of inertia are the same. Spectroscopists divide molecules into two classes of symmetric tops, oblate symmetric tops (frisbee or disc shaped) with $I_A = I_B < I_C$ and prolate symmetric tops (cigar shaped) with $I_A < I_B = I_C$. Symmetric tops have a three-fold or higher rotational symmetry axis.

Examples of oblate symmetric tops are: benzene (C_6H_6), cyclobutadiene (C_4H_4), and ammonia (NH₃). Prolate tops are: chloroform (CHCl₃) and methylacetylene (CH₃C=CH).

Spherical tops

A spherical top molecule is a special case of a symmetric tops with equal moment of inertia about all three axes $I_A = I_B = I_C$. The spherical top molecules have cubic symmetry.

Examples of spherical tops are: methane (CH₄), phosphorus tetramer (P₄), carbon tetrachloride (CCl₄), ammonium ion (NH₄⁺), and uranium hexafluoride (UF₆).

Asymmetric tops

BSc Physics

2017-2018-ODD

A rotor is an asymmetric top if all three moments of inertia are different. Most of the larger molecules are asymmetric tops. For such molecules a simple interpretation of the microwave spectrum usually is not possible. Sometimes asymmetric tops have rotational spectra that are similar to those of a linear molecule or a symmetric top, in which case the molecular structure must also be similar to that of a linear molecule or a symmetric top. In the determination of the molecular structure of asymmetric tops from microwave spectrum, isotopic substitution is invaluable.

Examples of asymmetric tops: anthracene ($C_{14}H_{10}$), water (H_2O), and nitrogen dioxide (NO_2).

Linkage between atoms

Ionic Bonding

This is the bond when one of the atoms is negative (has an extra electron) and another is positive (has lost an electron). Then there is a strong, direct Coulomb attraction. An example is NaCl. In the molecule, there are more electrons around Cl, forming Cl⁻ and less around Na, forming Na⁺. Ionic bonds are the strongest bonds. In real solids, ionic bonding is usually combined with covalent bonding. In this case, the fractional ionic bonding is defined as % ionic $= 100 \times [1 - \exp(-0.25 (X_A - X_B)^2)]$, where X_A and X_B are the electronegativities of the two atoms, A and B, forming the molecule.

Covalent Bonding

In covalent bonding, electrons are shared between the molecules, to saturate the valency. The simplest example is the H_2 molecule, where the electrons spend more time in between the nuclei than outside, thus producing bonding.
Metallic Bonding

In metals, the atoms are ionized, loosing some electrons from the valence band. Those electrons form a electron sea, which binds the charged nuclei in place, in a similar way that the electrons in between the H atoms in the H_2 molecule bind the protons.

Electrovalent and covalent atomic molecules

Electrovalent atomic molecule. In forming **electrovalent bonds** electrons are actually transferred from the outer orbit of one atom to the outer orbit of a second atom. In this process both atoms usually obtain completed outer orbits. For example, in sodium chloride the single electron in the outer orbit of the sodium atom is transferred to the outer orbit of the chlorine atom, completing its outer orbit. This leaves both the sodium and the chloride atoms with completed outer orbits. In this process the sodium atom becomes a sodium Na⁺ ion with a +1 charge and the chlorine atom becomes a chlorine Cl⁻ ion with a -1 charge. These two ions are bound together into a molecule by the force of electrostatic attraction existing between two opposite charges. Note that the process leaves the sodium atom with the electronic structure of the noble gas neon and the chlorine atom with the electronic structure of argon.



Another example of electrovalent bonding is found in the magnesium bromide $MgBr_2$ molecule. Here one of the two electrons in the outer orbit of magnesium is transferred to one bromine atom and the other is transferred to the other bromine atom. This gives a Mg^{++} ion and two Br^{-} ions. The ions are bound together as a molecule by the electrostatic forces existing between dissimilar charges.

BSc Physics	Unit –IV	Atomic and Molecular Physics
2017-2018-ODD	Molecular Structure	15PHU501

Covalent atomic molecule. In covalent bonds electrons are not transferred from one atom to another as in the electrovalent bond. Instead, two atoms share a pair of electrons with each other. Each of the two atoms contributes one of the electrons of the electron pair. Both electrons in the pair orbit both nuclei. This produces a bond between the two atoms. For the covalent bond of hydrogen gas. By this process of sharing pairs of electrons, the atoms involved achieve completed outer orbits which provide them with chemical stability. The bonds of most common gases including hydrogen (H₂), nitrogen (N₂), oxygen (O₂), fluorine (F₂), and chlorine (Cl₂) have covalent bonds. The bonds in water (H₂O) and ammonia (NH₃) are of the covalent type.



Metallic bonding

Metallic bonding is the strong attraction between closely packed positive metal ions and a 'sea' of delocalised electrons.

The attraction between the metal ions and the delocalised electrons must be overcome to melt or to boil a metal. Some of the attractions must be overcome to melt a metal and all of them must be overcome to boil it. These attractive forces are strong, so metals have high melting and boiling points.

The delocalised electrons are able to move through the metal structure. When a potential difference is applied, they will move together, allowing an electric current to flow through the metal.



Electric moments in molecules

The electric dipole moment is a measure of the separation of positive and negative electrical charges within a system, that is, a measure of the system's overall polarity. The electric field strength of the dipole is proportional to the magnitude of dipole moment. The SI units for electric dipole moment are coulomb-meter (C·m), however the most commonly used unit is the debye (D).

Theoretically, an electric dipole is defined by the first-order term of the multipole expansion, and consists of two equal and opposite charges infinitely close together. This is unrealistic, as real dipoles have separated charge.^[1] However, because the charge separation is very small compared to everyday lengths, the error introduced by treating real dipoles like they are theoretically perfect is usually negligible. The direction of dipole is usually defined from the negative charge towards the positive charge.

Often in physics the dimensions of a massive object can be ignored and can be treated as a pointlike object, i.e. a point particle. Point particles with electric charge are referred to as point charges. Two point charges, one with charge +q and the other one with charge -qseparated by a distance *d*, constitute an *electric dipole* (a special case of an electric multipole). For this case, the electric dipole moment has a magnitude and is directed from the negative charge to the positive one. Some authors may split *d* in half and use s = d/2 since this quantity is the distance between either charge and the center of the dipole, leading to a factor of two in the definition.

Dipole moments in molecules are responsible for the behavior of a substance in the presence of external electric fields. The dipoles tend to be aligned to the external field which can be constant or time-dependent. This effect forms the basis of a modern experimental technique called dielectric spectroscopy.

Size and shape of molecule

Lewis structures along with **Valence Shell Electron Pair Repulsion Theory** are used to predict the shape of molecules. The idea behind this is that electrons in filled orbitals will repel each other because they have the same charge (just as magnets with the same polarity repel).

- 1. All pairs of electrons, both bonding pairs and lone pairs, are important in determining the shape of a molecule.
- 2. Bonding pairs are smaller than lone pairs because there are 2 positively charged nuclei pulling them in.
- 3. Single bonds are smaller than double bonds and double bonds are smaller than triple bonds.
- 4. If a central atom (A) is surrounded by different atoms (B and C) in the molecule AB_xC_y , the relative sizes of B and C can affect the structure of the molecule.

The first step is to construct the best Lewis structure of the molecule. Let's look at a few examples: CH₄, NH₃, BH₃



The electron pairs on the central atom will be arranged in such a way as to maximize their distance to the others. Two pairs will always be 180 degrees apart, in a linear arrangement. Three pairs will be 120 degrees apart in a trigonal arrangement. Four pairs will be arranged in a tetrahedron, 109 degrees apart. When there are 5 pairs of electrons, there are two possible arrangements: trigonal bipyramidal (90 and 120 degree angles) and square pyramidal (90 degree angles). Trigonal bipyramidal is the lowest energy, but the square pyramidal structure is pretty close and is also important. When there are 6 pairs of electrons, they occupy the vertices of an octahedron (90 degree angles).



Photo chemical dissociation

When radiation is absorbed by a molecule sometimes the amount of energy becomes high enough to break bonds in the compound. This causes the atoms to photo-dissociate (break apart) forming radicals.

Photodissociation is the breakdown off molecules by High-energy light. Basically, a neutral molecule, say, Cl2, is hit by UV radiations. The Cl-Cl **bond is broken** and you get the formation of free radicals, in this case, the two Cl*- radicals. A free radical is atom or molecule with unpaired electrons, and is highly reactive

Intensity of Vibrational-Electronic Spectra: The Franck-Condon Principle.

Although quantum mechanics imposes no restrictions on the change in the vibrational quantum number during an electronic transition, the vibrational lines in a progression are not observed

to be of the same intensity. In some spectra, the (0,0) transition is the strongest, in others, the intensity of the spectrum increases to a maximum at some value of v', while yet in others, only a few vibrational lines with high v' are seen, followed by a continuum. All these types of spectra are readily explainable in terms of the Franck-Condon principle which states that an electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition.

We have already learned on the example of the description of a vibrating molecule with the anharmonic oscillator that the energy of a diatomic molecule varies with internuclear

BSc Physics	Unit –IV	Atomic and Molecular Physics
2017-2018-ODD	Molecular Structure	15PHU501

distance. This Morse potential represents the energy when one atom is fixed in place at r=0 and the other is allowed to oscillate between the limits of the curve. Classical theory would suggest that the molecule spends most of its time on the curve at the turning point of its motion, since it is moving most slowly there. Quantum theory, while agreeing this view for high values of the vibrational quantum number, shows that for v=0 the atom is most likely found at the center of this motion, i.e. at the equilibrium internuclear distance r_{eq} . For v=1, 2,

3, the most



Figure. Probability distribution of the internuclear distance of a diatomic molecule.

probable positions steadily approach the extremities until, for high v, the quantum and classical pictures merge (see figure below) where we plot the probability distribution in each vibrational state against internuclear distance.

If a diatomic molecule undergoes a transition into an upper electronic state in which the excited molecule is stable with respect to dissociation into its atoms, then we can represent the upper state by a Morse curve similar in outline to that of the ground state. There will probably (but not necessarily) be differences in such parameters as vibrational frequency, internuclear distance, or dissociation energy between the two states, but this simply means

that we should consider each excited molecule as a new, but rather similar molecule with a different, but also rather similar Morse Potential.

Below Figure shows three possibilities: In (a) we show the upper electronic state having the same equilibrium internuclear distance as the lower. Now the Franck-Condon principle suggests that a transition occurs vertically on this diagram, since the internuclear distance



Figure. Franck-Condon principle for electronic transitions

does not change, and so, if we consider the molecule to be initially in the ground state both electronically and vibrationally, then the most probable transition is that indicated by the vertical line in (a). Thus, the strongest spectral line of the v'' = 0 progression will be the (0,0). However, the quantum theory only says that the probability of finding the oscillating atom is greatest at the equilibrium distance in the v=0 state, it allows some, although small, chance of the atom being near the extremities of its vibrational motion. Hence there is some chance of the transition starting from the ends of the v''=0 and finishing in the v=1, 2, etc. states. The (1,0), (2,0), etc. lines diminish rapidly in intensity, however as shown in the foot of the figure above.

In part b of Figure above, it is shown a case where the excited electronic state has a slightly greater internuclear separation than the ground state. Now a vertical transition from the v=0

level will most likely occur into the upper vibrational state v'=2. Transitions to lower or higher v' states are less likely. In fact, the upper state most probably reached will depend on the difference between the equilibrium distances of the atoms in the lower and upper electronic states. In part c of the Figure above, the equilibrium distance of the upper state is drawn considerably greater than that of the lower state and we see that, firstly, the vibrational energy level to which the transition most probably takes place has a high v' vibrational quantum number. Further transitions can occur where the vibrational energy of the excited state is larger than the dissociation energy. From such a state, the molecule will dissociate without vibrations, since the atoms that are formed may take up any kind of value for kinetic energy. Such transitions are not quantized and a continuum results. This is again shown at the foot of the Figure.

Dissociation Energy and Heat Dissociation and photo dissociation.

Figure below shows two of the ways in which electronic excitation can lead to dissociation. Part a presents the case that we just discussed, where the equilibrium nuclear separation in the upper state is considerably greater than in the lower. The dashed line limits of the Morse curves represent the dissociation of the normal and excited molecule into atoms, the dissociation energies being D0" and D0' from the v=0 state in each case. We see that the total energy of the dissociation products (i.e.) atoms form the upper state is greater by an amount E_{ex} than that of the products of dissociation in the lower state. This energy is called the excitation energy of one (or rarely both) of the atoms produced on dissociation. We saw in the previous section that the spectrum of this system consists of some vibrational transitions (quantized) followed by a continuum (non-quantized transitions) representing dissociation. The lower wave number limit of this continuum must represent just sufficient energy to cause dissociation and no more (i.e. the dissociation products separate with virtually zero kinetic energy) and thus we have:

$$\overline{v}_{c.l.} = D_0'' + E_{ex} (\text{cm}^{-1})$$



A: Excitation into a stable upper state B: Excitation into a continous upper state

Figure. Dissociation upon electronic excitation of a diatomic molecule.

and we see that we can measure the dissociation energy, if we know E_{ex} , the excitation energy of the products. This excitation energy is readily measurable by atomic spectroscopy the precise state of dissociation products is not always obvious. There are several ways in which the total energy D0"+ E_{ex} may be separated into its two components, and one example shall be given. Thermochemical studies often lead to an approximate value of D0" and hence, since D0"+ E_{ex} is accurately measurable spectroscopically, a rough value for E_{ex} is obtained.

When the spectrum of the atomic products is studied, it usually happens that only one value of excitation energy corresponds at all well with E_{ex} . Thus the state of the products is known, E_{ex} measured accurately and a precise value of D0" is deduced.

In many electronic spectra, no continua appear at all — the internuclear distances in the upper and lower states are such that transitions near to dissociation limit are of negligible probability — but still it is possible to derive a value for the dissociation energy by noting how the vibrational lines converge. We have already seen that the vibrational levels may be written:

$$\varepsilon_v = (v + 1/2) \tilde{v}_e - x (v + 1/2) \text{ cm })$$

and so the separation between neighboring levels is

 $\Delta \varepsilon = \varepsilon_{v+1} - \varepsilon_v = \tilde{v}_e \{ 1 - 2x_e(v+1) \} \text{ (cm}^{-1} \text{)}$

This separation obviously decreases linearly with increasing v and the dissociation limit is reached when $\Delta \epsilon \rightarrow 0$. Thus the maximum value of v is given by v_{max} , where:

$$\tilde{v}_{e} \{ 1 - 2x_{e}(v_{\max} + 1) \} = 0,$$

Since the anharmonicity constant is of the order of 10^{-2} . Two vibrational transitions are sufficient to determine the x_e and \tilde{v}_e . Thus, an example given here for HCl yielded $\tilde{v}_e = 2990$ cm⁻¹ and x e = 0.0174. From the last equation we can calculate $v_{max} = 27.74$ and the next lowest integer is v = 27.

Possible questions (Part B- 8 Marks)

- 1. Explain the wave mechanical theory of covalent linkage.
- 2. Write a short note on Vander Waals type of binding and metallic binding.
- 3. Describe the molecular structure and classify the molecules.
- 4. Explain in detail the Franck Condon principle about molecules
- 5. Explain in detail about photo chemical disassociation and Frank –Condon principle.
- 6. Write a short note on metallic binding and electric moments of molecules.
- 7. Discuss the electronic structure in molecules and linkage between atoms.
- 8. How the size and shape of molecules determined and explain heat of dissociation of molecules

KARPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE-21

DEPARTMENT OF PHYSICS

CLASS:III BSC PHYSICS

Atomic and Molecular Physics (15PHI Batch 2015

MULIPLE CHOICE QUESTIONS

QUESTIONS	opt1	opt2	opt3	opt4	answer
The molecule having smallest bond					
angle is:	NC13	AsCl3	SbCl3	PC13	SbCl3
Elements in group III are likely to					
form	ionic bonds	covalent bonds	metallic bonds	diatic bonds	covalent bonds
Simple molecules or giant					
macromolecules are examples of	ionic bonds	covalent bonds	metallic bonds	diatic bonds	covalent bonds
Molecules having Van der Waals'		have high melting	have low melting	have high boiling	have low melting
forces have	higher stability	points	points	points	points
		arrangement of	arrangement of		arrangement of
Bonding structure refers to the	elements forming it	electrons	resulting particles	water of crystallization	resulting particles
Which sequence of Group 18					
elements demonstrates a gradual					
decrease in the strength of the Van					
der Waals forces? All the choices are					
elements in the liquid state.	Xe, Kr, Ar, Ne	Ne, Ar, Kr, Xe	Kr, Xe, Ar, Ne	Ar, Kr, Ne, Xe	Xe, Kr, Ar, Ne
A molecule with a single covalent					
bond is _	C12	Co2	N2	Co	C12
Which of the following diatomic					
molecules is joined by a double					
covalent bond?	N2	O2	He2	C12	02
Which of the following elements can					
form diatomic molecules held					
together by triple covalent bonds?	fluorine	carbon	nitrogen	oxygen	nitrogen
The model for metallic bonding is		the electron cloud			
known as	the quantum model	model	the rutherford model	the electron sea model	the electron sea model
Who discovered the interval rule	Pauli	Bhor	Rutherford	Lande	Lande
The selection rule for J is	$\Delta J = + \text{ or } - 1$	∆J=0	ΔJ = + or - 1 or 0	∆J=- 1	ΔJ = + or - 1 or 0
The selection rule for L is	ΔL =+ or - 1	$\Delta L=0$	$\Delta L = +1$	$\Delta L=-1$	ΔL =+ or - 1
The selection rule for L is	$\Delta S = + \text{ or } - 1$	$\Delta S = 0$	$\Delta S = +1$	$\Delta S = -1$	$\Delta S=0$
Molecular structure of SF ₆ is	linear	tetrahedral	hexagonal	octahedral	octahedral

Van der Waal's forces are directly					
proportional to the	temperature	pressure	electronegativity	boiling point	boiling point
Van der Waal's forces increase with			number of contact		
increase in	number of electrons	number of protons	points	All of Above	All of Above
Metals conduct electricity when they					
are	solid	molten	aqueous	both A and B	aqueous
strength of metallic bonding also					
increases with increase in	positive charge	mobile electrons	negative charge	both A and B	both A and B
	lose their outer	become positively	become negatively		
Metal atoms	electrons	charged	charged	both A and B	both A and B
		Temporary dipoles are		Temporary dipole	
		formed, because	More of charge cloud	induces a dipole in	More of charge cloud
In creation of Van der Waal's forces,	A temporary dipole is	electron clouds are	gathers on one side of	neighboring	gathers on one side of
series of actions that happens first is	set up	always moving	molecule/atom.	atom/molecule.	molecule/atom.
Molecular structure of an ammonia					
molecule is	tetrahedral	linear	triangular pyramidal	trigonal	triangular pyramidal
Word for three angles is	octahedra	tetrahedral	trigonal	trigonal planar	trigonal
Metallic bonding is very strong					
because of	lattice	volatility	electrostatic attraction	All of Above	electrostatic attraction
Degree of polarity of a molecule is		dipole-dipole			
measured as	dipole moment	interaction	dipole reaction	All of Above	dipole moment
			electrons in outer shells	electrons in outer shells	electrons in outer shells
			of metals are	of non-metals are	of metals are
When metals combine with non-	hydrogen gas is given	electrons of outer	transferred to non-	transferred to metals	transferred to non-
metals,	off	shells are shared	metals atoms	atoms	metals atoms
Molecules which have permanent					
dipole are known as	polar	non-polar	dipolar	tripolar	polar
The infrared spectrum of a diatomic					
molecule exhibit transitions at 2144,					
4262 and 6354 cm	2157	2170	2183	2196	2170
corresponding to excitation from the					
ground state to the first, second and					
third vibration states respectively.					
The different types of energies					
associated with a molecule are	Electronic energy	b) Vibrational energy	c) Rotational energy	All of the mentioned	All of the mentioned

During the motion, if the centre of					
gravity of molecule changes, the					
molecule possess	Electronic energy	b) Rotational energy	Translational energy	Vibrational energy	Translational energy
			decrease in bond length		decrease in bond length
	increase in bond length	decrease in bond length	and increase in bond		and increase in bond
The increase in bond order results in	and bond energy	and bond energy both	energy	none of the above	energy
Which of the following is the weakest					
bond?	Metallic	Covalent	Ionic	Н	Н
Higher the bond order greater is	bond energy	bond angle	bond length	paramagnetism	bond length
	good conductivity in	solubility in polar			solubility in polar
Ionic solids are characterised by	solid state	solvent	high vapour pressure	low melting point	solvent
Which of the following is a triatomic					
molecule?	Ammonia	Sulphurous anhydride	Sulphuric anhydride	Phosphine	Sulphurous anhydride
With the rise of temperature			may increase or		
conductivity of metals	increases	decreases	decrease	remains constant	increases
	both sigma and pi	neither sigma nor pi			
shape of the molecule is decided by	bonds	bonds	pi bonds	sigma bonds	sigma bonds
Maximum number of bonds between					
two atoms of a covalent bond can be	4	3	6	7	3
Metallic sodium is	conductor of electricity	insulator	semi-conductor	none of these	conductor of electricity
	non polar covalent				
A metallic bond is	bond	polar	covalent	electrostatic	electrostatic
When a molecule is formed by the	only repulsive forces	only attractive forces	none of these forces		
combination of atoms	operate	operate	operate	both A and B operate	both A and B operate
Molecular orbital theory was					
developed by	Rutherford	Millikan	Planck	Bohr	Millikan
Bond order is given by	3(na-nb)	3(nb+na)	2(nb-na)	(nb-na)/2	(nb-na)/2
Which combination of atomic orbitals					
is not allowed according to MO					
theory	Px - Px	Px - Py	Py - Py	Pz - Pz	Px - Py
In a homonuclear molecule, higher					
the bond order, larger will be	bond length	bond strength	paramagnetism	ionic character	bond strength
Covalent molecules are generally held					
in the crystal structures by	Van der Waals forces	electrostatic forces	covalent bonds	dipolar forces	electrostatic forces

During bond formation, normally all					
the elements in their outermost shell					
acquire	three electrons	ten electrons	eight electrons	sixteen electrons	eight electrons
VSEPR Theory was proposed by	Lewis	Lewis and Kossel	Nyhom and Gillipsie	Linus Pauling	Nyhom and Gillipsie
Which of the following molecule has			2, 2, 3, 3-tetramethyl		
dipole moment greater than zero?	3, 3-Diethylpentane	trans-2-pentene	butane	Neopentane	trans-2-pentene
Which of the following does not					
conduct electricity	Molten NaOH	Molten KOH	solid NaCl	Aqueous NaCl	solid NaCl
The carbon-carbon link in acetylene	One sigma and two pi	Two sigma and three pi	Two sigma and two pi		One sigma and two pi
contains	bonds	bonds	bonds	Three sigma bonds	bonds
Paramagnetism is exhibited by	are not attracted by	contain only paired	contain unpaired		contain unpaired
molecules which	magnetic field	electrons	electrons	carry positive charge	electrons
A simplified application of MO					
theory to the hypothetical "molecule"					
Of would give its bond order as	2	1.5	5	3	1.5
Strength of intermolecular forces					
from ionic or covalent bond is	weaker	stronger	equal	none of above	weaker
Among the following species					
octahedral shape is found in	SF6	PC15	HgCl2	BF4-	SF6
Which molecule has a trigonal					
pyramidal shape	AB4E	AB2E2	AB3E	AB2E	AB3E
Among the following molecules, the					
molecule with trigonal planar					
geometry is:	BF3	IF3	NH3	PC13	BF3
				Both bond pair as well	Both bond pair as well
				as lone pair of	as lone pair of
According to the VSEPR theory, the	Lone pair of electrons	Bond pair of electrons		electrons in the valence	electrons in the valence
geometry and shape of the molecule	present on the central	present on the central	Hybridization of the	shell of the central	shell of the central
depends upon	atom	atom	molecule	atom	atom
Among the following species linear					
shape is found in	SO2	03	NO2+	NO2-	NO2+

Unit:V Molecular spectra – experimental study – theoretical explanation – pure rotation spectra – rotation-vibration spectra – Fortrat diagram – Peculiarities of certain band spectra – Isotopic effect in molecular spectra

Pure rotation - Rotational-vibrational spectra

For a diatomic molecule, which we treat as a rigid rotator with a bond length fixed in the equilibrium position, the moment of inertia is $I_e = \mu r_e^2$. Here, μ is the reduced mass.

In the case of a rotator in vibrational motion, r_e needs to be replaced by the average of the square of the the internuclear distance. Consequently, the moment of inertia becomes $I_v = \mu < r^2 >$. Explicitly calculated with $r = r_e \pm s$:

Within one oscillation, the addend $2 < \mu sr_e >$ is compensated to zero. The third addend and the moment of inertia I_v remain for a molecule which has a vibration larger than μr_e^2 . In turn, the *rotational constant B* becomes dependent on the vibrational state. Note that $B_v < B_e$

with vibration: without vibration

$$B_v = h/4\pi c \mu r_v^2$$
 $B_e = h/4\pi c \mu r_e^2$.

Besides the approach from classical physics, the problem has as well been treated with purely mathematical means. A result of this is the following equation that represents a first approximation using a small correction coefficient α_e to quantify the influence of the vibrational states v on the rotational constant B_v .

$$B_v = B_e - \alpha_e (v + \frac{1}{2})$$

In addition to the influence of the molecule's oscillations, rotation itself affects molecular constants, i.e., centrifugation will stretch bonds (compare chapter <u>Elastic rotor</u>). The *centrifugal stretching constant D* introduces this phenomenon into our mathematical description of molecular energy levels. Note that, like B, constant D is function of the vibrational state and the correction coefficient β_e quantifies the respective dependency.

For $\Delta J = +1$ or $J + 1 \leftarrow J$, we speak of absorption peaks within the so-called **R-branch**. Their wavenumbers v are

For $\Delta J = -1$ or $J - 1 \leftarrow J$, we speak of absorption peaks within the so-called **P-branch**. Their wavenumbers v are

 $v = v_0 - (B_v + B_{v'}) J - (B_v - B_{v'}) J^2$ for J = 1, 2, 3, ...

The distance Δv between absorption line J and absorption line J+1 becomes

R-branch: $\Delta v = 2(2B_{v'} - B_{v}) - 2(B_v - B_{v'}) J$ distance decreases P-branch: $\Delta v = 2B_v + 2(B_v - B_{v'})J$ distance increases

For $B_v \approx B_{v'}$, this distance is approximately 2B. The distance between the first transitions of the two branches is $\Delta v \approx 4B_v$



Vibration and rotational energy levels of dia-atomic molecules

vibrational levels

 $E_v = (v + \frac{1}{2}) h\omega_0$

Rotation - vibrational levels

 $\mathbf{E}_{\mathbf{r}} = \mathbf{B} \cdot \mathbf{J} \left(\mathbf{J} + 1 \right)$

Some molecules display additional lines in the gap between the P- and the R-branch. These lines are connected to transitions with $\Delta J = 0$ and form the so-called **Q-branch**. As the rotation of the system is maintained, the axis of rotation must shift ($\Delta K \neq 0$) and a change of the angular momentum of electron orbitals must occur. If we consider **diatomics**, lines of a Q-branch must also have such an angular momentum which contributes to the total angular momentum of the molecule.

Projection of the electron's rotation onto the axis of the molecule: $\Lambda = 0, 1, 2, ...$



The quantum number Λ (recall chapter "<u>Term symbols and selection rules</u>") denotes the projection of this orbital's angular momentum onto the molecule's axis. For $\Lambda = 0$, nothing changes. For the molecular total momentum, which includes rotation of nuclei and electrons, the relation $|J| \ge |\Lambda|$ applies.

The respective energy levels are analogous to those of the <u>symmetric top</u>. Here, the constant A is in connection with the momentum of electron orbitals. Note that A >> B.

$$E_{J} = \begin{bmatrix} BJ (J+1) \\ due \text{ to rotation of nuclei} \end{bmatrix} + \begin{bmatrix} A & -B \end{bmatrix} \Lambda^{2}$$

$$due \text{ to electrons}$$

For $\Lambda \neq 0$, there are new selection rules: Besides $\Delta J = \pm 1$, as well transitions with $\Delta J = 0$ are allowed.

With the NO molecule, we have this situation, but due to spin-related phenomenona, a detailed analysis is quite complicated. With no regard to the spin, there is the following approach to the lines of the **Q-branch**:

$$E(v',J) - E(v,J) = v_0 + B_{v'}J(J+1) + (A-B_{v'})\Lambda^2 - B_vJ(J+1) - (A-B_v)\Lambda^2$$

$$v = v_0 - (B_v - B_{v'})J(J+1) + (B_v - B_{v'})\Lambda^2$$

As $B_v \approx B_{v'}$, the lines within this branch lie very close to each other.

$\Delta K = 0$	$\Delta J = \pm 1 \text{for } K$ $= 0$	diatomic molecules
parallel band	$\Delta J = 0, \pm 1 \text{ for } K$ $\neq 0$	diatomic molecules, electronic contribution to J
$\Delta K = \pm 1$ perpendicular band	$\Delta J = 0, \pm 1$	·

For the symmetric top, we have the following selection rules

Of course, the intensity of rovibronic lines depends on the probability of a transition and on the occupancy of the involved states. In cases where v = 0 is the only occupied vibrational level, the intensity of lines is proportional to the population N_J and the so-called <u>Hönl-London-Factor</u> S_J for this rotational state J.

$$\begin{split} I & \propto N_J \cdot |\mu_{J'J}|^2 \\ I & \propto N_J \cdot S_J \end{split}$$

As the transition probabilities for a simple rotator at high rotational states are in a quite narrow range, mainly the vibrational ground state distribution over J rules the intensity of lines. To find out the most probable rotational state, we fall back on *Boltzmann's* theory:

$$N_{J} \sim (2J+1)e^{\frac{-E_{ax}}{kT}} = (2J+1)e^{\frac{-BJ(J+1)}{kT}}$$

An estimation of the distribution is feasible if the distance betweeen the rotational levels is much smaller than the product kT, a condition which is fulfilled for temperatures around 300 Kelvin. We use $dN_J/dJ = 0$ as condition for a maximum.

$$\begin{array}{l} \displaystyle \frac{d}{dJ} \, N_J \,=\, 0 \quad \Rightarrow \\ \displaystyle \frac{d}{dJ} \, (2\,J+1) e^{-BJ(J+1)/kT} \,=\, 2\, e^{-BJ(J+1)/kT} - \frac{B}{kT} (2\,J+1)^2 e^{-BJ(J+1)/kT} \,=\, 0 \quad \Rightarrow \\ \displaystyle J_{max} \,=\, -\frac{1}{2} + \sqrt{\frac{kT}{2\,B}} \,\approx\, \sqrt{\frac{kT}{2\,B}} \end{array}$$

Isotope Effect in molecular spectra

In this section we will study a first astrophysical application of molecular spectroscopy, namely the determination of abundance ratios of different isotopes. Molecules serve as a much more ideal tool to distinguish different isotopes than atoms. This is because the presence of more or less neutrons in the nucleus of a specific chemical element does not strongly modify the electric field and thus has only a small influence on the electron configuration. The same is true for the electron configuration of molecules of course. However, the energy of nuclear motion in molecules due to vibration and rotation is influenced already to first order if the number of neutrons and thus the mass of the nucleus is changed. Thus, isotopic molecules have different frequencies of vibrations and rotations.

First we will consider the modification of molecular spectra due to the presence of different isotopes. Then we will look at several examples that illustrate how knowledge of isotope ratios allows us to gain insight into astrophysical objects and processes. Later, in Chapter 6 (Astrobiology), we will discuss an additional important example where knowledge of isotope ratios is crucial for determining the origin of water on Earth.

Vibration

For isotopic molecules, i.e. molecules that differ only by the mass of one or both of the nuclei but not by their atomic number (for example ${}^{1}\text{H}{}^{35}\text{C1}$ and ${}^{1}\text{H}{}^{37}\text{C1}$), the vibrational frequencies are obviously different. Assuming harmonic vibrations the (classical) vibrational frequency is given by

$$v_{\rm osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} ,$$

Where the force constant k, since it is determined by the electronic motion only, is exactly the same for different isotopic molecules, whereas the reduced mass is different. Therefore, if we let the superscript "i" distinguish an isotopic molecule from the "ordinary" molecule we have

$$\frac{v_{\rm osc}^{\rm i}}{v_{\rm osc}} = \sqrt{\frac{\mu}{\mu^{\rm i}}} = \rho$$

The heavier isotope has the smaller frequency. If the superscript "i" refers to the heavier isotope the constant will be smaller than 1. For example, the values for the pairs ${}^{1}\text{H}^{35}\text{Cl}$ and ${}^{1}\text{H}^{37}\text{Cl}$, ${}^{1}\text{H}^{35}\text{Cl}$ and ${}^{2}\text{H}^{35}\text{Cl}$, ${}^{10}\text{BO}$ and ${}^{11}\text{BO}$, and ${}^{16}\text{O}^{16}\text{O}$ and ${}^{16}\text{O}^{18}\text{O}$ are 0.99924, 0.71720, 0.97177, and 0.97176, respectively.

We find for the vibrational levels of two isotopic molecules (still assuming harmonic oscillations)

$$G^{i}(v) = \omega_{e}^{i}\left(v + \frac{1}{2}\right) = \rho \omega_{e}\left(v + \frac{1}{2}\right) = \rho G(v)$$

Therefore, the separation of corresponding vibrational levels in two isotopic molecules are somewhat shifted (and as a result spectral lines are also shifted). The levels of the lighter isotope always lie higher than those of the heavier isotope.

If anharmonicity is taken into account, the calculations become rather more involved and will not be reproduced here. The formulae for the energy levels are found to be in a very good approximation

$$G(\upsilon) = \omega_{\rm e} \left(\upsilon + \frac{1}{2}\right) - \omega_{\rm e} x_{\rm e} \left(\upsilon + \frac{1}{2}\right)^2 + \omega_{\rm e} y_{\rm e} \left(\upsilon + \frac{1}{2}\right)^3 + \dots ,$$

$$G^{\rm t}(\upsilon) = \rho \omega_{\rm e} \left(\upsilon + \frac{1}{2}\right) - \rho^2 \omega_{\rm e} x_{\rm e} \left(\upsilon + \frac{1}{2}\right)^2 + \rho^3 \omega_{\rm e} y_{\rm e} \left(\upsilon + \frac{1}{2}\right)^3 + \dots .$$

Dr. S. Esakki Muthu Department of Physics In other words, the vibrational constants are modified as

$$\omega_{\rm e}^{\rm l} = \rho \,\omega_{\rm e} \,,$$

$$\omega_{\rm e}^{\rm l} x_{\rm e}^{\rm l} = \rho^2 \,\omega_{\rm e} x_{\rm e} \,,$$

$$\omega_{\rm e}^{\rm l} y_{\rm e}^{\rm l} = \rho^3 \,\omega_{\rm e} y_{\rm e} \,.$$

Rotation

Since the reduced mass is inversely proportional to the rotational constant B, molecules containing heavy isotopes have rotational lines corresponding to lower quantum energies and smaller line spacing. Specifically, we find for the rotational constant B of the two isotopic molecules

$$B_{\rm e}^{\rm i} = \frac{\hbar^2}{2\mu^{\rm i} r_{\rm eq}^2 hc} = \rho^2 B_{\rm e}$$

Note that the internuclear distances in diatomic (and polyatomic) molecules are entirely determined by the electronic structure. They are therefore exactly equal in isotopic molecules as long as no vibration occurs. The rotational energies of the two isotopic molecules are thus connected by

$$F^{i} = B_{e}^{i}J(J+1) = \rho^{2}B_{e}J(J+1) = \rho^{2}F$$

Rotational levels of the heavier molecule have smaller energies. Furthermore, the separation of neighboring lines in the rotational spectrum (which is 2B in first approximation) differs for isotopic molecules. For example, for the ¹²CO molecule, 2B is found to be 3.842 cm⁻¹, and for the ¹³CO molecule containing the heavier isotope of carbon. 2B is found to be 3.673 cm⁻¹. Figure shows the resulting differences in the rotational spectra of CO containing the isotopes ¹²C and ¹³C.



Fig. The isotopic effect on the rotational energy levels and the corresponding rotational spectrum of the CO molecule

For simultaneous vibration and rotation, in a first approximation, we simply have to add the vibrational and rotational isotope effects. As a result, the lines of a rotation-vibration band of an isotopic molecule do not have exactly the same separations as the lines of the "normal" molecule. In other words, the isotope displacement between corresponding lines of the two bands is dependent on *J*.

Since the rotational energies are smaller than the vibrational energies, the rotational isotope shift is, in general, smaller than the vibrational one, despite the fact that the former scales with ρ^2 while the latter scales with ρ .

For more precise calculation, it is necessary to take into account the interaction of vibration and rotation, i.e. the rotational constants α , β , *D*, and possibly higher order ones. To a very good approximation we may use

$$D_{e}^{i} = \rho^{4} D_{e}^{i} ,$$

 $\alpha^{i} = \rho^{3} \alpha ,$
 $\beta^{i} = \rho^{5} \beta .$

Fortrait Diagram

In gases at low pressure (no Doppler broadening), we can observe a rotational structure to the vibrational transitions. By using the rotational constants B, see equations (6.02), (6.03), and (3.26), the rotation-vibration energy of a diatomic molecule in the harmonic approximation is $E(v, J)/h = (v + \frac{1}{2})v + B J(J + 1)$. (6.36) With " we label the ground state and with ' the

excited state. Let us now consider the transition $v' - v'' = \Delta v = 1$ and $J' - J'' = \Delta J = 0, \pm 1$. If we make the simplified assumption that the moment of inertia of the molecule remains constant during the transition between the two vibrational states, B in equ. (6.36) is constant. For arbitrary values of v" and variable values of J" we get the equation for the transition frequency discovered by Henry Alexandre Deslandres in 1885. E(v', J')/h - E(v'', J'')/h = v + vB m, (6.37) In which for the variable values of J", m = 0 when $\Delta J = 0$, m is a positive whole number when $\Delta J = +1$, and a negative whole number when $\Delta J = -1$. Spectroscopy \mathbb{O} D. Freude Chapter "Optical Spectroscopy", version June 2006 Chapter 6, page 13 Fig. 6.8 taken from Atkin 6th ed. Fig. A high-resolution vibration-rotation spectrum of HC1. The lines appear in pairs because both H35Cl and H37Cl contribute. Negative values of m ($\Delta J = -1$) are responsible for the P-branch, m = 0 ($\Delta J = 0$) determine the Q-branch, and positive values of m ($\Delta J = +1$) create the R-branch. A vibrational transition with a simultaneous rotational transition (Q-branch or $\Delta J = 0$) occur if a rotation around the interatomic axis has a non zero moment of inertia. For diatomic molecules, this is only observed in paramagnetic NO. From Fig. we can already see the discrepancy between the predictions of the Deslandres equation and reality. Equation describes a constant line separation B, but in Fig., the line separation gets smaller as the wave number increases (energy, frequency). This is due to the changing average distance in the transition from v" to v', and therefore $I' \neq I''$ or $B' \neq B''$.



Taking this into consideration, we conclude $\Delta E/h = v + (B' + B'') (J'' + 1) + (B' - B'') (J'' + 1)^2$ for J'' = 0, 1, 2, ... R-branch, $\Delta E/h = v + (B' - B'')J' + (B' - B'')J''^2$ for J'' = 0, 1, 2, ... Q-branch, (6.38) $\Delta E/h = v - (B' + B'')J'' + (B' - B'')J''^2$ for J'' = 1, 2, 3, ... P-branch. In a diatomic molecule, I' > I'', i.e. B' < B'', thus the final term is negative. With that it follows that

in the R-branch the second term is positive, but the third term is negative and whose magnitude increases with the square of J". From that we get a maximum or an edge, which has a shadow toward Red. In the P- and Q-branches, the frequency increases with J when I' > I". In multiatomic molecules, it is possible that r'e < r"e, i.e. I' < I" or B' > B". In this case, the P-branch has an edge which has a shadow toward Purple (violet). If the two considered vibrational states also belong to different electron states (additional electron transition), the moments of inertia differ all the more, and it can happen that in a diatomic molecule I' < I". It can also happen that $\Delta J = 0$ is forbidden, in which case the Q-branch does not apply.

Possible questions (Part B - marks 8)

- 1. Explain the experimental study of molecular spectra.
- 2. What is isotopic effect and explain the effect in molecular spectra.
- 3. Give the theoretical explanation of pure rotation spectra.
- 4. Discuss the rotation-vibration spectra in detail.
- 5. Describe the peculiarities of certain band spectra.
- 6. Explain the graphical representation of complex rotational structure.
- 7. How the pure rotational bands studied experimentally-Explain.
- 8. Discuss the Fortrat diagram about rotational structure.

KARPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE-21 DEPARTMENT OF PHYSICS

CLASS:III BSC PHYSICS

Atomic and Molecular Physics (15PHU501)

MULIPLE CHOICE QUESTIONS

Batch 2015

QUESTIONS	opt1	opt2	opt3	opt4	answer
Nuclei of isotopes will have the	same spin	different spins	zero spin	1/2 spins	different spins
An example of a triatomic molecule is	Ozone	Nitrogen	Carbon monoxide	Hydrogen	Ozone
Which one of the following exhibits rotational spectra	H2	N2	Со	Co2	Co
The microwave spectrum of a molecule yields three rotational	Prolate symmetric				
constants. The molecule is	top	Spherical top	Asymmetric top	Oblate symmetric top	Asymmetric top
he Q band in the vibrational spectrum of acetylene is observed		C - H symmetric		C-H antisymmetric	
in the	C-C streching mode	streching mode	Bending mode	streching mode	C-C streching mode
Which of the following spectroscopic techniques will be					
useful to distinguish between M-SCN & M-NCS binding					
modes	NMR	IR	EPR	Mass	IR
For a diatomic molecule AB, the energy for the rotational					
transition from J=0 to J=1 state is 3.9 cm ⁻¹ . The energy for the					
rotational transition from J=3 to J=4 state would be	3.9 cm- ¹	7.8 cm- ¹	11.7 cm- ¹	15.8 cm-1	15.8 cm-1
For the vibrational Raman spectrum of a homonuclear					
diatomic molecule, the selection rule under harmonic					
approximation is	$\Delta V = 0$ only	$\Delta V = \pm 1$ only	$\Delta V = \pm 2$ only	$\Delta v = 0, \pm 1$	$\Delta V = \pm 1$ only
In the vibrational spectrum of CO ₂ , the number of					
fundamental vibrational modes common in both infrared &					
Raman are	three	two	one	zero	zero
A triatomic molecule of the type AB ₂ shows two IR					
absorption lines & one IR-Raman line. The structure of the					
molecule is	B-B-A (linear)	B-A-B (linear)	B-B-A (bent)	B-A-B (bent)	B-A-B (linear)
If the component of the orbital angular momentum along the					
molecular axis of a heteronuclear diatomic molecule is	P and R branches	P and Q branches	Q and R branches	All the P,Q and R	All the P,Q and R
nonzero, the rotational – vibrational spectrum will show	only	only	only	branches	branches
	Rotational and	Rotational and	Rotational Raman	Vibrational and	Rotational Raman
Bond lengths of homonuclear diatomic molecules can be	vibrational	rotational	and electronic	electronic	and electronic
determined with the help of both	spectroscopy	spectroscopy	spectroscopy	spectroscopy	spectroscopy

he vibrational energy levels, $v=0$ and $v=1$ of a diatomic					
molecule are separated by 2143 cm. Its anharmonicity					
constant ($\omega \gamma$) is 14 cm. The values of ω (in cm) and first					
overtone (cm) of this molecule are respectively	2143 and 4286	2157 and 4286	2157 and 4314	2171 and 4258	2171 and 4258
EPR spectrum of free radical containing nuclei with non zero					
nuclear spin is obtained if the following selection rules are					
observed	$\Delta ms=0$, $\Delta ml=0$	$\Delta ms = \pm 1$, $\Delta ml = 0$	$\Delta ms = \pm 1$, $\Delta ml = \pm 1$	$\Delta ms=0$, $\Delta ml=\pm 1$	$\Delta ms = \pm 1$, $\Delta ml = 0$
	,	,	,	,	,
If the bond length of heteronuclear diatomic is greater in the					
upper vibrational state, the gap between the successive		Decreases non			
absorption lines of P-Branch	Increase non linearly	linearly	Increase linearly	Decrease linearl	Increase non linearly
1			<u>_</u>		
The molecule active in rotational microwave, infrared					
absorption as well as rotational Raman spectra is	CO2	SF6	HC1	Н2	HC1
The second se					
The selection rules for the appearance of P branch in the					
rotational vibrational absorption spectra of a diatomic					
molecule within rigid rotor-harmonic oscillator model are	$\Delta v = \pm 1$ and $\Delta J = \pm 1$	$\Delta v = +1$ and $\Delta J = +1$	$\Delta v = +1$ and $\Delta J = -1$	$\Delta v=-1$ and $\Delta J=-1$	$\Delta v = +1$ and $\Delta J = -1$
The most popular rotational state for HCl (B=8.5 cm) at 300					
K is	2	5	6	7	2
The number of IR active vibrational normal modes of CO	2	3	4	5	3
	Eel >> Evib >>	Eel >> Erot >>	Eel >> Evib >>	Etr >> Evib >>	Eel >> Evib >>
The correct order of different types of energies is	Erot >> E tr	Evib >> E tr	Etr >> E rot	Erot >> E el	Erot >> E tr
		Basis of	Study of		
Which of the following is an application of molecular	Structural	understanding of	energetically excited		
spectroscopy?	investigation	colors	reaction products	All of the mentioned	All of the mentioned
Vibrational spectroscopy involves the transitions falling in the					
spectral range of	100-1000 cm-1	300-3000 cm-1	400-4000 cm-1	500-5000 cm-1	400-4000 cm-1
Which of the following is not a type of bending molecular					
vibration?	Twisting	Stretching	Wagging	Rocking	Stretching
What is the degeneracy of the rotational energy level with $J =$					
4 for a heteronuclear diatomic molecule	1	2	4	9	9
Lines in the rotational microwave spectrum of carbon					
monoxide, CO, were observed at the following frequencies.					
Calculate the centrifugal distortion constant for carbon					
monoxide.	756Hz	189Hz	578Hz	1158Hz	189Hz

aleviate an environment of the Decoder with the feature it.					
alculate, as a wavenumber, the Doppler width of a transition					
in the vibration-rotation spectrum of carbon dioxide that					
occurs at a wavelength of 9.1µm for a temperature of 300 K.	0.205 m-1	0.002 cm-1	0.170 cm-1	0.059 cm-1	0.002 cm-1
How many normal modes of vibrational are possible for a					
benzene molecule?	6	30	12	31	30
Word for three angles is	octahedra	tetrahedral	trigonal	trigonal planar	trigonal
			electrostatic		electrostatic
Metallic bonding is very strong because of	lattice	volatility	attraction	All of Above	attraction
		dipole-dipole			
Degree of polarity of a molecule is measured as	dipole moment	interaction	dipole reaction	All of Above	dipole moment
			electrons in outer	electrons in outer	electrons in outer
			shells of metals are	shells of non-metals	shells of metals are
	hydrogen gas is given	electrons of outer	transferred to non-	are transferred to	transferred to non-
When metals combine with non-metals,	off	shells are shared	metals atoms	metals atoms	metals atoms
Molecules which have permanent dipole are known as	polar	non-polar	dipolar	tripolar	polar
The infrared spectrum of a diatomic molecule exhibit				-	-
transitions at 2144, 4262 and 6354 cm	2157	2170	2183	2196	2170
corresponding to excitation from the ground state to the first,					
second and third vibration states respectively.					
Which molecule has a bent shape	CO2	BeH2	H2O	NF3	H2O
Pick out the pair of species having identical shapes for both					
the molecules.	BF3, PCl3	PF, IF5	CF4,SF4	XeF2, CO2	XeF2, CO2

Time:2 hours

Maximum:50 marks

PART-A (20x1=20Marks) Answer all questions

1. Cathode rays produced yellow fluorescence when strike

a.Alumina b.sodium c.tin stone d.potassium chromate

2. By e/m ratio of cathode rays we deduce they are

a.Protons b.electrons c.neutrons d.anti neutron

- Magnetic properties of cathode rays were discovered in year a.1897 b.1895 c.1893 d.1890
- Aluminium foil causes cathode rays to a.pass through it b.struck in it c.distort d.loose their identity
- 5. Earliest version of Cathode Ray Tube which used cold cathode diode was invented by German Physicist is a.Thomas Edison b.Horace Day c.Fredinand Braun d.Oliver Evans
- Earliest version of Cathode Ray Tube was invented in a.1859 b.1839 c.1844 d.1897
- Number of electrons from grid reaching screen determines the

 a. bightness level b.picture quality c.sound quality d.both A and B
- In C.R.O, grid is connected to the a.positive potential b.negative potential c.AC source d.DC source
- The process of emission of electrons from metal by UV rays is a.Photoelectric emission b. Thermionic emission c. Secondary emission d. Field emission

- 10. The electrons are emitted in the photoelectric effect from a metal surface?a. only if the frequency of incident radiation above a certain threshold value b. Only if the temperature of the surface is high c. At the rate of independent of the nature of the metal d. None of these
- 11. Photoelectric effect can be explained by assuming that light?a.Is a form of transverse wave b.Is a form of longitudinal wave c.Can be polarized d. Consists of quanta
- 12. Scattered x-ray beams approach detector screena.perpendicularly b.parallel c.anti paralleld. at an angle
- 13. A good x-ray source should produce x-rays of narrow beam anda.parallel x-rays b. perpendicular x-rays c.anti parallel x-rays d. anti perpendicular x-rays
- 14. Pressure range which is applied in discharge tube is
 a.9000-10000 b.7000-9000 c.4000-5000
 d. 5000-10000
- 15. Voltage which is applied in discharge tube is dependent upon

a.length of tube b. width of tube c. tube nature d.wideness

16. To discover electrons gas discharge tube is fitted with

a. two electrodes b.three electrodes c.four electrodes d. $% \left({{{\bf{n}}_{{\rm{n}}}}} \right)$

five electrodes

- 17. Tube to discover electrons is fitted with a.vapors b.liquids c.solids d.none
- Rutherford in his atomic model could not explain behavior of

a.electrons b. protons c.neutrons d.neutrino

19. Particles which were deflected backwardsin Rutherford's experiment were hit uponby

a.lnucleus b.empty space c.electrons d.none

20. According to structure of atom electron should fall in

a. nucleus b.shell c.outer environment d.space

PART-B (3x10=(30Marks)

Answer all the questions

21. a).Write short note on Cathode rays, positive rays and x rays.

OR

b)Determine e/m by Thomson's method.

22. a)Explain in detail about Langevin's theory of diamagnetism.

OR

b)Explain electron theory and its applications.

23. a)Explain in detail about Bohr atom model and its applications.

OR

b) Give theory of Rutherford Model of the atom and explain the demerits.

PART-A (20x1=20Marks)

Answer all questions

- 1. Cathode rays produced yellow fluorescence when strike a.Alumina b.sodium c.**tin stone** d.potassium chromate
- 2. By e/m ratio of cathode rays we deduce they are a.Protons b.**electrons** c.neutrons d.anti neutron
- 3. Magnetic properties of cathode rays were discovered in year a.**1897** b.1895 c.1893 d.1890
- 4. Aluminium foil causes cathode rays to a.**pass through it** b.struck in it c.distort d.loose their identity
- Earliest version of Cathode Ray Tube which used cold cathode diode was invented by German Physicist is

 a. Thomas Edison b. Horace Day c. Fredinand Braun d. Oliver Evans
- Earliest version of Cathode Ray Tube was invented in a.1859 b.1839 c.1844 d.1897
- 7. Number of electrons from grid reaching screen determines the a. **bightness level** b.picture quality c.sound quality d.both A and B
- 8. In C.R.O, grid is connected to the a.positive potential b.**negative potential** c.AC source d.DC source
- The process of emission of electrons from metal by UV rays is

 a.Photoelectric emission b. Thermionic emission c. Secondary emission d. Field
 emission
- 10. The electrons are emitted in the photoelectric effect from a metal surface?a. only if the frequency of incident radiation above a certain threshold value b. Only if the temperature of the surface is high c. At the rate of independent of the nature of the metal d. None of these
- 11. Photoelectric effect can be explained by assuming that light?a.Is a form of transverse wave b.Is a form of longitudinal wave c.Can be polarized d.Consists of quanta
- 12. Scattered x-ray beams approach detector screen a.perpendicularly b.parallel c.anti parallel d. at an angle
- 13. A good x-ray source should produce x-rays of narrow beam anda.parallel x-raysb. perpendicular x-raysc. anti parallel x-raysd. anti perpendicular x-rays
- 14. Pressure range which is applied in discharge tube is

a.**9000-10000** b.7000-9000 c.4000-5000 d. 5000-10000

- 15. Voltage which is applied in discharge tube is dependent upon a.**length of tube** b. width of tube c. tube nature d.wideness
- 16. To discover electrons gas discharge tube is fitted witha. two electrodes b.three electrodes c.four electrodes d. five electrodes
- 17. Tube to discover electrons is fitted with a.vapors b.liquids c.solids d.none
- 18. Rutherford in his atomic model could not explain behavior of a.electrons b. protons c.neutrons d.**neutrino**
- 19. Particles which were deflected backwards in Rutherford's experiment were hit upon by

a.nucleus b.empty space c.electrons d. none

20. According to structure of atom electron should fall in

a. nucleus b.shell c.outer environment d.space

PART-B (3x10=30Marks)

Answer all the questions

21.a).Write short note on Cathode rays, positive rays and x rays.

Cathode rays, positive rays and X rays

Cathode rays are streams of fast moving electrons.

Properties:

(i) Cathode rays are emitted normally from the cathode surface. Their direction is independent of the position of the anode.

(ii) Cathode rays travel in straight lines. (Cast shadows of objects placed in their path).

(iii) Cathode rays exert mechanical force on the objects they strike.

(iv) Cathode rays produce heat when they strike a material surface.

(v) Cathode rays produce fluorescence when they strike a number of crystals, minerals and slats.

(vi) When cathode ray strikes a solid object, specially a metal, X-rays are emitted from the object. (It is not safe to use Geissler tube at potential differences above about 5-6 kV because of this X-ray emission, generated by striking of cathode rays of metal anode).

(vii) Cathode rays are deflected by an electric field and also by a magnetic field. The direction of deflection is the same as that of a stream of negatively charged particles.

(viii) Cathode rays ionize the gas through which they are passed.

(ix) Cathode rays can penetrate thin foils of metal.

(x) Cathode rays affect photographic plates.

(xi) Cathode rays are found to have velocity upto one tenth of the velocity of light. The e/m of electrons was measured by J.J. Thomson (so credit of discovering electron is given to Thomson).

The e of electron was measured by R.A./Millikan e/m = 1.759×10^{11} c/kg e = 1.602×10^{-19} C m = 9.09×10^{-31} kg

The e/m of an electron is called the specific charge of an electron.

If one includes the relativistic variation of mass with speed then specific charge of an electron decreases with the increase in the velocity of the electron.

Positive Rays :

Positive rays are sometimes known as the canal rays. These were discovered in 1896 by Goldstein. If the cathode of a discharge tube has holes in it and the pressure of the gas is around 1 mm of mercury than faint luminous glow come out from each hole on the backside of the cathode.

This shows that something is coming out of the holes. These are called canal rays or positive rays.



Origin of positive rays :

When potential difference is applied across the electrodes, electrons (cathode rays) are emitted from the cathode. As they move towards anode, they gain energy.

These energetic electrons which collide with the atoms of the gas in the discharge tube, they ionize the atoms. The positive ions formed at various places between cathode and anode, travel towards the cathode. Since during their motion, the positive ions when reach the

cathode, some pass through the holes in the cathode. These stream of positive ions are the positive rays or canal rays.

If the discharge tube is totally evacuated then no positive rays are produced. Thus positive rays are positive ions of the gas in the tube. Properties of positive rays were studied by Thomson. The q/m of the hydrogen was found to be $\sim 10^8$ C/kg much less then the e/m of electron $\sim 10^{11}$ C/kg indicating that mass of positive rays is much greater than that of electrons.

Properties of Positive Rays :

(i) These are positive ions having same mass if the experimental gas does not have isotopes. However if the gas has isotopes then positive rays are group of positive ions having different masses.

(ii) They travel in straight lines and cast shadows of objects placed in their path. But the speed of the positive rays is much smaller than that of cathode rays.

(iii) They are deflected by electric and magnetic fields but the deflections are small as compared to that of cathode rays.

(iv) They show a spectrum of velocities. Different positive ions move with different velocities.

(v) q/m ratio of these rays depends on the nature of the gas in the tube (while in case of the cathode rays q/m is constant and does not depend on the gas in the tube).

(vi) They carry energy and momentum.

(vii) They cause ionization (which is much more than that produced by cathode rays).

(viii) They cause fluorescence (in ZnS or CdS screen) and affect photographic plates.

(ix) They have a little penetration power (but much less in comparison to cathode rays)

X-Rays

W. C. Rontgen conducted various experiments to study the discharge of electricity through gases and accidently discovered X-rays. He used a glass tube fitted with two electrodes cathode and anode. An exhaust pump was connected through a side tube and a high electric potential of about 25 kV was applied across the electrodes. Rontgen made the following important observations:



(a) When air inside the tube was at atmospheric pressure there was no discharge of electricity through it.

(b) When pressure inside the tube was reduced to few cm of mercury, a feeble discharge of electricity occurred between the electrodes. At the same time air inside the tube started giving visible light.

(c) When air pressure was reduced to 10^{-3} mm of mercury, air lumininescence gets disappeared but the glass walls of the tubes starts glowing. Rontgen concluded that this glow was due to some invisible penetrating radiations from anode that were falling on the glass and producing fluorescence. Rontgen did not know much about the nature of these rays and therefore, he called them X-rays.

(B) Explanations: Rontgen explained the production of these X-rays due to the bombardment of high velocity electrons on anode. Due to low pressure (10^{-3} mm) inside the tube, the air gets ionised producing a few electrons and the positive ions.

The positive ions are highly accelerated towards the cathode, these ions knock out electrons from the cathode. The released electrons move with tremendous speed towards highly positive anode. They strike the anode surface and produce X-rays. On his experimental basis, Rontgen observed that in order to produce X-rays, the following three things are required.

- (a) The source of electron
- (b) Means of accelerating these electrons to high speeds.
- (c) Anode or target on which these high speed electrons should strike to produce X-rays.

OR

b)Determine e/m by Thomson's method.

Introduction

J.J Thomson was the first scientist who measured charge to mass ratio (e/m) of an electron.

Principle

When a narrow beam of charged particles are projected at constant speed (v) across a magnetic field in a direction perpendicular to the field, the beam of particles experiences a force, which makes them move in a circular path.

Apparatus

It consists of a highly evacuated glass tube, fitted with electrodes. Electrons are produced by heating a tungsten filament electrically. Electrons are made to accelerate and form a beam by passing through discs A and B. They are passed through electric and magnetic field. Finally they fall on zinc sulphide screen.



Theory

Actually electrons moving side ways are also directed towards the screen by applying a –ve potential on a hollow cylinder (c) open on both sides surrounding the filament. Electrons are accelerated by applying a potential difference of above 1000 V between the filament and disc A. A further potential difference of 500 V is applied between the discs A and B. The arrangement focuses the beam to the hole of the disc B from where it is further proceeds to a straight line. When beam of electrons enters a magnetic field it moves in a circular track. The force experienced by the electron is

$$\mathbf{F}_{\mathbf{m}} = \mathbf{evB} - \cdots - (1)$$

This magnetic field provides necessary centripetal force to electron so that it follows a
i.e. $F_m = F_c$ $evB = mv^2/r$ eB = mv/r

e/m = v/Br ----(2)

By knowing the values of v, B and r, value of e/m can be determined.

Radius of curvature of the path

If r is the radius of curvature of circular path, 'a' is the distance b/w 'O' and 'O'', and 'b' is the distance b/w electron gun and screen then by using the property of chord:

$AD \times OD = BD \times DO$

(2r-a)(a) = b.b

 $2\mathbf{ra}\cdot\mathbf{a}^2 = \mathbf{b}$

Since 'a' is very small as compared to '2r', so we neglect 'a²'. $2ra = b^2$

 $r = b^2/2a$

Determination of the velocity (First Method)

The electrons are first accelerated by applying a potential (V) b/w discs A and B before entering the magnetic field.

A 2r-a b a o 0

K.E = V.e Or $1/2mv^2 = Ve$ $v = (2Ve/m)^{1/2}$ Putting the value of v in eq. (2) e/m = v/Br $e/m = (2Ve/m)^{1/2}/Br$ Squaring on both sides $e^2/m^2 = 2Ve/m/B^2r^2$ Or $e/m = 2Ve/B^2r^2$

22.a)Explain in detail about Langevin's theory of diamagnetism.

Langevin gave a satisfactory explanation of diamagnetism on the basis of electron theory the basic principle of which ia Lenz's law in electromagnetic induction which states that when a magnetic flux linked with electric current due to revolving electrons is changed, an induced current is set up in such a direction as to oppose the change in flux. It is manifested by the very small and negative value of magnetic susceptibility.

If ω_0 be the frequency of electron in the absence of applied field and r is the radius of the loop then:

$$\mathbf{F}_{o} = \mathbf{m}\omega_{o}^{2} \mathbf{r} = \mathbf{Z}\mathbf{e}^{2}/4\pi\varepsilon_{o}\mathbf{r}^{2}$$

Lorentz force acting on the electron moving with velocity v is given by

$$\mathbf{F}_{\mathrm{L}} = -\mathbf{B}\mathbf{e}\mathbf{v} = -\mathbf{B}\mathbf{e}\boldsymbol{\omega}\mathbf{r}$$

 $\boldsymbol{\omega} = \pm \boldsymbol{\omega}_{\mathrm{o}} - \mathbf{e}\mathbf{B}/2\mathbf{m}$

The -ve sigm indicates that these electrons whise orbital magnetic moments are parallel to the magnetic field are slowed downand those with moments antiparallel are speeded by an amount eB/2m : LARMOR THEOREM.

The additional current produced due to change in frequency of the electron is given by $I = -e^2B/4\pi m$ and the change in magnetic moment is given by $\Delta Ma = -e^2r^2B/4m$

$$<\mathbf{r}^{2}> = <\mathbf{x}^{2}> +<\mathbf{y}^{2}>$$
 and $<\mathbf{r}_{0}^{2}> = <\mathbf{x}^{2}> +<\mathbf{y}^{2}> +<\mathbf{z}^{2}>$

Magnetization,

Susceptibility,

 $< r^{2} > = 2/3 < r_{0}^{2} >$ $M = -e^{2} Z \mu_{0} HN < r_{0}^{2} > /6m$ $\chi = M/H$ $= -e^{2} Z \mu_{0} N < r_{0}^{2} > /6m$

Since χ is independent of temperature so the diamagnetic behavior of the material does not change into temperature.

According to quantum theory, the magnetic moments are quantized, so they can orient only in specific direction with respect to the magnetic field.

 $\mu = -g \mu_B J$ μ_B is called Bohr magneton

g = 1 + (J(J+1) + S(S+1) - L(L+1))/2J(J+1)

Using Maxwell Boltzmann statistics, magnetization is given as

 $M = N \sum m_I g \mu_B e^{mJ g \mu B/k\beta T} / e^{mJ g \mu B/k\beta T}$

CASE I At ordinary temperatures $Bm_J g \mu_B / k_\beta T \ll 1$ Using the exponential series and $\sum m_J^2 = (1/3)(J+1)(2J+1)$

$$\begin{split} M &= Ng^2 \mu_B{}^2 \mu_0 \ H \ J(J+1)/3k_\beta T \\ \chi &= M/H \qquad \qquad \chi_{para} = Ng^2 \mu_B{}^2 \mu_0 \ P_{eff}{}^2 \qquad \qquad Peff = g \sqrt{J(J+1)} \end{split}$$

CASE II At low temperature and strong magnetic field $Bm_J g \mu_B / k_\beta T$ is not less than unity

Let $x=B g \mu_B / k_\beta T$ $M = \sum Bm_J g \mu_B emJx$

As $\sum mJ x$ is a geometric progression with (2J+1) terms

$$\begin{split} M &= Ng\mu_B \ d/dx \ (ln(\ e^{Jx} \ (1-e^{-(2J+1)x}/(1-e^{-x})))) \\ &= NgJ\mu_B \ B_J(a) \\ BJ(a) &= (2J+1)/2J \ coth \ (2J+1)a/2J \ - 1/2J \ coth \ (a/2J), \\ Brillouin \ function \ a &= Jg\mu B/k_BT \end{split}$$

In the limit J tends to ∞ Brillouin function approaches the Langevin function i.e., infinite number of possible orientations are allowed.

OR

b) Explain electron theory and its applications.

In solid-state physics, the **free electron theory** is a simple model for the behaviour of valence electrons in a crystal structure of a metallicsolid. It was developed in 1927, principally by Arnold Sommerfeld who combined the classical Drude model with quantum mechanical Fermi–Dirac statistics and hence it is also known as the **Drude–Sommerfeld model**.

Given its simplicity, it is surprisingly successful in explaining many experimental phenomena, especially

- the Wiedemann–Franz law which relates electrical conductivity and thermal conductivity;
- the temperature dependence of the electron heat capacity;
- the shape of the electronic density of states;
- the range of binding energy values;
- electrical conductivities;
- Thermal electron emission and field electron emission from bulk metals.

The free model follows the Drude model in which four basic assumptions are taken into account:

- Free electron approximation: The interaction between the ions and the valence electrons is mostly neglected, except in boundary conditions. The ions only keep the charge neutrality in the metal. In contrast with Drude model, the ions are not necessarily the source of collisions.
- **Independent electron approximation**: The interactions between electrons are ignored. The electrostatic fields in metals are weak because of the screening effect.
- Relaxation-time approximation:: There is some unknown scattering mechanism such

that the electron probability of collision is , where is known as the relaxation time and represents the average time between collisions. The collisions do not depend on the electronic configuration.

• **Pauli exclusion principle:** each quantum state of the system must be occupied by a single electron. This restriction of available electron states is taken into account by Fermi–Dirac statistics (see also Fermi gas). Main predictions of the free-electron model are derived by the Sommerfeld expansion of the Fermi–Dirac occupancy for energies around the Fermi level.

The crystal lattice is not explicitly taken into account in the free electron model, but a quantum-mechanical justification is given by Bloch's Theorem: an unbound electron moves in a periodic potential as a free electron in vacuum, except for the electron mass m becoming an effective mass m^* which may deviate considerably from m (one can even use negative effective mass to describe conduction by electron holes). Effective masses can be derived

from band structure computations that were not originally taken into account in the free electron model.

23.a)Explain in detail about Bohr atom model and its applications.

Niels Bohr proposed the Bohr Model of the Atom in 1915. Because the Bohr Model is a modification of the earlier Rutherford Model, some people call Bohr's Model the Rutherford-Bohr Model.

The modern model of the atom is based on quantum mechanics. The Bohr Model contains some errors, but it is important because it describes most of the accepted features of atomic theory without all of the high-level math of the modern version. Unlike earlier models, the Bohr Model explains the Rydberg formula for the spectral emission lines of atomic hydrogen. The Bohr Model is a planetary model in which the negatively-charged electrons orbit a small, positively-charged nucleus similar to the planets orbiting the Sun (except that the orbits are not planar). The gravitational force of the solar system is mathematically akin to the Coulomb (electrical) force between the positively-charged nucleus and the negatively-charged electrons.

MAIN POINTS OF THE BOHR MODEL

- Electrons orbit the nucleus in orbits that have a set size and energy.
- The energy of the orbit is related to its size. The lowest energy is found in the smallest orbit.
- Radiation is absorbed or emitted when an electron moves from one orbit to another

BOHR MODEL OF HYDROGEN

The simplest example of the Bohr Model is for the hydrogen atom (Z = 1) or for a hydrogenlike ion (Z > 1), in which a negatively-charged electron orbits a small positively-charged nucleus. Electromagnetic energy will be absorbed or emitted if an electron moves from one orbit to another.

Only certain electron orbits are permitted. The radius of the possible orbits increases as n^2 , where n is the principal quantum number. The $3 \rightarrow 2$ transition produces the first line of the Balmer series. For hydrogen (Z = 1) this produces a photon having wavelength 656 nm (red light).

PROBLEMS WITH THE BOHR MODEL

- It violates the Heisenberg Uncertainty Principle because it considers electrons to have both a known radius and orbit.
- The Bohr Model provides an incorrect value for the ground state orbital angular momentum.
- It makes poor predictions regarding the spectra of larger atoms.
- It does not predict the relative intensities of spectral lines.
- The Bohr Model does not explain fine structure and hyperfine structure in spectral lines.
- It does not explain the Zeeman Effect.

OR

b) Give theory of Rutherford Model of the atom and explain the demerits.

Also called **nuclear atom** or **planetary model of the atom**, description of the structure of atoms proposed (1911) by the New Zealand-born physicist Ernest Rutherford. The model described the atom as a tiny, dense, positively charged core called a nucleus, in which nearly all the mass is concentrated, around which the light, negative constituents, called electrons, circulate at some distance, much like planets revolving around the Sun.



Diagram of the Rutherford atomic model

The nucleus was postulated as small and dense to account for the scattering of alpha particles from thin gold foil, as observed in a series of experiments performed by undergraduate Ernest Marsden under the direction of Rutherford and German physicist Hans Geiger in 1909. A radioactive source capable of emitting alpha particles (i.e., positively charged particles, identical to the nucleus of the helium atom and 7,000 times more massive than electrons) was enclosed within a protective lead shield. The radiation was focused into a narrow beam after passing through a slit in a lead screen. A thin section of gold foil was

placed in front of the slit, and a screen coated with zinc sulfide to render it fluorescentserved as a counter to detect alpha particles. As each alpha particle struck the fluorescent screen, it would produce a burst of light called scintillation, which was visible through a viewing microscope attached to the back of the screen. The screen itself was movable, allowing Rutherford and his associates to determine whether or not any alpha particles were being deflected by the gold foil.

Problems with the Rutherford Model

In the years after Rutherford discovered the nucleus, chemists and particle physicists discovered that electron behavior was much more complicated than depicted in the Rutherford model. Electrons did not travel in set paths, their speeds were inconsistent, and their location around the nucleus could change based on how much energy they had. It was no longer accurate to depict electrons as traveling in straight paths. Instead, physicists began to represent them by an electron cloud that could suggest where electrons might be at any given time. The electron cloud model is the current model of the atom.

The Bohr Model has an atom consisting of a small, positively-charged nucleus orbited by negatively-charged electrons. Here's a closer look at the Bohr Model, which is sometimes called the Rutherford-Bohr Model.

		Atomic and more	ecular Physics Reg. No. :				
Ouration: 2 hours Maximum: 60 marks		Maximum: 60 marks	9. The rate of radioactive disintegration at any instant directly proportional to number of				
	PART – A (2	20 x 1=20 Marks)	a. atoms b. protons c. electrons d. neutrons				
Ans wer all questions			10. The vector atom model is an extension of the				
1.	In continuous X	-Ray spectra the minimum	a.Rutherford model b. Bohr model				
	wavelength is		c. Sommerfield atom model d. Rutherford-Bohr Sommerfeld atom model				
	a. proportional proportional tc. zero d. one	to applied voltage b. inversely to applied voltage	11. The original unit for measuring the amour of radioactivity was				
2.	The wavelength	of the continuous spectrum	a. Ohm. b. Kelvin c. Watt d. Curie				
	a. dependent or independent of	n target b. equal to target c. of target d. none	12. For the structural analysis of the crystal, X-rays are used because				
3.	The features of studied in the ye	f continuous spectrum was ear of	a. X-rays have wavelengths of the order o interatomic spacingb. X-rays are highly penetrating radiation				
	a. 1920 b. 1965	c. 1915 d. 1925	c. wavelength of X-rays are of the order o nuclear size				
4.	The waveleng spectrum is	th of the characteristic	d. the wavelength of X-rays is of the order of 546 nm				
	a. dependent or independent of	n target b. equal to target c. of target d. none	13. The phenomenon of radio activity wa discovered by				
5.	The characterist	tic spectrum was studied in	a. H. Becquerel b. Einstein c. Thomson of Edison				
	a. 1987 b. 1908.	c. 1876 d. 1879	14. What elements did Marie Curie and Piere Curi discovered.				
6.	Systematic and characteristic sp	comprehensive study of the ectrum was made by	a. radium and polonium b. radium an cesium c. carbon d. argon				
	a. Einstein b. Thomson c. Rutherford d.		15. The substance which emit radiations are called				
7.	According to S electron around	ommerfeld the path of the the nucleus is	a. radioactive elements b. carbon active elements c. fluorescence elements of none of above.				
	a. Ellipse b. Cir	cle c. square d. Spiral	16. Alpha particle is anucleus				
8.	Sommerfeld mo	del did not explain the	a. helium b. hydrogen c. oxygen o nitrogen				
	a. Zeeman effe	ct b. Thermoelectric effect. c.	17. Gamma particle havewavelengt				

CIA-II

B.Sc Degree Examinations

15PHU501

- a. long b. short c. very long d. none of above
- 18. Beta particle are deflected by
 - a. electric field b. magnetic field c. electric and magnetic field d. all of above
- 19. The half life period is inversely proportional to its
 - a. decay constant b. time constant c. number of atoms d. number of electrons
- 20. In alpha disintegration number of atoms decreaseswith increase of time.
 - a. linearly b. elliptically c. logarithmically d. exponentially

PART – B $(3 \times 10 = 30 \text{ Marks})$ Answer all the questions

21. (a) Write a note on continuous and characteristic X- ray spectra..

(OR)

(b) Describe a Sommerfeld atom model and give the drawbacks of it.

22. (a) Describe the vector atom model of the atom and explain the different quantum numbers associated with it

(OR)

(b) Explain the electronic structure of atoms and fine structure of spectral lines.

- 23. (a) Explain in detail the alpha disintegration. (OR)
 - (b) What is beta disintegration and explain it.

PART – A (20 x 1=20 Marks)

Answer all questions

- 1. In continuous X-Ray spectra the minimum wavelength is
 - a. proportional to applied voltage **b. inversely proportional to applied voltage**
 - c. zero d. one
- 2. The wavelength of the continuous spectrum is
 - a. dependent on target b. equal to target c. independent of target d. none
- 3. The features of continuous spectrum was studied in the year of
 - a. 1920 b. 1965 c. 1915 d. 1925
- 4. The wavelength of the characteristic spectrum is
 - a. dependent on target b. equal to target c. independent of target d. none
- 5. The characteristic spectrum was studied in the year of
 - a. 1987 b. 1908. c. 1876 d. 1879
- 6. Systematic and comprehensive study of the characteristic spectrum was made by
 - a. Einstein b. Thomson c. Rutherford d. Moseley
- 7. According to Sommerfeld the path of the electron around the nucleus is
 - a. Ellipse b. Circle c. square d. Spiral
- 8. Sommerfeld model did not explain the
 - a. Zeeman effect b. Thermoelectric effect. c. Seebeck effect. d. all of above
- 9. The rate of radioactive disintegration at any instant directly proportional to number of
 - a. **atoms** b. protons c. electrons d. neutrons
- 10. The vector atom model is an extension of the

 a.Rutherford model
 b. Bohr model

 c. Sommerfield atom model
 d. Rutherford-Bohr Sommerfeld atom model
- 11. The original unit for measuring the amount of radioactivity was
 - a. Ohm. b. Kelvin c. Watt d. Curie
- 12. For the structural analysis of the crystal, X-rays are used because

a. X-rays have wavelengths of the order of interatomic spacing

- b. X-rays are highly penetrating radiation
- c. wavelength of X-rays are of the order of nuclear size
- d. the wavelength of X-rays is of the order of 546 nm
- 13. The phenomenon of radio activity was discovered by
 - a. **H. Becquerel** b. Einstein c. Thomson d. Edison
- 14. What elements did Marie Curie and Piere Curie discovered.
 - a. radium and polonium b. radium and cesium c. carbon d. argon
- 15. The substance which emit radiations are called
 - a. **radioactive elements** b. carbon active elements c. fluorescence elements d. none of above.
- 16. Alpha particle is anucleus
 - a. helium b. hydrogen c. oxygen d. nitrogen
- 17. Gamma particle havewavelength
 - a. long b. **short** c. very long d. none of above
- 18. Beta particle are deflected by
 - a. electric field b. magnetic field c. electric and magnetic field d. all of above
- 19. The half life period is inversely proportional to its
 - a. decay constant b. time constant c. number of atoms d. number of electrons
- 20. In alpha disintegration number of atoms decreaseswith increase of time.
 - a. linearly b. elliptically c. logarithmically d. exponentially

$PART - B (3 \times 10 = 30 Marks)$

Answer all the questions

- 21.(a) Write a note on continuous and characteristic X- ray spectra
- X-ray spectra continuous and characteristic X-ray spectra

The spectrum from an X-ray tube contains two distinct parts :

(i) Continuous X-ray spectra (ii) Characteristic X-ray spectra

X-ray spectra - continuous and characteristic X-ray spectra.

The spectrum from an X-ray tube contains two distinct parts :

(i) Continuous X-ray spectra

It consists of radiations of all possible wavelengths, from a certain lower limit to higher value continuously, as in the case of visible light.

Origin - Continuous X-ray spectra

X-rays are produced, when high velocity electrons strike the target material of high atomic number. It has also been mentioned in the production of X-rays, that most of the energy of the electrons goes into the heating of the target material.



A few fast moving electrons penetrate deep into the interior of the atoms of the target material and are attracted towards the nuclei by the attractive forces of their nuclei. Due to these forces, the electrons get deflected from their original path. As a result of this, the electrons are decelerated, and hence energy of the electron decreases continuously. This loss of energy during retardation is given off in the form of X-rays of continuously varying wavelength. The X - rays consist of continuous range of frequencies upto a maximum frequency λ_{max} or minimum wave length λ_{min} . This is called as continuous X - rays. The minimum wave length depends on the anode voltage. If V is the potential difference between the anode and the cathode

$$eV = hv_{max} = hc / \lambda_{min}$$

The minimum wavelength of the given radiation is,

 $\lambda_{min} = hc \ /e \, V$

where h is Planck's constant, c is the velocity of light and e, the charge of the electron. Substituting the known values in the above equation.

$$\lambda_{\rm min} = 12400/{\rm V}~{\rm A}^0$$

For the given operating voltage, the minimum wave length is same for all metals.

(ii) Characteristic X-ray spectra

It consists of definite, well defined wavelengths superimposed on the continuous spectrum. These spectral lines generally occur in the form of small groups and are characteristic of the material of the target.



Origin - Characteristic X-ray spectra

Few of the fast moving electrons having velocity of about $(1/10)^{th}$ of the velocity of light may penetrate the surface atoms of the target materials and knock out the tightly bound electrons even from the inner most shells (like K, L shells) of the atom. Fig shows the case, when the fast moving electrons knock off one electron from K-Shell and the vacancy is filled by the nearby electron from the L shell. During this transition, the energy difference is radiated in the form of X-rays of very small wave length. This corresponds to K_{α} - line of the series. The frequency v_1 of this line is given by the relation ($E_K - E_L$) = hv_1 . Suppose, the electron from M shell jumps to the K shell, it gives out K_{β} line and so on. If an electron jumps from the M-Shell to the vacant state in L-Shell, it contributes L_{β} and so on. The frequency of radiation depends upon the target material. The X-ray spectra consists of sharp lines and is the characteristic of target material. Hence this spectra is known as characteristic spectra.

(OR)

b) Describe a Sommerfeld atom model and give the drawbacks of it.

Sommerfeld atom model and its Drawbacks



In order to explain the observed fine structure of spectral lines, Sommerfeld introduced two main modifications in Bohr's theory.

Sommerfeld atom model

In order to explain the observed fine structure of spectral lines, Sommerfeld introduced two main modifications in Bohr's theory.

(i) According to Sommerfeld, the path of an electron around the nucleus, in general, is an ellipse with the nucleus at one of its foci.

(ii) The velocity of the electron moving in an elliptical orbit varies at different parts of the orbit. This causes the relativistic variation in the mass of the moving electron.

Now, when elliptical orbits are permitted, one has to deal with two variable quantities.

(i) The varying distance of the electron from the nucleus (r).

(ii) The varying angular position of the electron with respect to the nucleus i.e the azimuthal angle φ (Fig).

To deal with these two variables, two quantum numbers are introduced

(i) The principal quantum number n of Bohr's theory, which determines the energy of the electrons, and

(ii) a new quantum number called orbital (or azimuthal) quantum number (l) which has been introduced to characterize the angular momentum in an orbit i.e., it determines the orbital angular momentum of the electron. Its values vary from zero to (n-1) in steps of unity.

This orbital quantum number (l) is useful in finding the possible elliptical orbits. The possible elliptical orbits are such that

b/a = l+1/n

where a and b are semi-major and semi-minor axes respectively of the ellipse.

According to Sommerfeld's model, for any principal quantum number n, there are n possible orbits of varying eccentricities called sub-orbits or sub-shells. Out of n subshells, one is circular and the remaining (i.e., n-1) are elliptical in shape.

These possible sub-orbits possess slightly different energies because of the relativistic variation of the electron mass.

Consider the first energy level (n=1). When n = 1, l = 0 i.e., in this energy level, there is only one orbit or sub-shell for the electron. Also, when a = b, the two axes of the ellipse are equal. As a result of this, the orbit corresponding to n=1 is circular. This subshell is designated as *s* sub-shell. Since, this sub-shell belongs to n=1, it is designated as 1s (Fig a).



Similarly, for the second energy level n=2, there are two permissible sub-shells for the electrons. For n=2, l can take two values, 0 and 1.

When n = 2, l = 0.

b/a= 0+1/2 =1/2

or

$$b=a/2$$

This subshell corresponding to l = 0 is elliptical in shape and is designated as 2s.

when n = 2, l = 1.

b/a= 1+1/2 =2/2 =1

or

b=a

This sub-shell corresponding to l = 1 is circular in shape and is designated as 2p (Fig b).

For n = 3, *l* has three values 0, 1 and 2, i.e. there are three permissible sub-shells for the electrons.

when n = 3, l = 0. b/a = (0+1)/3 = 1/3 = 1 or b=a/3when n = 3, l = 1. b/a = (1+1)/3 = 2/3 = 1 or b=2a/3and when n = 3, l = 2. b/a = (2+1)/3 = 3/3 = 1 or b=a

The sub-shells corresponding to l = 0, 1 and 2 are designated as 3s, 3p and 3d respectively. The circular shell is designated as 3d and the other two are elliptical in shape (Fig c).

It is common practice to assign letters to *l*-values as given below:

Orbital quantum number 1	:	0	1	2	3	4
electron state :		S	р	d	f	g

Hence, electrons in the l = 0, 1, 2, 3 states are said to be in the s, p, d, f states.

22.(a) Describe the vector atom model of the atom and explain the different quantum numbers associated with it.

The vector atom model

The vector atom model basically deals with the *total angular momentum* of an atom, which is results of the combination of orbital and spin angular momenta. The two fundamental features of the vector atom model are (i) space quantization of orbits and (ii) spinning electron hypothesis.

Space Quantization

The angular momentum is a vector quantity, hence its direction must be specified to describe it completely. To specify the orientation or direction of an orbit, a reference is required. The direction of the magnetic field applied to the atom is chosen as the reference line.

The rotating electron about the nucleus forms a current loop which has a magnetic moment $\mu = IA$, where I is the current in the loop and A is the area vector. The energy of loop-field system is given by $U = -\mu$. $B = -|\mu| |B| \cos\theta$, where θ is the angle between the magnetic moment θ and magnetic field B. As such classically any energy value between $-\mu B$ to $+\mu B$ is possible for the loop.

An electron orbiting around the nucleus in an atom possess angular momentum L which interacts with external applied magnetic field B. According to quantum theory, there are fixed directions of magnetic moment 1.1. of magnetic dipole (formed by closed loop motion of electron about nucleus) with respect to the magnetic field B. The magnetic moment μ and angular momentum L can be related as

$$\mu = \left(\frac{e}{2m_e}\right)L$$

This relationship is true from both classical and quantum mechanical point of view. Since discrete directions of μ are allowed, as such the direction of L will also be quantized in space. Here, the quantization refers the projection of L along the Z-direction (L₂) which can have discrete values only. The orbital magnetic quantum number m_l gives the direction of L and tells the possible components of L in the Z-direction (the field direction). The phenomenon of quantization of L in the direction of magnetic field B is commonly known as **space quantization.** The direction of B is along the Z axis. As such the component of L along Z-direction is given as $L_Z = m_l$, h, the m_l can table the values from -l to +l including zero.

The above discussed space quantization of orbits and possible components of L can be understood with the following example.

Let us calculate the allowed projections of L for 1 = 2. The L can be visualized as a vector lying on the surface of a cone (see Figure a).



The possible values of m_l for l = 2 can be -2, -1, 0, 1, 2 hence $L_Z = m_l h = -2h - h$, 0, h, 2h. Figure (b) and (c) show space quantization of L for l=2.

Spin Quantization

Goudsmit and Uhlenbeck in 1925 proposed that electron 'spins' about an axis through its centre of mass and further it has both angular momentum and a magnetic moment. The spin of electron is analogous to the planetary motion about the Sun in our solar system. Quantum mechanical treatment has demonstrated that the spin of electron should be quantized. As such a new quantum number 5 has been introduced. The spin angular momentum S is related with spin quantum number s as

$$s = \sqrt{s(s+1)h} \qquad \dots (1)$$

The spin can be either clockwise or anticlockwise as such s can have two values *i.e.*, $\pm \frac{1}{2}$

$$S = \sqrt{\frac{1}{2}(\frac{1}{2}+1)} h = \frac{\sqrt{3}}{2} h$$

Component of S along the direction of magnetic field is governed by quantum, number m_s as

$$S_z = m_s h$$
 ... (2)

where m_s is the spin magnetic quantum number. The m_s can take (2s + 1) values.

```
as such m_s \operatorname{can} be 2 \times \frac{1}{2} + 1 = 2 values m_s = \pm \frac{1}{2}
```

Hence $S_z = \pm \frac{1}{2}h$

We have seen that the orbital and spin motions of an electron are quantized in magnitude as well as in direction. These motions are represented by quantized vectors, as such the atomic model is termed as *vector atom model*.

The Quantum Numbers and Spectroscopic Notations

The Bohr-Sommerfeld atomic theory uses four quantum numbers which are (i) Principal quantum number (n) (*ii*) Orbital quantum number (1) (*iii*) Spin quantum number (s) and (iv). Total angular momentum quantum number (j). In addition to these, three other quantum numbers have been introduced in vector atom model which are (i) Magnetic orbital quantum number (m_l) , (*ii*) Magnetic spin quantum number (m_s) and (*iii*) Magnetic total an momentum quantum number (m_j) . The general description and possible values of these quantum numbers is given below.

Principal Quantum Number (n): This quantum number represents the serial number of the atomic shells starting from the innermost. The 'n' can have only positive integral values excluding zero.

n = 1, 2, 3, 4

Orbital Quantum Number (I): The Orbital quantum number 'l' can have the values from a to (n - 1), where 'n' is the principal quantum number. For example, if n = 3, then l = 0, 1, 2. I Conventionally we call 1 = 0 s electron l = 1 p electron l = 2 d electron l = 3 f electron Spin Quantum Number (s): Spin quantum number s has only one value

i.e. $\frac{1}{2} \Rightarrow s = \frac{1}{2}$

Total Angular Momentum Quantum Number (j): The total angular momentum quantum number *j* is the sum of orbital angular momentum 'l' and spin quantum number's'. As such *j* can have $l \pm s$ or $l \pm \frac{1}{2}$ values.

Magnetic Orbital Quantum Number ' m_l **'**: As discussed previously in article 10.3.1, the magnetic orbital quantum number m_l can have 2l + 1 values. For example, I = 2, m_l can have -2, -1, 0, 1, 2 *i.e.*, total 5 values.

Magnetic Spin Quantum Number 'm_s': The magnetic spin quantum number take (2s + 1) values. We know that $s = \frac{1}{2}$ and hence m_s , can take $(2 \times \frac{1}{2} + 1) = 2$ in total. The values of m_s ' therefore are -s and +s or $-\frac{1}{2}$ and $+\frac{1}{2}$.

Magnetic Total Angular Momentum Quantum Number m_j : The total momentum J of an atom is a vector quantity and is the vector sum of orbital momentum L and spin angular momentum S *i.e.*, J = L + S. We define quantum number m_j which is known as the magnetic total angular mom quantum number and specify the orientation of J in space with respect to Z-axis.

According to quantum mechanics

$$J = \sqrt{J(J+1)} h \qquad \qquad \dots (1)$$
 and $J_s = m_j h$

The possible values of m_j are 2j + 1 *i.e.*, m_j can take values from -j to +j including zero in integral steps.

Now $J_z = L_z \pm S_z$

which implies that $m_j = m_l \pm m_s$. Now m_l is an integer and m_s is $\pm \frac{1}{2}$ as such m_j will have the half integral values only. The m_j , m_l and m_s can have the maximum value j, l and s respectively.

(OR)

b) Explain the electronic structure of atoms and fine structure of spectral lines.

Electronic structure of atoms and fine structure of spectral lines

Recall that the energy levels of a hydrogen atom are given by

 $E_n = -13.6/n^2$

This will give rise to a series of spectral lines at a set of allowed transition frequencies when the electron in the atom is excited.

 W_{ni} - $W_{nf} = E_{ni}$ - E_{nf}/h

Here, ni and nf represent the initial energy level to which the electron is excited and represents the final level to which it decays. In the decay process, electromagnetic radiation is emitted which can be detected in a spectrometer.

If one examines, the Lyman spectrum, for example, which corresponds to nf = 1 and produces spectral lines in the ultraviolet part of the electromagnetic spectrum, one finds that the individual lines are actually several lines of nearly identical frequency. For example, the 2p to 1s transition is actually a doublet, with the two components being separated by ~10⁻⁴ eV which is also on the order of a few tens of wavenumbers, which is about 10⁵ times smaller than the splitting predicted from the formula, i.e., 10.2 eV. Clearly, the simple theory based on the above formulae is not sufficient to explain the multiplicity of lines actually observed.

- o Fine structure of H-atom is due to spin-orbit interaction:
- o If L is parallel to S => J is a maximum => high energy configuration.
- o Angular momenta are described in terms of quantum numbers, s, l and j:

23.(a) Explain in detail the alpha disintegration.

Alpha disintegration

Alpha decay or α -decay is a type of radioactive decay in which an atomic nucleus emits an alpha particle (helium nucleus) and thereby transforms or 'decays' into an atom with a mass number that is reduced by four and an atomic number that is reduced by two. An alpha particle is identical to the nucleus of a helium-4 atom, which consists of two protons and two neutrons. It has a charge of +2e and a mass of 4u. For example, uranium-238 decays to form thorium-234. Alpha particles have a charge +2, but as a nuclear equation describes a nuclear reaction without considering the electrons – a convention that does not imply that the nuclei necessarily occur in neutral atoms – the charge is not usually shown.

Alpha decay typically occurs in the heaviest nuclides. Theoretically, it can occur only in nuclei somewhat heavier than nickel (element 28), where the overall binding energy per nucleon is no longer a minimum and the nuclides are therefore unstable toward spontaneous fission-type processes. In practice, this mode of decay has only been observed in nuclides considerably heavier than nickel, with the lightest known alpha emitters being the lightest isotopes (mass numbers 106–110) of tellurium (element 52). Exceptionally, however, beryllium-8 decays to two alpha particles.

Alpha decay is by far the most common form of cluster decay, where the parent atom ejects a defined daughter collection of nucleons, leaving another defined product behind. It is the most common form because of the combined extremely high binding energy and relatively small mass of the alpha particle. Like other cluster decays, alpha decay is fundamentally a quantum tunneling process. Unlike beta decay, it is governed by the interplay between both the nuclear force and the electromagnetic force.

Alpha particles have a typical kinetic energy of 5 MeV (or $\approx 0.13\%$ of their total energy, 110 TJ/kg) and have a speed of about 15,000,000 m/s, or 5% of the speed of light. There is surprisingly small variation around this energy, due to the heavy dependence of the half-life of this process on the energy produced (see equations in the Geiger-Nuttall law). Because of their relatively large mass, +2 electric charge and relatively low velocity, alpha particles are very likely to interact with other atoms and lose their energy, and their forward motion can be stopped by a few centimeters of air. Approximately 99% of the helium produced on Earth is the result of the alpha decay of underground deposits

of minerals containing uranium or thorium. The helium is brought to the surface as a byproduct of natural gas production.

Alpha particles were first described in the investigations of radioactivity by Ernest Rutherford in 1899, and by 1907 they were identified as He^{2+} ions.

By 1928, George Gamow had solved the theory of alpha decay via tunneling. The alpha particle is trapped in a potential well by the nucleus. Classically, it is forbidden to escape, but according to the (then) newly discovered principles of quantum mechanics, it has a tiny (but non-zero) probability of "tunneling" through the barrier and appearing on the other side to escape the nucleus. Gamow solved a model potential for the nucleus and derived, from first principles, a relationship between the half-life of the decay, and the energy of the emission, which had been previously discovered empirically, and was known as the Geiger–Nuttall law.

The nuclear force holding an atomic nucleus together is very strong, in general much stronger than the repulsive electromagnetic forcesbetween the protons. However, the nuclear force is also short range, dropping quickly in strength beyond about 1 femtometre, while the electromagnetic force has unlimited range. The strength of the attractive nuclear force keeping a nucleus together is thus proportional to the number of nucleons, but the total disruptive electromagnetic force trying to break the nucleus apart is roughly proportional to the square of its atomic number. A nucleus with 210 or more nucleons is so large that the strong nuclear force holding it together can just barely counterbalance the electromagnetic repulsion between the protons it contains. Alpha decay occurs in such nuclei as a means of increasing stability by reducing size.

One curiosity is why alpha particles, helium nuclei, should be preferentially emitted as opposed to other particles like a single proton or neutron or other atomic nuclei.^[note 1] Part of the answer comes from conservation of wave function symmetry, which prevents a particle from spontaneously changing from exhibiting Bose–Einstein statistics (if it had an even number of nucleons) to Fermi–Dirac statistics (if it had an odd number of nucleons) or vice versa. Single proton emission or the emission of any particle with an odd number of nucleons would violate this conservation law. The rest of the answer comes from the very high binding energy of the alpha particle. Computing the total disintegration energy given by the equation:

Where is the initial mass of the nucleus, is the mass of the nucleus after particle emission, and is the mass of the emitted particle, shows that alpha particle emission will usually be possible just with energy from the nucleus itself, while other decay modes will require

CIA-II Answer Key Atomic and Molecular Physics

additional energy. For example, performing the calculation for uranium-232 shows that alpha particle emission would need only 5.4 MeV, while a single proton emission would require 6.1 MeV. Most of this disintegration energy becomes the kinetic energy of the alpha particle itself, although to preserve conservation of momentum part of this energy becomes the recoil of the nucleus itself. However, since the mass numbers of most alpha emitting radioisotopes exceed 210, far greater than the mass number of the alpha particle (4) the part of the energy going to the recoil of the nucleus is generally quite small.



These disintegration energies however are substantially smaller than the potential barrier provided by the nuclear force, which prevents the alpha particle from escaping. The energy needed is generally in the range of about 25 MeV, the amount of work that must be done against electromagnetic repulsion to bring an alpha particle from infinity to a point near the nucleus just outside the range of the nuclear force's influence. An alpha particle can be thought of as being inside a potential barrier whose walls are 25 MeV. However, decay alpha particles only have kinetic energies of 4 MeV to about 9 MeV, far less than the energy needed to escape.

Quantum mechanics, however, provides a ready explanation, via the mechanism of quantum tunnelling. The quantum tunnelling theory of alpha decay, independently developed by George Gamow^[3] and Ronald Wilfred Gurney and Edward Condon in 1928,^[4] was hailed as a very striking confirmation of quantum theory. Essentially, the alpha particle escapes from the nucleus by quantum tunnelling its way out. Gurney and Condon made the following observation in their paper on it:

It has hitherto been necessary to postulate some special arbitrary 'instability' of the nucleus; but in the following note it is pointed out that disintegration is a natural consequence of the laws of quantum mechanics without any special hypothesis... Much has been written of the explosive violence with which the α -particle is hurled from its place in the nucleus. But from

the process pictured above, one would rather say that the α -particle almost slips away unnoticed.^[4]

The theory makes the assumptions that the alpha particle can be considered an independent particle within a nucleus that is in constant motion, but held within the nucleus by nuclear forces. There is, in addition, a very small but decidedly non-zero probability that it will tunnel its way out. An alpha particle with a speed of 1.5×10^7 m/s within a nuclear diameter of approximately 10^{-14} m will thus collide against the potential barrier of the nuclear force more than 10^{21} times per second, and yet for some radioisotopes it will need to keep doing this for as long as 13 billion years before managing to escape, so the probability of escape is extremely low.

Working out the details of the theory leads to an equation relating the half-life of a radioisotope to the decay energy of its alpha particles, a theoretical derivation of the empirical Geiger–Nuttall law.

(OR)

(b) What is beta disintegration and explain it.

Beta disintegration

Beta decay, any of three processes of radioactive disintegration by which some unstable atomic nuclei spontaneously dissipate excess energy and undergo a change of one unit of positive charge without any change in mass number. The three processes are electron emission, positron (positive electron) emission, and electron capture. Beta decay was named (1899) by Ernest Rutherford when he observed that radioactivity was not a simple phenomenon. He called the less penetrating rays alpha and the more penetrating rays beta. Most beta particles are ejected at speeds approaching that of light.

All atoms heavier than ordinary hydrogen have a nucleus consisting of neutrons and protons (neutral and positively charged particles, respectively), surrounded by negative electrons; these orbital electrons are not involved in the electron emission associated with beta decay. In electron emission, also called negative beta decay (symbolized β^- -decay), an unstable nucleus emits an energetic electron (of relatively small mass) and an antineutrino (with little or possibly no rest mass), and a neutron in the nucleus becomes a proton that remains in the product nucleus. Thus, negative beta decay results in a daughter nucleus, the proton number (atomic number) of which is one more than its parent but the mass number

(total number of neutrons and protons) of which is the same. For example, hydrogen-3(atomic number 1, mass number 3) decays to helium-3 (atomic number 2, mass number 3). The energy lost by the nucleus is shared by the electron and the antineutrino, so that beta particles (the electrons) have energy ranging from zero to a distinct maximum that is characteristic of the unstable parent.

In positron emission, also called positive beta decay (β^+ -decay), a proton in the parent nucleus decays into a neutron that remains in the daughter nucleus, and the nucleus emits a neutrino and a positron, which is a positive particle like an ordinary electron in mass but of opposite charge. Thus, positive beta decay produces a daughter nucleus, the atomic number of which is one less than its parent and the mass number of which is the same. Positron emission was first observed by Irène and Frédéric Joliot-Curie in 1934.



In electron capture, an electron orbiting around the nucleus combines with a nuclear proton to produce a neutron, which remains in the nucleus, and a neutrino, which is emitted. Most commonly the electron is captured from the innermost, or K, shell of electrons around the atom; for this reason, the process often is called K-capture. As in positron emission, the nuclear positive charge and hence the atomic number decreases by one unit, and the mass number remains the same.

Each chemical element consists of a set of isotopes the nuclei of which have the same number of protons but differ in the number of neutrons. Within each set the isotopes of intermediate mass are stable or at least more stable than the rest. For each element, the lighter isotopes, those deficient in neutrons, generally tend toward stability by positron emission or electron capture, whereas the heavier isotopes, those rich in neutrons, usually approach stability by electron emission.

In comparison with other forms of radioactivity, such as gamma or alpha decay, beta decay is a relatively slow process. Half-lives for beta decay are never shorter than a few milliseconds.

BSc Degree Examinations

Model Exam

15PHU501

be Degree Examinations	WIUUCI LIAd	,	151 110501
Α	tomic and mol	ecular Physics	Reg. No. :
Duration: 3 hours Maximum PART – A (20 x 1=20 Marks	n: 60 marks s)	 b. X-rays are c. wavelength size 	highly penetrating radiation of X-rays are of the order of nuclear
1. The nature of positive ray depends on		d. the waveler nm	ngth of X-rays is of the order of 546
a. The nature of electrode b. The discharge tube c. The nature of residuate above	ne nature of al gas d. all of	9. Monatomic ma a. rotational	blecules can havemotion b. circular c. translator d. elliptic
 2. The nature of cathode rays were identian. a. J.J. Thomson b. William crook J. Perrin 	ified by c.Hitiroff d.	10. If two of the molecule is ca a. Symmetric linear rotator	moments of inertia are equal, the lled rotator b. antisymmetry rotator c. d. circular rotator
a. line spectra b. continuous spect spectra d. reflection of light	tra c. band	11. Photo electric a. dual nature	emission confirms of radiation
4. Depolarization factor is the ratio of the a. Frequencies of the vertical an components	e Id horizontal	c. wave nature d. electromagn	of radiation etic nature of radiation
 b. Frequencies of the horizontal components c. Intensities of the horizontal components d. Intensities of the vertical and 	and vertical and vertical d horizontal	12. Franck Condoa. photochemb. electrocherc. physical dia	n principle explains ical dissociation nical dissociation ssociation d. none of above
components 5. Photoelectric effect can be explained that light	by assuming	13. The electronic a. visible reg region d. bo	bands occur in ion b. infrared region c. ultraviolet th a and c
a. Is a form of transverse wave b longitudinal wave c. Can be polarised quanta	o. Is a form of d. Consists of	14. The total inter a. rotational of above	nal energy of molecule is partly o. vibrational c. both a and b d. none
 6. The vector atom model is an extension a.Rutherford model b. Bohr model c. Sommerfield atom model d. Rutherford-Bohr Sommerfeld atom 	n of the el m model	15. Compound radioisotope is a. Tracer c. non radioac	containing some amount of b. radioactive compound tive d. linear active compound
7. The original unit for measuring the radioactivity was	e amount of	16. Radiations en a. alpha b. bet	itted by different elements are a c. gamma d. all of above

- a. Ohm. b. Kelvin c. Watt d. Curie
- 8. For the structural analysis of the crystal, X-rays are used because
 - a. X-rays have wavelengths of the order of interatomic spacing
- 17. Quantum number values for 2p sub shell are?

a. n = 1, L = 1 b. n = 1, L = 0 c. n = 2, L = 1 d. n = 2, L = 1

18. According to Bohr's postulates, which of the following quantities take discrete values?

- a. kinetic energy b. potential energy c. angular momentum d. momentum
- 19. The energy of an electron in the n^{th} orbit of the hydrogen atom E_n is

a. $-13.6/n^2$ b. $15.6n^2$ c. n^2 d. 13

20. cathode rays are deflected bya. neither electric not magnetic field b. bothelectric and magnetic field.c.electric field only d. magnetic field only

$$PART - B (5 \times 8 = 40 Marks)$$

Answer all the questions

21. (a) Discuss in detail about cathode rays, positive rays, x-rays.

(OR)

(b) Drive the susceptibility equation in Langevin's theory of diamagnetism.

22. (a) Describe in detail about Thomson atom model and Rutherford atom model (OR)

(b) Explain in detail about Sommerfeld relativistic atom model and drawback of it.

23.(a) Drive the expression for number of atoms in alpha disintegration method.

(OR)

(b) What is gamma ray and explain in detail about the origin of gamma rays.

24. (a) Explain the wave mechanical theory of covalent linkage.

(OR)

(b) Write a short note on Vander Waals type of binding and metallic binding.

25. (a) Explain the experimental study of molecular spectra.

(OR)

(b) What is isotopic effect and explain the effect in molecular spectra.

Reg. No. : ------

PART - A (20 x 1=20 Marks)

1. The nature of positive ray depends on

a. The nature of electrode b. The nature of discharge tube c. **The nature of residual gas** d. all of above

- 2. The nature of cathode rays were identified by
 - a. **J.J. Thomson** b. William crook c. Hitiroff d. J. Perrin
- 3. Atomic spectra is an example of
 - a. line spectra b. continuous spectra c. band spectra d. reflection of light
- 4. Depolarization factor is the ratio of the
 - a. Frequencies of the vertical and horizontal components
 - b. Frequencies of the horizontal and vertical components
 - c. Intensities of the horizontal and vertical components
 - d. Intensities of the vertical and horizontal components
- 5. Photoelectric effect can be explained by assuming that light
 - a. Is a form of transverse wave b. Is a form of longitudinal wave
 - c. Can be polarised d. **Consists of quanta**
- 6. The vector atom model is an extension of the
 - a.Rutherford model b. Bohr model
 - c. Sommerfield atom model
 - d. Rutherford-Bohr Sommerfeld atom model
- 7. The original unit for measuring the amount of radioactivity was
 - a. Ohm. b. Kelvin c. Watt d. Curie
- 8. For the structural analysis of the crystal, X-rays are used because

a. X-rays have wavelengths of the order of interatomic spacing

- b. X-rays are highly penetrating radiation
- c. wavelength of X-rays are of the order of nuclear size
- d. the wavelength of X-rays is of the order of 546 nm
- 9. Monatomic molecules can havemotion a. **rotational** b. circular c. translator d. elliptic
- 10. If two of the moments of inertia are equal, the molecule is calleda. Symmetric rotator b. antisymmetry rotator c. linear rotator d. circular rotator
- 11. Photo electric emission confirmsa. dual nature of radiation

- b. corpuscular nature of radiation
- c. wave nature of radiation
- d. electromagnetic nature of radiation
- 12. Franck Condon principle explains
 - a. photochemical dissociation
 - b. electrochemical dissociation
 - c. physical dissociation d. none of above
- 13. The electronic bands occur ina. visible region b. infrared region c. ultraviolet region d. both a and c
- 14. The total internal energy of molecule is partlya. rotational b. vibrational c. both a and b d. none of above
- 15. Compound containing some amount of radioisotope is
 a. Tracer
 b. radioactive compound
 d. linear active compound
- 16. Radiations emitted by different elements are a. alpha b. beta c. gamma d. **all of above**
- 17. Quantum number values for 2p sub shell are?

a. n = 1, L = 1 b. n = 1, L = 0 c. n = 2, L = 1 d. n = 2, L = 1

18. According to Bohr's postulates, which of the following quantities take discrete values?

a. kinetic energy b. potential energy c. angular momentum d. momentum

19. The energy of an electron in the n^{th} orbit of the hydrogen atom E_n is

a. **-13.6/n²** b. $15.6n^2$ c. n^2 d. 13

20. cathode rays are deflected bya. neither electric not magnetic field b. both electric and magnetic field.c.electric field only d. magnetic field only

$$PART - B (5 \times 8 = 40 Marks)$$

Answer all the questions

21. (a) Discuss in detail about cathode rays, positive rays, x-rays.

Cathode rays, positive rays and X rays

Cathode rays are streams of fast moving electrons.

Properties:

2017-2018-ODD

(i) Cathode rays are emitted normally from the cathode surface. Their direction is independent of the position of the anode.

(ii) Cathode rays travel in straight lines. (Cast shadows of objects placed in their path).

(iii) Cathode rays exert mechanical force on the objects they strike.

(iv) Cathode rays produce heat when they strike a material surface.

(v) Cathode rays produce fluorescence when they strike a number of crystals, minerals and slats.

(vi) When cathode ray strikes a solid object, specially a metal, X-rays are emitted from the object. (It is not safe to use Geissler tube at potential differences above about 5-6 kV because of this X-ray emission, generated by striking of cathode rays of metal anode).

(vii) Cathode rays are deflected by an electric field and also by a magnetic field. The direction of deflection is the same as that of a stream of negatively charged particles.

(viii) Cathode rays ionize the gas through which they are passed.

(ix) Cathode rays can penetrate thin foils of metal.

(x) Cathode rays affect photographic plates.

(xi) Cathode rays are found to have velocity upto one tenth of the velocity of light. The e/m of electrons was measured by J.J. Thomson (so credit of discovering electron is given to Thomson).

The e of electron was measured by R.A./Millikan e/m = 1.759×10^{11} c/kg e = 1.602×10^{-19} C m = 9.09×10^{-31} kg

The e/m of an electron is called the specific charge of an electron.

If one includes the relativistic variation of mass with speed then specific charge of an electron decreases with the increase in the velocity of the electron.

Positive Rays :

Positive rays are sometimes known as the canal rays. These were discovered in 1896 by Goldstein. If the cathode of a discharge tube has holes in it and the pressure of the gas is around 1 mm of mercury than faint luminous glow come out from each hole on the backside of the cathode.

This shows that something is coming out of the holes. These are called canal rays or positive rays.



Origin of positive rays :

When potential difference is applied across the electrodes, electrons (cathode rays) are emitted from the cathode. As they move towards anode, they gain energy.

These energetic electrons which collide with the atoms of the gas in the discharge tube, they ionize the atoms. The positive ions formed at various places between cathode and anode, travel towards the cathode. Since during their motion, the positive ions when reach the cathode, some pass through the holes in the cathode. These stream of positive ions are the positive rays or canal rays.

If the discharge tube is totally evacuated then no positive rays are produced. Thus positive rays are positive ions of the gas in the tube. Properties of positive rays were studied by Thomson. The q/m of the hydrogen was found to be $\sim 10^8$ C/kg much less then the e/m of electron $\sim 10^{11}$ C/kg indicating that mass of positive rays is much greater than that of electrons.

Properties of Positive Rays :

(i) These are positive ions having same mass if the experimental gas does not have isotopes. However if the gas has isotopes then positive rays are group of positive ions having different masses.

(ii) They travel in straight lines and cast shadows of objects placed in their path. But the speed of the positive rays is much smaller than that of cathode rays.

(iii) They are deflected by electric and magnetic fields but the deflections are small as compared to that of cathode rays.

(iv) They show a spectrum of velocities. Different positive ions move with different velocities.

(v) q/m ratio of these rays depends on the nature of the gas in the tube (while in case of the cathode rays q/m is constant and does not depend on the gas in the tube).

(vi) They carry energy and momentum.

(vii) They cause ionization (which is much more than that produced by cathode rays).

(viii) They cause fluorescence (in ZnS or CdS screen) and affect photographic plates.

(ix) They have a little penetration power (but much less in comparison to cathode rays)

X-Rays

W. C. Rontgen conducted various experiments to study the discharge of electricity through gases and accidently discovered X-rays. He used a glass tube fitted with two electrodes cathode and anode. An exhaust pump was connected through a side tube and a high electric potential of about 25 kV was applied across the electrodes. Rontgen made the following important observations:



(a) When air inside the tube was at atmospheric pressure there was no discharge of electricity through it.

(b) When pressure inside the tube was reduced to few cm of mercury, a feeble discharge of electricity occurred between the electrodes. At the same time air inside the tube started giving visible light.

(c) When air pressure was reduced to 10^{-3} mm of mercury, air lumininescence gets disappeared but the glass walls of the tubes starts glowing. Rontgen concluded that this glow was due to some invisible penetrating radiations from anode that were falling on the glass and producing fluorescence. Rontgen did not know much about the nature of these rays and therefore, he called them X-rays.

(B) Explanations: Rontgen explained the production of these X-rays due to the bombardment of high velocity electrons on anode. Due to low pressure (10^{-3} mm) inside the tube, the air gets ionised producing a few electrons and the positive ions.

The positive ions are highly accelerated towards the cathode, these ions knock out electrons from the cathode. The released electrons move with tremendous speed towards highly positive anode. They strike the anode surface and produce X-rays. On his experimental basis, Rontgen observed that in order to produce X-rays, the following three things are required.

(a) The source of electron

(b) Means of accelerating these electrons to high speeds.

(c) Anode or target on which these high speed electrons should strike to produce X-rays.

(OR)

(b) Drive the susceptibility equation in Langevin's theory of diamagnetism.

Langevin gave a satisfactory explanation of diamagnetism on the basis of electron theory the basic principle of which ia Lenz's law in electromagnetic induction which states that when a magnetic flux linked with electric current due to revolving electrons is changed, an induced current is set up in such a direction as to oppose the change in flux. It is manifested by the very small and negative value of magnetic susceptibility.

If ω_0 be the frequency of electron in the absence of applied field and r is the radius of the loop then:

$$\mathbf{F}_{o} = \mathbf{m}\omega_{o}^{2} \mathbf{r} = \mathbf{Z}\mathbf{e}^{2}/4\pi\varepsilon_{o}\mathbf{r}^{2}$$

Lorentz force acting on the electron moving with velocity v is given by

 $F_L = -Bev = -Be\omega r$ $\omega = \pm \omega_0 - eB/2m$

The –ve sigm indicates that these electrons whise orbital magnetic moments are parallel to the magnetic field are slowed downand those with moments antiparallel are speeded by an amount eB/2m : LARMOR THEOREM.

The additional current produced due to change in frequency of the electron is given by $\mathbf{I} = -\mathbf{e}^2 \mathbf{B}/4\pi \mathbf{m}$ and the change in magnetic moment is given by $\Delta \mathbf{M} \mathbf{a} = -\mathbf{e}^2 \mathbf{r}^2 \mathbf{B}/4\mathbf{m}$

 $<\mathbf{r}^{2}> = <\mathbf{x}^{2}> +<\mathbf{y}^{2}> \text{ and } <\mathbf{r}_{0}^{2}> = <\mathbf{x}^{2}> +<\mathbf{y}^{2}> +<\mathbf{z}^{2}>$ $<\mathbf{r}^{2}> = 2/3 < \mathbf{r}_{0}^{2}>$ $\mathbf{M} = -\mathbf{e}^{2}\mathbf{Z}\mu_{0}\mathbf{H}\mathbf{N} < \mathbf{r}_{0}^{2}> /6\mathbf{m}$ $\boldsymbol{\chi} = \mathbf{M}/\mathbf{H}$

Magnetization,

$$= -e^{2}Z\mu_{0}N < r_{0}^{2} > /6m$$

Since χ is independent of temperature so the diamagnetic behavior of the material does not change into temperature.

According to quantum theory, the magnetic moments are quantized, so they can orient only in specific direction with respect to the magnetic field.

 $\mu = -g \mu_B J$ μ_B is called Bohr magneton

g = 1+(J(J+1)+S(S+1)-L(L+1))/2J(J+1)

Using Maxwell Boltzmann statistics, magnetization is given as

 $\mathbf{M}{=}\;N\sum\,m_{J}\;g\;\mu_{B}\;e^{mJ\;g\;\mu B\,\textit{\textit{k}}\beta\;T}{/}\;e^{\;mJ\;g\;\mu B\textit{\textit{k}}\beta\;T}$

CASE I At ordinary temperatures $\mathbf{Bm}_{J} \mathbf{g} \mu_{B} / \mathbf{k}_{\beta} \mathbf{T} \ll 1$ Using the exponential series and $\sum \mathbf{m}_{J}^{2} = (1/3)(J+1)(2J+1)$

$$\chi = M/H \qquad \qquad \chi_{para} = Ng^2 \mu_B^2 \mu_0 P_{eff}^2 \qquad \qquad Peff = g\sqrt{J(J+1)}$$

 $M = Ng^{2}\mu_{B}^{2}\mu_{0} H J(J+1)/3k_{B}T$

CASE II At low temperature and strong magnetic field $Bm_J g \mu_B / k_\beta T$ is not less than unity

Let $x=B g \mu_B / k_\beta T$ $M = \sum Bm_J g \mu_B emJx$

As $\sum mJ x$ is a geometric progression with (2J+1) terms

```
\begin{split} M &= Ng\mu_B \ d/dx \ (ln(\ e^{Jx} \ (1-e^{-(2J+1)x}/(1-e^{-x})))) \\ &= NgJ\mu_B \ B_J(a) \\ BJ(a) &= (2J+1)/2J \ coth \ (2J+1)a/2J \ - 1/2J \ coth \ (a/2J), \\ Brillouin \ function \ a &= Jg\mu B/k_BT \end{split}
```

In the limit J tends to ∞ Brillouin function approaches the Langevin function i.e., infinite number of possible orientations are allowed.

22. (a) Describe in detail about Thomson atom model and Rutherford atom model

Thomson model: Introduction

In 1897, J.J.Thomson discovered a negatively charged particle known as an electron. Thomson discovered electron by cathode ray tube experiment. Cathode ray tube is a vacuum tube. Thomson assumed that an electron is two thousand times lighter than a proton and believed that an atom is made up of thousands of electrons having the negative charge. In this atomic structure model, he considered atoms to have a cloud of negative charge and the positive charges. He along with Rutherford was also the first to demonstrate the ionization of air by Xrays. Thomson's model of an atom is similar to plum pudding model or a watermelon.



Thomson's Model of Atom

Postulates of Thomson's atomic model

- An atom consists of a positively charged sphere with electrons filled into it. The negative and positive charge present inside an atom are equal and as a whole, an atom is electrically neutral.
- Thomson's model of the atom was compared to plum pudding and watermelon. He compared the red edible part of the watermelon to positively charged sphere whereas the seeds of watermelon to negatively charged particles.

Limitations of Thomson's atomic model

- This model of atom failed to explain how a positive charge holds the negatively charged electrons in an atom. Therefore, it failed to explain the stability of an atom.
- This theory also failed to account for the position of the nucleus in an atom.
- Thomson's model failed to explain the scattering of alpha particles.
Although Thomson's model was not an accurate model to account for the atomic structure, it proved to be the base for the development of other atomic structure models

Drawbacks

(i) According electromagnetic theory, the vibrating electron to should radiate the frequency of the emitted spectral line energy and should be the the electron. In the case of hydrogen same as atom, Å. But Thomson's model gives only one spectral line of about 1300 the experimental observations reveal that hydrogen spectrum consists of five different series with several lines each series. in (ii) It could not account for the scattering of α -particles through large angles.

Also called **nuclear atom** or **planetary model of the atom**, description of the structure of atoms proposed (1911) by the New Zealand-born physicist Ernest Rutherford. The model described the atom as a tiny, dense, positively charged core called a nucleus, in which nearly all the mass is concentrated, around which the light, negative constituents, called electrons, circulate at some distance, much like planets revolving around the Sun.



Diagram of the Rutherford atomic model

The nucleus was postulated as small and dense to account for the scattering of alpha particles from thin gold foil, as observed in a series of experiments performed by undergraduate Ernest Marsden under the direction of Rutherford and German physicist Hans Geiger in 1909. A radioactive source capable of emitting alpha particles (i.e., positively charged particles, identical to the nucleus of the helium atom and 7,000 times more massive than electrons) was enclosed within a protective lead shield. The radiation was focused into a narrow beam after passing through a slit in a lead screen. A thin section of gold foil was placed in front of the slit, and a screen coated with zinc sulfide to render it fluorescentserved as a counter to detect alpha particles. As each alpha particle struck the fluorescent screen, it would produce a burst of light

called scintillation, which was visible through a viewing microscope attached to the back of the screen. The screen itself was movable, allowing Rutherford and his associates to determine whether or not any alpha particles were being deflected by the gold foil.

Problems with the Rutherford Model

In the years after Rutherford discovered the nucleus, chemists and particle physicists discovered that electron behavior was much more complicated than depicted in the Rutherford model. Electrons did not travel in set paths, their speeds were inconsistent, and their location around the nucleus could change based on how much energy they had. It was no longer accurate to depict electrons as traveling in straight paths. Instead, physicists began to represent them by an electron cloud that could suggest where electrons might be at any given time. The electron cloud model is the current model of the atom.

The Bohr Model has an atom consisting of a small, positively-charged nucleus orbited by negatively-charged electrons. Here's a closer look at the Bohr Model, which is sometimes called the Rutherford-Bohr Model.

(OR)

(b) Explain in detail about Sommerfeld relativistic atom model and drawback of it.

Sommerfeld atom model and its Drawbacks



In order to explain the observed fine structure of spectral lines, Sommerfeld introduced two main modifications in Bohr's theory.

Sommerfeld atom model

In order to explain the observed fine structure of spectral lines, Sommerfeld introduced two main modifications in Bohr's theory.

(i) According to Sommerfeld, the path of an electron around the nucleus, in general, is an ellipse with the nucleus at one of its foci.

(ii) The velocity of the electron moving in an elliptical orbit varies at different parts of the orbit. This causes the relativistic variation in the mass of the moving electron.

Now, when elliptical orbits are permitted, one has to deal with two variable quantities.

(i) The varying distance of the electron from the nucleus (r).

(ii) The varying angular position of the electron with respect to the nucleus i.e the azimuthal



angle φ (Fig).

To deal with these two variables, two quantum numbers are introduced

(i) The principal quantum number n of Bohr's theory, which determines the energy of the electrons, and

(ii) a new quantum number called orbital (or azimuthal) quantum number (l) which has been introduced to characterize the angular momentum in an orbit i.e., it determines the orbital angular momentum of the electron. Its values vary from zero to (n-1) in steps of unity.

This orbital quantum number (l) is useful in finding the possible elliptical orbits. The possible elliptical orbits are such that

b/a = l+1/n

where a and b are semi-major and semi-minor axes respectively of the ellipse.

According to Sommerfeld's model, for any principal quantum number n, there are n possible orbits of varying eccentricities called sub-orbits or sub-shells. Out of n subshells, one is circular and the remaining (i.e., n-1) are elliptical in shape.

These possible sub-orbits possess slightly different energies because of the relativistic variation of the electron mass.

Consider the first energy level (n=1). When n = 1, l = 0 i.e., in this energy level, there is only one orbit or sub-shell for the electron. Also, when a = b, the two axes of the ellipse are equal. As a result of this, the orbit corresponding to n=1 is circular. This subshell is designated as *s* subshell. Since, this sub-shell belongs to n=1, it is designated as 1s (Fig a).



Similarly, for the second energy level n=2, there are two permissible sub-shells for the electrons. For n=2, l can take two values, 0 and 1.

When n = 2, l = 0.

b/a= 0+1/2 =1/2

or

b=a/2

This subshell corresponding to l = 0 is elliptical in shape and is designated as 2s.

when n = 2, l = 1.

b/a= 1+1/2 =2/2 =1

or

b=a

This sub-shell corresponding to l = 1 is circular in shape and is designated as 2p (Fig b).

For n = 3, *l* has three values 0, 1 and 2, i.e. there are three permissible sub-shells for the electrons.

when n = 3, l = 0.

b/a = (0+1)/3 = 1/3 = 1 or b = a/3

when n = 3, l = 1.

b/a = (1+1)/3 = 2/3 = 1 or b = 2a/3

and when n = 3, l = 2.

b/a = (2+1)/3 = 3/3 = 1 or b=a

The sub-shells corresponding to l = 0, 1 and 2 are designated as 3s, 3p and 3d respectively. The circular shell is designated as 3d and the other two are elliptical in shape (Fig c).

It is common practice to assign letters to *l*-values as given below:

Orbital quantum number 1	:	0	1	2	3	4
electron state :		S	р	d	f	g

Hence, electrons in the l = 0, 1, 2, 3 states are said to be in the s, p, d, f states.

Based on this idea, Sommerfeld successfully explained the fine structure of spectral lines of hydrogen atom.

Drawbacks

- (i) Though Sommerfeld's modification gave a theoretical background of the fine structure of spectral lines of hydrogen, it could not predict the correct number of observed fine structure of these lines.
- (ii) It could not explain the distribution and arrangement of electrons in atoms.
- Sommerfeld's model was unable to explain the spectra of alkali metals such as sodium, potassium etc.
- (iv) It could not explain Zeeman and Stark effect.

- (v) This model does not give any explanation for the intensities of the spectral lines
- 23. (a) Drive the expression for number of atoms in alpha disintegration method.

Alpha disintegration

Alpha decay or α -decay is a type of radioactive decay in which an atomic nucleus emits an alpha particle (helium nucleus) and thereby transforms or 'decays' into an atom with a mass number that is reduced by four and an atomic number that is reduced by two. An alpha particle is identical to the nucleus of a helium-4 atom, which consists of two protons and two neutrons. It has a charge of +2e and a mass of 4u. For example, uranium-238 decays to form thorium-234. Alpha particles have a charge +2, but as a nuclear equation describes a nuclear reaction without considering the electrons – a convention that does not imply that the nuclei necessarily occur in neutral atoms – the charge is not usually shown.

Alpha decay typically occurs in the heaviest nuclides. Theoretically, it can occur only in nuclei somewhat heavier than nickel (element 28), where the overall binding energy per nucleon is no longer a minimum and the nuclides are therefore unstable toward spontaneous fission-type processes. In practice, this mode of decay has only been observed in nuclides considerably heavier than nickel, with the lightest known alpha emitters being the lightest isotopes (mass numbers 106–110) of tellurium (element 52). Exceptionally, however, beryllium-8 decays to two alpha particles.

Alpha decay is by far the most common form of cluster decay, where the parent atom ejects a defined daughter collection of nucleons, leaving another defined product behind. It is the most common form because of the combined extremely high binding energy and relatively small mass of the alpha particle. Like other cluster decays, alpha decay is fundamentally a quantum tunneling process. Unlike beta decay, it is governed by the interplay between both the nuclear force and the electromagnetic force.

Alpha particles have a typical kinetic energy of 5 MeV (or $\approx 0.13\%$ of their total energy, 110 TJ/kg) and have a speed of about 15,000,000 m/s, or 5% of the speed of light. There is surprisingly small variation around this energy, due to the heavy dependence of the half-life of this process on the energy produced (see equations in the Geiger–Nuttall law). Because of their relatively large mass, +2 electric charge and relatively low velocity, alpha particles are very likely to interact with other atoms and lose their energy, and their forward motion can be stopped

by a few centimeters of air. Approximately 99% of the helium produced on Earth is the result of the alpha decay of underground deposits of minerals containing uranium or thorium. The helium is brought to the surface as a by-product of natural gas production.

Alpha particles were first described in the investigations of radioactivity by Ernest Rutherford in 1899, and by 1907 they were identified as He^{2+} ions.

By 1928, George Gamow had solved the theory of alpha decay via tunneling. The alpha particle is trapped in a potential well by the nucleus. Classically, it is forbidden to escape, but according to the (then) newly discovered principles of quantum mechanics, it has a tiny (but non-zero) probability of "tunneling" through the barrier and appearing on the other side to escape the nucleus. Gamow solved a model potential for the nucleus and derived, from first principles, a relationship between the half-life of the decay, and the energy of the emission, which had been previously discovered empirically, and was known as the Geiger–Nuttall law.

The nuclear force holding an atomic nucleus together is very strong, in general much stronger than the repulsive electromagnetic forcesbetween the protons. However, the nuclear force is also short range, dropping quickly in strength beyond about 1 femtometre, while the electromagnetic force has unlimited range. The strength of the attractive nuclear force keeping a nucleus together is thus proportional to the number of nucleons, but the total disruptive electromagnetic force trying to break the nucleus apart is roughly proportional to the square of its atomic number. A nucleus with 210 or more nucleons is so large that the strong nuclear force holding it together can just barely counterbalance the electromagnetic repulsion between the protons it contains. Alpha decay occurs in such nuclei as a means of increasing stability by reducing size.

One curiosity is why alpha particles, helium nuclei, should be preferentially emitted as opposed to other particles like a single proton or neutron or other atomic nuclei.^[note 1] Part of the answer comes from conservation of wave function symmetry, which prevents a particle from spontaneously changing from exhibiting Bose–Einstein statistics (if it had an even number of nucleons) to Fermi–Dirac statistics (if it had an odd number of nucleons) or vice versa. Single proton emission or the emission of any particle with an odd number of nucleons would violate this conservation law. The rest of the answer comes from the very high binding energy of the alpha particle. Computing the total disintegration energy given by the equation:

Where is the initial mass of the nucleus, is the mass of the nucleus after particle emission, and is the mass of the emitted particle, shows that alpha particle emission will usually be possible just with energy from the nucleus itself, while other decay modes will require additional energy. For example, performing the calculation for uranium-232 shows that alpha particle emission would need only 5.4 MeV, while a single proton emission would require 6.1 MeV. Most of this disintegration energy becomes the kinetic energy of the alpha particle itself, although to preserve conservation of momentum part of this energy becomes the recoil of the nucleus itself. However, since the mass numbers of most alpha emitting radioisotopes exceed 210, far greater than the mass number of the alpha particle (4) the part of the energy going to the recoil of the nucleus is generally quite small.



These disintegration energies however are substantially smaller than the potential barrier provided by the nuclear force, which prevents the alpha particle from escaping. The energy needed is generally in the range of about 25 MeV, the amount of work that must be done against electromagnetic repulsion to bring an alpha particle from infinity to a point near the nucleus just outside the range of the nuclear force's influence. An alpha particle can be thought of as being inside a potential barrier whose walls are 25 MeV. However, decay alpha particles only have kinetic energies of 4 MeV to about 9 MeV, far less than the energy needed to escape.

Quantum mechanics, however, provides a ready explanation, via the mechanism of quantum tunnelling. The quantum tunnelling theory of alpha decay, independently developed by George Gamow and Ronald Wilfred Gurney and Edward Condon in 1928, was hailed as a very striking confirmation of quantum theory. Essentially, the alpha particle escapes from the nucleus by quantum tunnelling its way out. Gurney and Condon made the following observation in their paper on it:

It has hitherto been necessary to postulate some special arbitrary 'instability' of the nucleus; but in the following note it is pointed out that disintegration is a natural consequence of the laws of quantum mechanics without any special hypothesis... Much has been written of the explosive violence with which the α -particle is hurled from its place in the nucleus. But from the process pictured above, one would rather say that the α -particle almost slips away unnoticed.^[4]

The theory makes the assumptions that the alpha particle can be considered an independent particle within a nucleus that is in constant motion, but held within the nucleus by nuclear forces. There is, in addition, a very small but decidedly non-zero probability that it will tunnel its way out. An alpha particle with a speed of 1.5×10^7 m/s within a nuclear diameter of approximately 10^{-14} m will thus collide against the potential barrier of the nuclear force more than 10^{21} times per second, and yet for some radioisotopes it will need to keep doing this for as long as 13 billion years before managing to escape, so the probability of escape is extremely low.

Working out the details of the theory leads to an equation relating the half-life of a radioisotope to the decay energy of its alpha particles, a theoretical derivation of the empirical Geiger–Nuttall law.

(OR)

(b) What is gamma ray and explain in detail about the origin of gamma rays.

Origin of gamma rays

Sources through currently unidentified mechanisms.

 \geq The term gamma ray was coined by British physicist Ernest Rutherford in 1903 following early studies of the emissions of radioactive nuclei. Just as atoms have discrete energy levels associated with different configurations of the orbiting electrons, atomic nuclei level structures determined configurations have energy by the of the protons and neutrons that constitute the nuclei. While energy differences between atomic Dr. S. Esakki Muthu Karpagam Academy of Higher Education Page 17/27 **Department of Physics**

energy levels are typically in the 1- to 10-eV range, energy differences in nuclei usually fall in the 1-keV (thousand electron volts) to 10-MeV (million electron volts) range. When a nucleus makes a transition from a high-energy level to a lower-energy level, a photon is emitted to carry off the excess energy; nuclear energy-level differences correspond to photon wavelengths in the gamma-ray region.

When an unstable atomic nucleus decays into a more stable nucleus (*see* radioactivity), the "daughter" nucleus is sometimes produced in an excited state. The subsequent relaxation of the daughter nucleus to a lower-energy state results in the emission of a gamma-ray photon. Gamma-ray spectroscopy, involving the precise measurement of gamma-ray photon energies emitted by different nuclei, can establish nuclear energy-level structures and allows for the identification of trace radioactive elements through their gamma-ray emissions. Gamma rays are also produced in the important process of pair annihilation, in which an electron and its antiparticle, a positron, vanish and two photons are created. The photons are emitted in opposite directions and must each carry 511 keV of energy—the rest mass energy (*see* relativistic mass) of the electron and positron. Gamma rays can also be generated in the decay of some unstable subatomic particles, such as the neutral pion.

Source and the gamma ray's energy transferred to a single ejected electron. Higher-energy gamma rays are more likely to scatter from the atomic electrons, depositing a fraction of their energy in each scattering event. Standard methods for the detection of gamma rays are based on the effects of the liberated atomic electrons in gases, crystals, and semiconductors

Gamma rays can also interact with atomic nuclei. In the process of pair production, a gamma-ray photon with an energy exceeding twice the rest mass energy of the electron (greater than 1.02 MeV), when passing close to a nucleus, is directly converted into an electron-positron pair (*see* photograph). At even higher energies (greater than 10 MeV), a gamma ray can be directly absorbed by a nucleus, causing the ejection of nuclear particles or the splitting of the nucleus in a process known as photofission

24. (a) Explain the wave mechanical theory of covalent linkage.

(OR)

(b) Write a short note on Vander Waals type of binding and metallic binding.

Van Der Waals Bonding

Secondary bonds are weak in comparison to primary bonds.

They are found in most materials, but their effects are often overshadowed by the strength of the primary bonding. Secondary bonds are not bonds with a valence electron being shared or donated. They are usually formed when an uneven charge distribution occurs, creating what is known as a dipole (the total charge is zero, but there is slightly more positive or negative charge on one end of the atom than on the other).

These dipoles can be produced by a random fluctuation of the electrons around what is normally an electrically symmetric field in the atom.

Once a random dipole is formed in one atom, an induced dipole is formed in the adjacent atom. This is the type of bonding present in N2 molecules, and is known as Van Der Waals Bonding.



Secondary bonding may also exist when there is a permanent dipole in a molecule due to an asymmetrical arrangement of positive and negative regions.

Molecules with a permanent dipole can either induce a dipole in adjacent electrically symmetric molecules or thus form a weak bond, or they can form bonds with other permanent dipole molecules.

Metallic bonding

Metallic bonding is the strong attraction between closely packed positive metal ions and a 'sea' of delocalised electrons.

The attraction between the metal ions and the delocalised electrons must be overcome to melt or to boil a metal. Some of the attractions must be overcome to melt a metal and all of them must be overcome to boil it. These attractive forces are strong, so metals have high melting and boiling points. The delocalised electrons are able to move through the metal structure. When a potential difference is applied, they will move together, allowing an electric current to flow through the metal.

25. (a) Explain the experimental study of molecular spectra.

Molecular spectra

For a diatomic molecule, which we treat as a rigid rotator with a bond length fixed in the equilibrium position, the moment of inertia is $I_e = \mu r_e^2$. Here, μ is the reduced mass.

In the case of a rotator in vibrational motion, r_e needs to be replaced by the average of the square of the the internuclear distance. Consequently, the moment of inertia becomes $I_v = \mu < r^2 >$. Explicitly calculated with $r = r_e \pm s$:

Within one oscillation, the addend $2 < \mu sr_e >$ is compensated to zero. The third addend and the moment of inertia I_v remain for a molecule which has a vibration larger than μr_e^2 . In turn, the *rotational constant B* becomes dependent on the vibrational state. Note that $B_v < B_e$

with vibration: without vibration $B_v = h/4\pi c \mu r_v^2$ $B_e = h/4\pi c \mu r_e^2$.

Besides the approach from classical physics, the problem has as well been treated with purely mathematical means. A result of this is the following equation that represents a first approximation using a small correction coefficient α_e to quantify the influence of the vibrational states v on the rotational constant B_v .

$$B_v = B_e - \alpha_e(v + \frac{1}{2})$$

In addition to the influence of the molecule's oscillations, rotation itself affects molecular constants, i.e., centrifugation will stretch bonds (compare chapter Elastic rotor). The *centrifugal stretching constant* D introduces this phenomenon into our mathematical description of

molecular energy levels. Note that, like B, constant D is function of the vibrational state and the correction coefficient β_e quantifies the respective dependency.

For $\Delta J = +1$ or $J + 1 \leftarrow J$, we speak of absorption peaks within the so-called **R-branch**. Their wavenumbers v are

For $\Delta J = -1$ or $J - 1 \leftarrow J$, we speak of absorption peaks within the so-called **P-branch**. Their wavenumbers v are

$$v = v_0 - (B_v + B_{v'}) J - (B_v - B_{v'}) J^2$$
 for $J = 1, 2, 3, ...$

The distance Δv between absorption line J and absorption line J+1 becomes

R-branch:
$$\Delta v = 2(2B_{v'} - B_{v}) - 2(B_{v} - B_{v'}) J$$
 distance decreases
P-branch: $\Delta v = 2B_{v} + 2(B_{v} - B_{v'})J$ distance increases

For $B_v \approx B_{v'}$, this distance is approximately 2B. The distance between the first transitions of the two branches is $\Delta v \approx 4B_v$



Vibration and rotational energy levels of dia-atomic molecules

vibrational levels

 $\mathbf{E}_{\mathbf{v}} = (\mathbf{v} + \frac{1}{2}) h \boldsymbol{\omega}_0$

Rotation - vibrational levels

 $\mathbf{E}_{\mathbf{r}} = \mathbf{B} \cdot \mathbf{J} \left(\mathbf{J} + 1 \right)$

Some molecules display additional lines in the gap between the P- and the R-branch. These lines are connected to transitions with $\Delta J = 0$ and form the so-called **Q-branch**. As the rotation of the system is maintained, the axis of rotation must shift ($\Delta K \neq 0$) and a change of the angular momentum of electron orbitals must occur. If we consider **diatomics**, lines of a Q-branch must also have such an angular momentum which contributes to the total angular momentum of the molecule.

Projection of the electron's rotation onto the axis of the molecule: $\Lambda = 0, 1, 2, ...$



The quantum number Λ (recall chapter "<u>Term symbols and selection rules</u>") denotes the projection of this orbital's angular momentum onto the molecule's axis. For $\Lambda = 0$, nothing changes. For the molecular total momentum, which includes rotation of nuclei and electrons, the relation $|J| \ge |\Lambda|$ applies.

The respective energy levels are analogous to those of the <u>symmetric top</u>. Here, the constant A is in connection with the momentum of electron orbitals. Note that A >> B.

$$E_{J} = \begin{array}{c} BJ (J+1) \\ due \text{ to rotation of nuclei} \end{array} + \begin{array}{c} (A - B) & \Lambda^{2} \\ due \text{ to electrons} \end{array}$$

For $\Lambda \neq 0$, there are new selection rules: Besides $\Delta J = \pm 1$, as well transitions with $\Delta J = 0$ are allowed.

With the NO molecule, we have this situation, but due to spin-related phenomenona, a detailed analysis is quite complicated. With no regard to the spin, there is the following approach to the lines of the **Q-branch**:

$$E(v',J) - E(v,J) = v_0 + B_{v'}J(J+1) + (A-B_{v'})\Lambda^2 - B_vJ(J+1) - (A-B_v)\Lambda^2$$

$$v = v_0 - (B_v - B_{v'})J(J+1) + (B_v - B_{v'})\Lambda^2$$

As $B_v \approx B_{v'}$, the lines within this branch lie very close to each other.

$\Delta K = 0$	$\Delta J = \pm 1 \text{for } K$ $= 0$	diatomic molecules	
parallel band	$\Delta J = 0, \pm 1 \text{ for } K$ $\neq 0$	diatomic molecules, electronic contribution to J	
$\Delta K = \pm 1$ perpendicular band	$\Delta J = 0, \pm 1$		

For the symmetric top, we have the following selection rules

Of course, the intensity of rovibronic lines depends on the probability of a transition and on the occupancy of the involved states. In cases where v = 0 is the only occupied vibrational level, the intensity of lines is proportional to the population N_J and the so-called <u>Hönl-London-Factor</u> S_J for this rotational state J.

$$\begin{split} I &\propto N_J \cdot |\mu_{J'J}|^2 \\ I &\propto N_J \cdot S_J \end{split}$$

As the transition probabilities for a simple rotator at high rotational states are in a quite narrow range, mainly the vibrational ground state distribution over J rules the intensity of lines. To find out the most probable rotational state, we fall back on *Boltzmann's* theory:

$$N_J \sim (2J+1)e^{\frac{-E_{ax}}{kT}} = (2J+1)e^{\frac{-BJ(J+1)}{kT}}$$

An estimation of the distribution is feasible if the distance betweeen the rotational levels is much smaller than the product kT, a condition which is fulfilled for temperatures around 300 Kelvin. We use $dN_J/dJ = 0$ as condition for a maximum.

$$\begin{aligned} \frac{d}{dJ} N_J &= 0 \quad \Rightarrow \\ \frac{d}{dJ} (2J+1) e^{-BJ(J+1)/kT} &= 2 e^{-BJ(J+1)/kT} - \frac{B}{kT} (2J+1)^2 e^{-BJ(J+1)/kT} = 0 \quad \Rightarrow \\ J_{max} &= -\frac{1}{2} + \sqrt{\frac{kT}{2B}} \approx \sqrt{\frac{kT}{2B}} \end{aligned}$$

(OR)

(b) What is isotopic effect and explain the effect in molecular spectra.

Isotope Effect in molecular spectra

In this section we will study a first astrophysical application of molecular spectroscopy, namely the determination of abundance ratios of different isotopes. Molecules serve as a much more ideal tool to distinguish different isotopes than atoms. This is because the presence of more or less neutrons in the nucleus of a specific chemical element does not strongly modify the electric field and thus has only a small influence on the electron configuration. The same is true for the electron configuration of molecules of course. However, the energy of nuclear motion in molecules due to vibration and rotation is influenced already to first order if the number of neutrons and thus the mass of the nucleus is changed. Thus, isotopic molecules have different frequencies of vibrations and rotations.

First we will consider the modification of molecular spectra due to the presence of different isotopes. Then we will look at several examples that illustrate how knowledge of isotope ratios allows us to gain insight into astrophysical objects and processes. Later, in Chapter 6 (Astrobiology), we will discuss an additional important example where knowledge of isotope ratios is crucial for determining the origin of water on Earth.

Vibration

For isotopic molecules, i.e. molecules that differ only by the mass of one or both of the nuclei but not by their atomic number (for example ${}^{1}\mathrm{H}^{35}\mathrm{C1}$ and ${}^{1}\mathrm{H}^{37}\mathrm{C1}$), the vibrational frequencies are obviously different. Assuming harmonic vibrations the (classical) vibrational frequency is given by

$$v_{\rm osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$
,

Where the force constant k, since it is determined by the electronic motion only, is exactly the same for different isotopic molecules, whereas the reduced mass is different. Therefore, if we let the superscript "i" distinguish an isotopic molecule from the "ordinary" molecule we have

$$\frac{v_{\rm osc}^{\rm i}}{v_{\rm osc}} = \sqrt{\frac{\mu}{\mu^{\rm i}}} = \rho$$

The heavier isotope has the smaller frequency. If the superscript "i" refers to the heavier isotope the constant will be smaller than 1. For example, the values for the pairs ${}^{1}\text{H}{}^{35}\text{C1}$ and ${}^{1}\text{H}{}^{37}\text{C1}$, ${}^{1}\text{H}{}^{35}\text{C1}$ and ${}^{2}\text{H}{}^{35}\text{C1}$, ${}^{10}\text{BO}$ and ${}^{11}\text{BO}$, and ${}^{16}\text{O}{}^{16}\text{O}$ and ${}^{16}\text{O}{}^{18}\text{O}$ are 0.99924, 0.71720, 0.97177, and 0.97176, respectively

We find for the vibrational levels of two isotopic molecules (still assuming harmonic oscillations)

$$G^{i}(v) = \omega_{e}^{i}\left(v + \frac{1}{2}\right) = \rho\omega_{e}\left(v + \frac{1}{2}\right) = \rho G(v)$$

Therefore, the separation of corresponding vibrational levels in two isotopic molecules are somewhat shifted (and as a result spectral lines are also shifted). The levels of the lighter isotope always lie higher than those of the heavier isotope

If anharmonicity is taken into account, the calculations become rather more involved and will not be reproduced here. The formulae for the energy levels are found to be in a very good approximation

$$G(v) = \omega_{e}\left(v + \frac{1}{2}\right) - \omega_{e} x_{e}\left(v + \frac{1}{2}\right)^{2} + \omega_{e} y_{e}\left(v + \frac{1}{2}\right)^{3} + \dots ,$$

$$G^{I}(v) = \rho \omega_{e}\left(v + \frac{1}{2}\right) - \rho^{2} \omega_{e} x_{e}\left(v + \frac{1}{2}\right)^{2} + \rho^{3} \omega_{e} y_{e}\left(v + \frac{1}{2}\right)^{3} + \dots ,$$

In other words, the vibrational constants are modified as

$$\begin{split} & \omega_{\rm e}^{\rm i} = \rho \, \omega_{\rm e} \ , \\ & \omega_{\rm e}^{\rm i} x_{\rm e}^{\rm i} = \rho^2 \, \omega_{\rm e} \, x_{\rm e} \ , \\ & \omega_{\rm e}^{\rm i} y_{\rm e}^{\rm i} = \rho^3 \, \omega_{\rm e} \, y_{\rm e} \ . \end{split}$$

Rotation

Since the reduced mass is inversely proportional to the rotational constant B, molecules containing heavy isotopes have rotational lines corresponding to lower quantum energies and smaller line spacing. Specifically, we find for the rotational constant B of the two isotopic molecules

$$B_{\rm e}^{\rm i} = \frac{\hbar^2}{2\mu^{\rm i} r_{\rm eq}^2 hc} = \rho^2 B_{\rm e}$$

Note that the internuclear distances in diatomic (and polyatomic) molecules are entirely determined by the electronic structure. They are therefore exactly equal in isotopic molecules as long as no vibration occurs. The rotational energies of the two isotopic molecules are thus connected by

$$F' = B_{e}^{i}J(J+1) = \rho^{2}B_{e}J(J+1) = \rho^{2}F$$

Rotational levels of the heavier molecule have smaller energies. Furthermore, the separation of neighboring lines in the rotational spectrum (which is 2*B* in first approximation) differs for isotopic molecules. For example, for the ¹²CO molecule, 2*B* is found to be 3.842 cm^{-1} , and for the ¹³CO molecule containing the heavier isotope of carbon. 2*B* is found to be 3.673 cm^{-1} . Figure shows the resulting differences in the rotational spectra of CO containing the isotopes ¹²C and ¹³C.



Fig. The isotopic effect on the rotational energy levels and the corresponding rotational spectrum of the CO molecule

For simultaneous vibration and rotation, in a first approximation, we simply have to add the vibrational and rotational isotope effects. As a result, the lines of a rotation-vibration band of an isotopic molecule do not have exactly the same separations as the lines of the "normal" molecule. In other words, the isotope displacement between corresponding lines of the two bands is dependent on J.

Since the rotational energies are smaller than the vibrational energies, the rotational isotope shift is, in general, smaller than the vibrational one, despite the fact that the former scales with ρ^2 while the latter scales with ρ .

For more precise calculation, it is necessary to take into account the interaction of vibration and rotation, i.e. the rotational constants α , β , *D*, and possibly higher order ones. To a very good approximation we may use

$$D_{e}^{i} = \rho^{4} D_{e} ,$$

$$\alpha^{i} = \rho^{3} \alpha ,$$

$$\beta^{i} = \rho^{5} \beta .$$