Atomic Structure

Basics

Mass number (A) = number of protons + number of neutrons

Note that atomic weight of an element is approximately equal to the mass number

Mass of an electron(m_e) $= \frac{1}{1873}$ amu (1 amu =1.66 $\times 10^{-24}$ g)

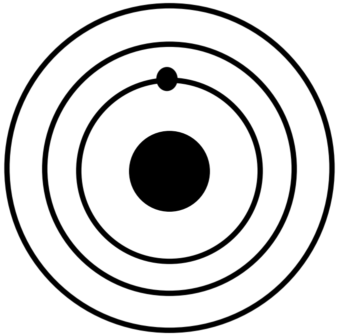
$= \mathbf{9.1 \times 10^{-31}}\ \boldsymbol{kg}$ (In SI units)

Think of comparing mass of electron with mass of a proton or a neutron which is equal to 1 amu

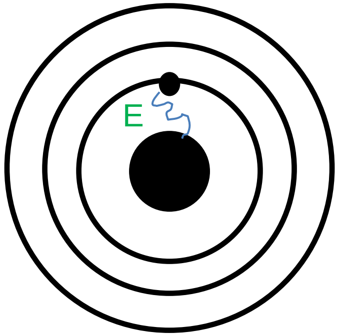
$m_e + m_p \approx m_p$

Bohr's Postulates

1. Electrons revolve around the nucleus in certain orbits without losing energy



2. Energy is absorbed / emitted only when an atom jumps from one orbit to another



3. Electron is restricted to those orbits in which electrons angular momentum is an integral multiple of $\frac{h}{2\pi}$

$$\textbf{Angular momentum of electron} = n \times \frac{h}{2\pi}$$

Where n is an integer

Note that these are valid only for one electron species like H , He^{+}

Hydrogen Spectral Lines

Wavenumber for e^- going from n_2 to n_1

$$\frac{1}{\lambda} = RZ^2\left(\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right)$$

Note that here R is in SI units

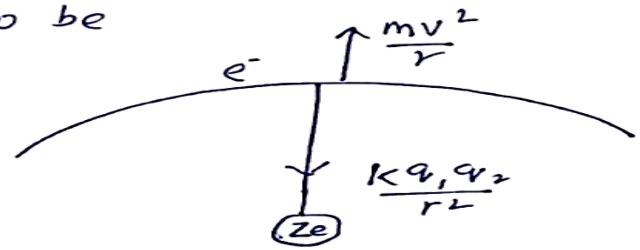
Lines	n_1	n_2	Spectral Region
Lyman	1	2,3,4,.....	Ultraviolet (UV)
Ballmer	2	3,4,5.....	Visible
Paschen	3	4,5,6.....	Infrared (IR)
Brackett	4	5,6,7.....	Infrared (IR)
Pfund	5	6,7,8.....	IR
Pfund	6	7,8,9....	———

Note that from the observed line in the spectrum , wavenumber of energy required for transition or absorption can be calculated

(1)

① Concept of Centrepetal and Centrifugal force

For e^- to revolve in an orbit the two forces has to be balanced



$$\frac{K q_1 q_2}{r^2} = \frac{mv^2}{r}$$

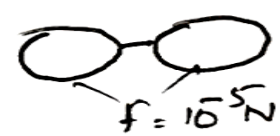
(Ze), e

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

Q1) Two Carbon disc of 1g each are 1 cm apart have equall and opposite charges. if FOA between them is 10^{-5} N. Calculate the ratio of excess e^- to total atoms on −ve charged disc.

a) $4.17\times10^{-4}\, e^-/atom$ b) $9.25\times10^{-17}\, e^-/atom$

c) $4.17\times10^{-14}\, e^-/atom$ d) $3.25\times10^{14}\, e^-/atom$



Concept Apply $F = \frac{K q_1 q_2}{r^2}$ $q_1 = q_2 = q$

$$10^{-5} = \frac{K(9\times10^9)\, q^2}{(10^{-2})^2}, \quad q = 3.3\times10^{-10}C \text{ on each disc}$$

now 1.6×10^{-19} C —— $1e^-$

3.3×10^{-10} C —— ? 2.08×10^9

now no of atoms in 1g Carbon $= \frac{2.08\times10^9}{5\times10^{22}}$

$= 4.17\times10^{-14}\, e^-/atom$

no of atoms in 1g C $= \frac{6.022\times10^{23}}{12}$

$= 5\times10^{22}$

(2) Concept of Quantum Theory of Radiation

$E = nh\nu$, $E = \frac{nhc}{\lambda}$, $E = \frac{n \times 20 \times 10^{-26}}{\lambda}$

E → Joules, λ → meters

$E = \frac{n \times 12400}{\lambda\ (Å)}$

E → eV

$400\ nm \rightarrow 400 \times 10^{-9}\ m \rightarrow 4000\ Å$

Remember: Intensity is no of photons falling on a unit area per sec

$I_{Radiation} \uparrow$ no of photons $\uparrow$

to comment on Energy we need to calculate

$E = \frac{n \times 20 \times 10^{-26}}{\lambda}$

Q The dissociation energy of H_2 is 430 kJ mol^{-1}. if H_2 is exposed to radiation of λ (254 nm) what % of radiation is converted to KE

Solve H — H

$\frac{430 \times 10^3}{6 \times 10^{23}}$ J/molecule — x

$E_{photon} = \frac{hc}{\lambda} = \frac{20 \times 10^{-26}}{254 \times 10^{-9}}$ — y

$y > x$ to have KE

$y - x = z$, $\frac{z}{y} \times 100 =$ % Radiation Converted into KE

Nearly 8 – 9 %.

Q3) A certain dye absorbs light of $\lambda = 4530\,\text{Å}$ and emits light of $5080\,\text{Å}$. Assuming that under given conditions 47% of absorbed energy is emitted out as light. Calculate the ratio of quanta of energy emitted to the quanta of energy absorbed

a) 1.897 b) 0.527 c) 2.384 d) 5.27

Concept $E_{absorbed} \times \frac{47}{100} = E_{emitted\ out}$

$$\frac{n_{ab} \times hc}{\lambda_{ab}} \times \frac{47}{100} = \frac{n_{emi} \times hc}{\lambda_{emi}}$$

$$\frac{n_{emi}}{n_{ab}} = \frac{47}{100} \times \frac{\lambda_{emitted}}{\lambda_{absorbed}}$$

$$= \frac{47}{100} \times \frac{5080}{4530} = 0.527$$

Q4) A photon of 300 nm is absorbed by a gas and then reemits two photons. One re-emitted photons has wavelength 496 nm calculate energy of other photon

a) 2.6×10^{-19} J b) 4.8×10^{-19} J c) 5.3×10^{4} J d) 7.3×10^{5} J

Concept : $E_{absorbed} = E_{emitted}$

$$E = E_1 + E_2$$

$$\frac{hc}{\lambda_{ab}} = \frac{hc}{\lambda_1} + \frac{hc}{\lambda_2}$$

find out λ_2 and then

$$E_2 = \frac{20 \times 10^{-26}}{\lambda_2}$$

(4)

(3) Bohrs Model (H and H Like species)

(a) $r = \frac{0.529 n^2}{Z}$ b) $V = \frac{2.18 \times 10^6 Z}{n}$

(c) $TE = \frac{-13.6 Z^2}{n^2}$ d) $T \propto \frac{n^3}{Z^2}$ (e) $\nu \propto \frac{Z^2}{n^3}$

(F) $\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

R_H = 109677 cm^{-1}, n_1 = GS, n_2 = ES

Q5) Calculate the ratio of difference between 1st and 2nd to that of 2nd and 3rd Bohrs radius, velocity and Total energy for H atom

$r = 3:5$ $V = 3:1$ $TE = 27:5$

$r = \frac{x n^2}{Z}$ $V = \frac{x Z}{n}$

$r_1 = x$
$r_2 = 4x$] 3
$r_3 = 9x$] 5

$V_1 = x$
$V_2 = x/2$] $x/2$
$V_3 = x/3$] $x/6$

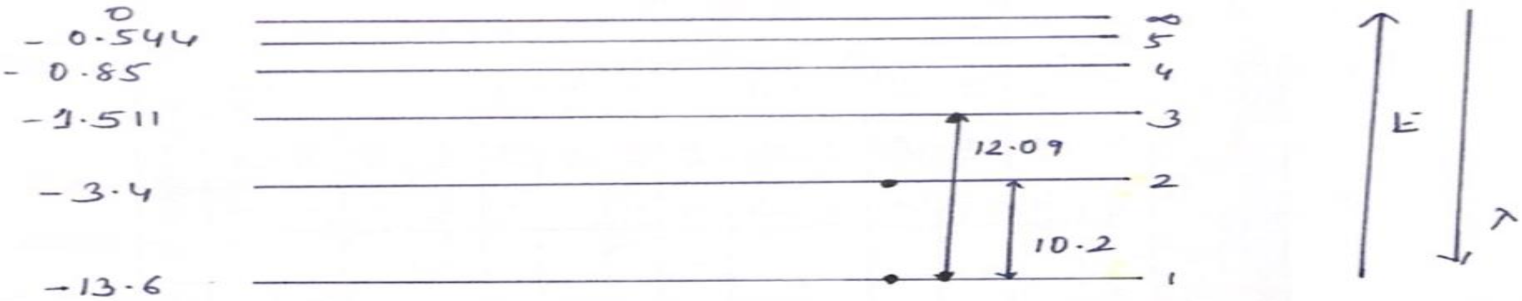
$TE = \frac{-x Z^2}{n^2}$
$TE_1 = +x$
$TE_2 = +x/4$
$TE_3 = +x/9$

(4) Relation between Total energy, KE and PE

1) $TE = -KE$ 2) $TE = \frac{PE}{2}$ 3) $\frac{KE}{PE} = -\frac{1}{2}$

$T_E = \frac{-kze^2}{2r}$ $KE = \frac{kze^2}{2r}$ $T_E = \frac{PE}{2}$

Spectrum :



Relation between IE, EE, and SE

IE	EE	SE
$E_\infty - E_1$	$E_2 - E_1$	$E_\infty - E_2$
$0 - (-13.6)$		
$= 13.6$	$= 10.2$	3.4

IE = EE + SE

$$\frac{13.6 z^2}{n^2} \qquad \frac{10.2 z^2}{n^2} \qquad \frac{3.4 z^2}{n^2}$$

Q6) Calculate EE in eVolt for 1st orbit of Li^{2+}

$10.2 \times 9 = 91.8$ ✓

Q7) IE He^+ = 19.6×10^{-18} J/atom.

Calculate IE of 1st stationary state of Li^{2+} (44.1×10^{-18} J/atom)

IE for Li^{2+} = IE of H × 9 ①

IE for He^+ = IE of H × 4 ②

IE of Li^{2+} = $\frac{\text{IE of } He^+}{4} \times 9$

Calculation of wavelength in the spectrum

Q6) $\frac{\lambda max}{\lambda min}$ or $\frac{E max}{E min}$ in Lyman Series for H

Maximum E
Maximum T
Minimum λ

$n_1 = 1 \quad n_2 = \infty$

$\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{1^2} - \frac{1}{\infty^2} \right), \quad \frac{1}{\lambda} = R_H$

minimum E
minimum T
Maximum λ

$n_1 = 1, \quad n_2 = 2$

$\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{3 R_H}{4}$

8Q) if Shortest wavelength for H atom in Lyman Series is x then longest wavelength for He^+ in Balmer Series

a) $\frac{9x}{5}$ b) $\frac{5x}{9}$ c) $\frac{3x}{4}$ d) $\frac{27x}{5}$

Shortest (minimum) λ, so Max E, so Max T

$n_1 = 1, \quad n_2 = \infty$

$x \leftarrow \frac{1}{\lambda_{min}} = R_H$

longest λ, min E, min T, $n_1 = 2$, $n_2 = 3$

$\frac{1}{\lambda_{max}} = R_H\, 4 \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = \frac{5 R_H}{9}$

Q8) Wavelength of high energy transition of H atom is 91.2 nm. Calculate corresponding wavelength for He^+

a) 22.8 nm b) 91.2 nm c) 40.6 nm d) 74.8 nm

Concept : high Energy (Max Energy) Max T

so for both transitions are same

$$\underset{91.2}{\frac{1}{\lambda_H}} = R_H \quad (1) \qquad \frac{1}{\lambda_{He^+}} = R_H \, 4$$

$$\lambda_{He^+} = 22.8\,nm$$

Q9) What transition in the Hydrogen spectrum would have same λ as Balmer transition $n=4$ to $n=2$ of He^+

a) $n_1 = 1,\ n_2 = 2$ b) $n_1 = 3,\ n_2 = 4$

c) $n_1 = 3,\ n_2 = 5$ d) $n_1 = 4,\ n = 6$

Concept $\frac{1}{\lambda} = R_H\, 4\left(\frac{1}{2^2} - \frac{1}{4^2}\right) = \frac{3R_H}{4}$ For He^+

For H, $\frac{1}{\lambda} = \frac{3R_H}{4}$ will only come when u take $n_1 = 1,\ n_2 = 2$

$$\frac{1}{\lambda} = R_H\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$

De- Broglie Equation

Particles of matter such as electrons, protons etc. have properties of waves

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

$\boldsymbol{M}$ is mass of particle,

$\boldsymbol{v}$ is its velocity

OR

$$\boldsymbol{\lambda = \frac{h}{p}}$$

$\boldsymbol{p}$ is momentum

Note that λ will be significant only when mass m of particle is very small like that of electron or proton

Example: For a block say of 100 g mass , λ will be insignificant and wave characteristic of the particle can be ignored

Quantization Of Angular Momentum

Note that electron is assumed to exhibit wave characteristics

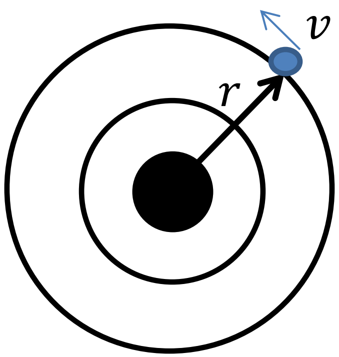
$$2\pi r = n\lambda$$
$$= n\frac{h}{mv}$$

Note that circumference of the circle must be an integral multiple of the wavelength

Or

$$mvr = n \cdot \frac{h}{2\pi} \quad (angular\ momentum\ )$$

This is the mechanical picture of de-Broglie equation



Relation Between Wavelength (λ) And Potential (V)

$$K.E. = \frac{1}{2}mv^2$$

$$= V.e$$ (where V is the potential)

Note that electron posses matter characteristic as well along with its wave nature

$$\boldsymbol{v = \sqrt{\frac{2V.e}{m}}}$$

$$\boldsymbol{= \sqrt{\frac{2E}{m}}}$$

$$\lambda = \frac{h}{\sqrt{2.V.e.m}}$$

Since, $E = \frac{hc}{\lambda}$

$$\lambda = \frac{1.226}{\sqrt{V}}\ \text{nm}$$

Here V is in Volts

Quantum Mechanical Picture Of An Atom

Very small particle like electrons do not follow law of classical mechanics

As wave properties at negligible mass are significant

Wave mechanics or Quantum mechanics describe their properties properly

In this approach electron in an atom is treated as a standing or stationary wave

Standing wave does not travel and has at least one node

Schrodinger Wave Equation

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

ψ is the waveform

- Must be finite
- Must be single valued
- Must be continuous

$$\nabla^2 (laplacian\ operator\ ) = \frac{\delta^2}{\delta x^2} + \frac{\delta^2}{\delta y^2} + \frac{\delta^2}{\delta z^2}$$

E is total energy

V is P.E. of the particle

Note that interpretation of ψ is that it describes wave characteristics of a particle

And its value at a point relates the possibility of particle being there at that time

Heisenberg Uncertainly Principle

It is impossible to determine precisely both the position and momentum of a subatomic particle simultaneously

Note that it is applicable to subatomic particles only and not to large objects

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

Δx and Δp represent uncertainties in position and momentum respectively

Or

$$\Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$$

Similarly

$$\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$$

Note that the principle goes against the concept of Bohr's definite orbit which is only region of probability of finding an electron

Hiesenberg Uncortanity Principle

(8)

$\Delta x \times \Delta p \geq \frac{h}{4\pi}$ or $\Delta x \times m\Delta v \geq \frac{h}{4\pi}$

$\rightarrow \Delta f \times \Delta t$, $\Delta x \times \Delta f$ $\leftarrow$ $\Delta E \times \Delta t \geq \frac{h}{4\pi}$

Q) if $\Delta x = \Delta p$ than $\Delta v =$

a) $\sqrt{h/\pi}$ b) $\sqrt{h/2\pi}$ c) $\frac{1}{2m}\sqrt{h/\pi}$ d) $\frac{1}{m}\sqrt{h/\pi}$

Use $\Delta x \times \Delta p \geq \frac{h}{4\pi}$, $(\Delta p)^2 = \frac{h}{4\pi}$, $\Delta p = \sqrt{\frac{h}{4\pi}}$

$m\Delta v = \sqrt{\frac{h}{4\pi}}$, $\Delta v = \sqrt{\frac{h}{4\pi}} \times \frac{1}{m}$ $= \frac{1}{2m}\sqrt{\frac{h}{\pi}}$

de broglie nalue (dual nature of e^-)

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

for e^- $\lambda = \frac{h}{mv}$

$\underbrace{2\pi r = n\lambda}$ $\rightarrow$ no of waves in an orbit

$\downarrow$

Constructive waves (waves in phase)

$2\pi r \neq n\lambda$

destructive waves not in phase

$E = eV$

for e^-

$KE = \frac{mv^2}{2} = eV$

$v^2 = \frac{2eV}{m} = \sqrt{\frac{2eV}{m}}$

$\lambda = \frac{h}{mv} = \frac{h}{m\sqrt{\frac{2eV}{m}}}$

$= \frac{h}{\sqrt{2eVm}}$

Q) With what velocity must an e^- travel so that its momentum is equals to that of a photon of wavelength $\lambda = 5200\,\mathring{A}$

$\Rightarrow$ momentum of e^- = momentum of photon

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

$$9.1\times10^{-31} \times V = \frac{6.626\times10^{-34}}{5200\times10^{-10}}$$

$V = 1400\ m/sec$

Q) An electron practically at rest in initially accelerated by a PD of 100 Volt. has de broglie wavelength $\lambda_1\,\mathring{A}$. it then get retarted by 19 volt has dB $\lambda = \lambda_2\,\mathring{A}$. a further retardation by 32 volt changes wavelength to $\lambda_3\,\mathring{A}$ find out $\frac{\lambda_3 - \lambda_2}{\lambda_1}$

Solution

$e^- \xrightarrow{100V} \lambda_1$

$49 \longleftarrow\ \longleftarrow 81$

$\lambda_3 \qquad \lambda_2$

$$\lambda_1 = \sqrt{\frac{150}{100}}$$

$$\lambda_2 = \sqrt{\frac{150}{81}}$$

$$\lambda_3 = \sqrt{\frac{150}{49}}$$

$\frac{20}{63}$

(4)

$$\lambda = \frac{h}{\sqrt{2eVm}} = \sqrt{\frac{150}{V}} = \frac{h}{\sqrt{2KEm}}$$

Q) $\frac{\lambda p}{\lambda \alpha}$ (both having same P.D) $\frac{h}{\sqrt{2eVm}} \Big/ \frac{h}{\sqrt{2(2e)4mV}}$

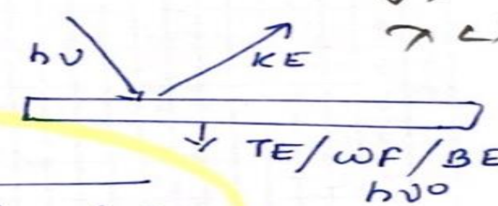
Q) $\frac{\lambda p}{\lambda \alpha}$ (both having same KE) $\frac{h}{\sqrt{2KEm}} \Big/ \frac{h}{\sqrt{2KE\,4m}}$

Photo electric effect

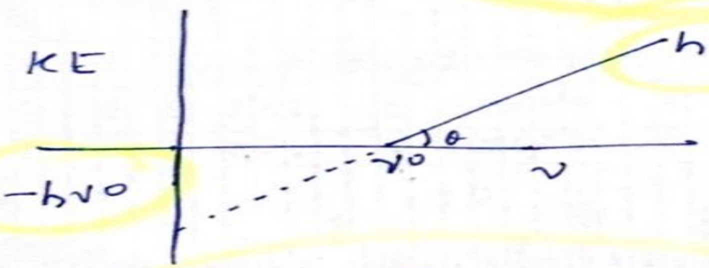
$$KE = h\nu - h\nu_0$$
$$= h(\nu - \nu_0)$$
$$= \frac{hc}{\lambda} - \frac{hc}{\lambda_0}$$

$\nu > \nu_0$

$\lambda < \lambda_0$



$$\frac{mv^2}{2} = \frac{hc}{\lambda} - \frac{hc}{\lambda_0}, \quad V = \sqrt{\frac{2hc}{m}\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)}$$



Intercept $= -h\nu_0$

Slope $= h$

$$KE = h\nu - h\nu_0$$
$$= h(\nu - \nu_0)$$

y $\quad$ x

Note: Stopping Potential is KE

$$KE = eV$$

Q Energy required to stop the ejection of $\bar{e}$ from Cu plate is 0.24 eV. Calculation the work functi when radiation of $\lambda = 254\ nm$ strikes the plate

Approach :

$$KE = h\nu - h\nu^0$$

$$0.24 \qquad \frac{12400}{2540} - wf$$

$$\hookrightarrow 4.88$$

$$wf = 4.88 - 0.24 = 4.64\ eV$$

Q Photoelectric emission is observed from a surface for frequncies ν_1 and ν_2 $(\nu_1 > \nu_2)$ if max KE of photoelectric is in the ratio $1:k$ then threshold frequency ν_0 is given by

$$\Rightarrow \quad KE_1 = h\nu_1 - h\nu^0 \qquad KE_2 = h\nu_2 - h\nu^0 \qquad \left\{ \quad \frac{1}{k} = \frac{\nu_1 - \nu_0}{\nu_2 - \nu^0} \right.$$

$$k\nu_1 - k\nu_0 = \nu_2 - \nu^0$$

$$\nu^0 =$$

Principle Quantum Number

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

Solution of Schrodinger equation gives a set of numbers called quantum numbers

Principle quantum number (n):

It describes the main energy level on electron occupies

n:	1	2	3	4 ....
Known as:	K	L	M	N ....

Note that n is always a positive integer

Azimuthal Quantum Number (l)

Also called angular momentum quantum number

Tells a sublevel or specific shape of atomic orbital than an electron occupies

l:	0	1	2	3 ……… (n-1)
known as:	s	p	d	f …………

Note that for a given value of n, l can take integral values from 0 to (n-1)

Maximum value of l depend on value of n

Orbital angular momentum (L)

$$\sqrt{\boldsymbol{l(l+1)}} \cdot \frac{\boldsymbol{h}}{\boldsymbol{2\pi}} \qquad l = 0,1,2,3 \ \cdots\cdots$$

$$\hbar(Dirac) = \frac{\boldsymbol{h}}{\boldsymbol{2\pi}}$$

Magnetic Quantum Number (m)

m designates specific orbital within a subshell (l)

Within each subshell m can take any integral values from – l to $+l$

Note that orbitals within a given subshell differ in their orientation in space but not in their energies

$$\mathbf{m} = (-l), \cdots\cdots\cdots\cdots\ 0, 1, 2, \cdots\cdots\cdots\cdots, (+l)$$

Maximum value of m depends on value of l

Example : for $\mathrm{l} = 1,\quad m = -1\ ,\quad 0\ ,\quad +1$

p -subshell $\quad p_x \quad p_y \quad p_z$

Magnetic Dipole Moment (μ)

$$\boldsymbol{\mu_B} = \frac{\boldsymbol{eh}}{\boldsymbol{4\pi m}}$$

m is mass of electron

$$= \frac{\boldsymbol{e\hbar}}{\boldsymbol{2m}} \quad \text{in Bohrs Magneton(BM)}$$

$$\therefore \boldsymbol{\mu_B} = 9.27 \times 10^{-24}\ JT^{-1}$$

In SI units

$$= 9.27 \times 10^{-21} ergG^{-1}$$

In CGS units

Note that when an atom has angular momentum L , it acts like a small magnet with magnetic dipole moment (μ)

Spin Quantum Number (s)

's' refers to the spin of an electron and orientation of magnetic field produced by this spin

For every set of $\boldsymbol{n}$, $\boldsymbol{l}$ and $\boldsymbol{m}$ values; s can take two values → $+\frac{1}{2}$ **or** $-\frac{1}{2}$

Note that the value of n , l and m describe a particular atomic orbital therefore each atomic orbital can accommodate no more than two electrons;

One with s= $+\frac{1}{2}$ and another with s $= -\frac{1}{2}$

↓

From Pauli exclusion principle

Spin Angular Momentum (S)

$$\boldsymbol{S = \sqrt{s(s+1)} \cdot \frac{h}{2\pi}}$$

where s =spin quantum number

Since, $s = \frac{1}{2}$,

$$S = \frac{\sqrt{3}}{2}\frac{h}{2\pi}$$

$$\boldsymbol{S = \frac{\sqrt{3}\hbar}{2}}$$

Quantum Numbers :

n, l, m, s (Energy, Shape, Orientation, Spin)

n: $-\infty$

l: $0 \to (n-1)$

m: $-l \;\; 0 \;\; +l$

s: $(+\frac{1}{2}, -\frac{1}{2})$

$l = 0$ s
$l = 1$ p
$l = 2$ d
$l = 3$ f

For $4s^1$ ($n=4$, $l=0$, $m=0$; $s = \pm \frac{1}{2}$)

For $4p^1$ ($n=4$, $l=1$, $m = -1, 0, +1$, $s = \pm \frac{1}{2}$)

For $4d^1$ ($n=4$, $l=2$, $m = -2, -1, 0, +1, +2$) $s = \pm \frac{1}{2}$

For finding out Period, Groups block

$4s^1$ → Gp no = 1
→ s block
4 → Period

$4p^1$ → Gp = 1+12 = 13
→ p block
4 → Period

$4d^1$ → Gp no = 1+2 = 3
→ d block
4+1 = Period no

$4f^1$ → Gp no = 3
→ f block
4+2 = P no

Calculation of Magnetic Moment

$\mu = \sqrt{n(n+2)}$

μ → BM

n → no of unpaired e^-

For eg Fe^{2+} $4s^2 \; 3d^6$

$4s^2$ → lost

$3d^6$ → means 4 unpaired e^-

Mn_{25} $4s^2 3d^5 = 5$

Fe_{26} $4s^2 3d^6 = 4$

Co_{27} $4s^2 3d^7 = 3$

Ni_{28} $4s^2 3d^8 = 2$

Q A Compound of Vanadium has a magnetic moment of 1.73 BM. the electronic Configuration of Vanadium ion in the Compound

$\Rightarrow$ $\mu = \sqrt{n(n+2)}$

$1.73 = \sqrt{n(n+2)}$

$n = 1$

$_{23}V$ | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$

$3d^1$ ✓✓

and if they ask OS of V^{n+} $n = 4$ ✓