Unit: III

Vector Atom Model

Magnetic Dipole moment of electron due to orbital and spin motion – Bohr magneton:–

(சுற்றுப்பாதை மற்றும் சுழற்சி இயக்கத்தால் எலக்ட்ரானின் காந்தத்திருப்புத்திறன் போர் மேக்னட்டான்)

Consider the $\bar{e}$ moving in an elliptical orbit of Area A with a period T. The electron crosses any point orbit $1/T$ times in unit time.

Current $i = e/T$

Area $\Rightarrow A$

$e \Rightarrow$ charge of the $\bar{e}$

Applying Ampere's theorem, this current gives rise to a magnetic dipole moment μ_l given by,

$$\mu_l = iA = eA/T \rightarrow (1)$$

$A \rightarrow$ area of the orbit.

velocity in central orbit $\frac{1}{2} r^2 \, d\phi/dt$, the area,

$$A = \int_0^T \frac{1}{2} r^2 (d\phi/dt) \cdot dt \rightarrow (2)$$

Angular momentum of the $\bar{e}$,

$$P_l = mr^2 \, d\phi/dt = \text{constant} \rightarrow (3)$$

(or)

$$\frac{1}{2} r^2 \left(\frac{d\phi}{dt}\right) = P_l/2m = \text{const} \rightarrow (4)$$

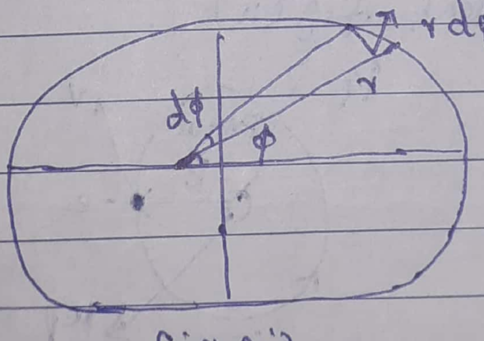

fig (i)

$$A = \int_0^T \left(\frac{P_l}{2m}\right) dt = \frac{P_l T}{2m} \rightarrow (5)$$

Sub in equ (5), $\mu_l = e/2m \, P_l \rightarrow (6)$

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We have, $P_l = l\hbar$ → (7)

$$\mu_l = \frac{e}{2m} \times l\hbar = \frac{e\hbar}{2m} l \rightarrow (8)$$

μ_l is directly proportional to l.

$\frac{e\hbar}{2m}$ is the smallest unit of magnetic dipole moment is called the Bohr electron magneton (μ_B).

$$\mu_B = \frac{e\hbar}{2m} = \frac{(1.602 \times 10^{-19}) \times (1.055 \times 10^{-34})}{2 \times (9.109 \times 10^{-31})} = 9.274 \times 10^{-34} \; J_T \rightarrow (9)$$

The ratio magnetic dipolemoment and angular momentum is called the gyromagnetic ratio.
(ഗൈറോമാഗ്നറ്റിക് റേഷ്യോ)

ie, $\frac{\mu_l}{P_l} = e/2m = 8.8 \times 10^{9} \, C/kg$ → (10)

equ (10) canbe written as,

$$\frac{\mu_l}{P_l} = \frac{e}{2m} \cdot g \rightarrow (10-a)$$

$g \rightarrow$ Lande's splitting factor.

$$g = 1 \; ; \; \frac{\mu_l}{P_l} = \frac{e}{2m}.$$

The electronic charge is -ve, the magnetic dipole moment vector is directed opposite to that angular moment fig (ii)

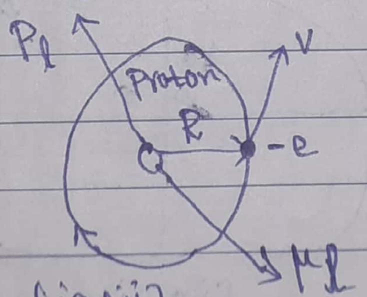

fig (ii)

equ (10-a) canbe written as,
μ_ly

$$\frac{\mu_l}{P_l} = -g_l \frac{e}{2m} \quad \text{with } g_l = 1$$

||ly

$$\frac{\mu_s}{P_s} = -g_s\, e/2m \quad \text{with } g_s = 2$$

$$\frac{\mu_J}{P_J} = -g_j\, e/2m \qquad \rightarrow (11)$$

Here, g is called Lande's Splitting factor.

Magnetic Dipole Moment Due to Spin:-

(சுழற்சியின் காந்த இருமுனை திருப்புத்திறன்)

An $\bar{e}$ spinning about its axis should also behave as a tiny magnet and possess a magnetic dipole moment due to the spin. This is known as magnetic dipole moment of spin. The Spin magnetic dipole moment (μ_s) is,

$$\mu_s = 2 \cdot (e/2m) \cdot P_s \rightarrow (12)$$

Where, $P_s = s\hbar$

$$\therefore \mu_s = \frac{2 \cdot e}{2m} \times s\hbar \rightarrow (13)$$

$$\mu_s = \frac{\cancel{2} \cdot e}{\cancel{2}m} \times s \cdot \frac{h}{2\pi}$$

$$\mu_s = \frac{e}{m} \cdot s \cdot \frac{h}{2\pi} \rightarrow (14)$$

Sub in the value $S = 1/2$, we get

$$\therefore \mu_s = \frac{e}{m} \cdot \frac{h}{2\pi} \cdot \frac{1}{2}$$

equ (13) in

$$\mu_s = 2 \cdot \left(\frac{e}{2m}\right) \cdot s \cdot \frac{h}{2\pi} = 2 \cdot \left(\frac{eh}{4\pi m}\right) \cdot s \rightarrow (15)$$

$$\mu_s = 2 \cdot \mu_B \cdot s \rightarrow (16).$$

ie, $S = 1/2$ $\quad \mu_s = \mu_B = 1$ Bohr Magnetron equ (12) we get

$$\frac{\mu_s}{p_s} = 2(e/2m) \rightarrow (17)$$

It is const,

$$\frac{\mu_s}{p_s} = g_s(e/2m) \rightarrow (18)$$

$\therefore g_s$ is called the lande's splitting factor.

Various Quantum Numbers:~

(வெவ்வேறு வகையான குவாண்டம் எண்கள்)

There are 7 types of Quantum Numbers associated with Vector Atom Model.

(i) The principal Quantum Number (n)
(ii) The Orbital " " (l)
(iii) The Spin " " (s)
(iv) Total Angular momentum " " (j)
(v) Magnetic Orbital " " (m_l)
(vi) Magnetic spin " " (m_s)
(vii) Magnetic total angular momentum " " (m_j).

(i) the principal Quantum Number (n):~

This is identical with the One used in Bohr Sommerfield theory. The letter was (n). It can take only integer values excluding zero. i.e, $n = 1, 2, 3 \ldots$

(ii) The Orbital Quantum number (l):~

This may take any integer value $0, 1, 2, \ldots (n-1)$. If $n = 4$, l can take four values $0, 1, 2, 3$. By convention an $\bar{e}$ for which,

$l = 0 \rightarrow s\bar{e}$; $l = 1 \rightarrow p\bar{e}$; $l = 2 \rightarrow d\bar{e}$.
$l = 3 \rightarrow f\bar{e}$.

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The Orbital angular momentum P_l.

So, $P_l = l\hbar$

$\therefore \hbar = h/2\pi$.

According Wave mechanics, $P_l = \sqrt{l(l+1)}\,\hbar$.

(ii) The Spin Quantum number (S):-

Only one Value, $S = \frac{1}{2}$

Spin angular momentum, $P_s = s\hbar$, wave mechanics

$P_s = \sqrt{s(s+1)}\,\hbar$.

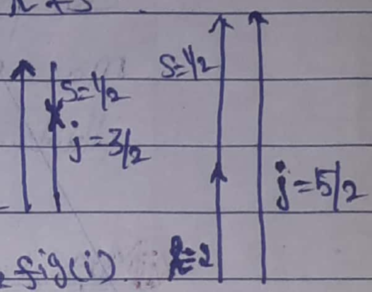
(iii) Total angular momentum quantum number (j):-

Sum of Orbital angular momentum and Spin angular momentum. It's defined as $\vec{j} = \vec{l} + \vec{s}$.

also j is +ve. $S = \pm 1/2$

$S = +$ → Parallel

$S = -$ → Antiparallel.



Thus $l = 2$ and $s = 1/2$, j can have values $5/2$ & $3/2$ fig(i)

fig(i)

Total angular momentum of $\bar{e} = P_j = j\hbar$

According to Wave Mechanics, $P_j = \sqrt{j(j+1)}\,\hbar$

To explain the splitting of spectral lines a mag. field, 3 more Quantum numbers are introduced.

(iv) Magnetic Orbital Quantum number (m_l):-

The projection of the Orbital Quantum number l on the mag. field direction is called the mag. Orbital Quantum no. (m_l). It's possible Values, m_l are $l, l-1, l-2, \ldots 0, -1, -2, \ldots -l$.

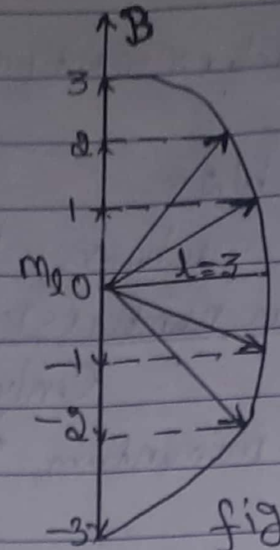
ie, there are $(2l+1)$ possible Value of m_l.

The angle θ between l & B is given by

$\cos\theta = \frac{m_l}{l}$. For eg:- $l = 3$; $m_l = 3, 2, 1, 0, -1, -2, -3$

Hence the l vector can take only 7 directions as shown in fig (a). l cannot be inclined to B at any other angle. This is known as 'Spatial

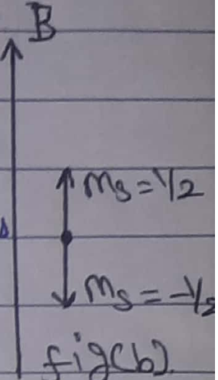
"Quantisation"



fig(a)

(ii) Magnetic Spin Quantum number (m_s):-

The spin angular momentum (s) two possible positions, $\parallel^{el}$ and Anti $\parallel^{el}$, m_s can have only two values $+\frac{1}{2}$ (or) $-\frac{1}{2}$, as illustrated in fig(b).



fig(b).

(iii) Magnetic total angular momentum Quantum number (m_j):-

Total angular momentum vector j on the direction of mag. field, j can have only odd half integral values. ($\because j = l \pm \frac{1}{2}$); m_j must have only half integral values. m_j can have only $(2j+1)$ values, from $+j$ to $-j$ and zero excluded.

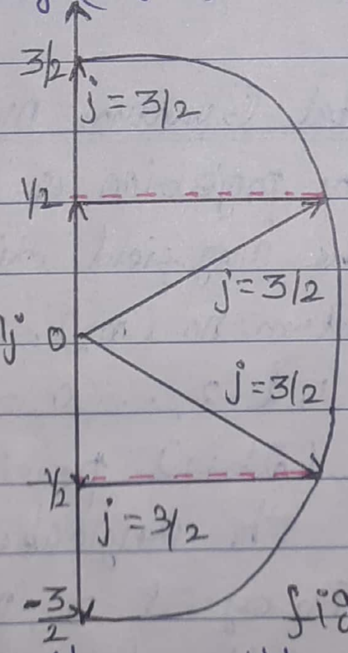


fig (c).

Fig (c), shows the possible values of $j = 3/2$.

Pauli's exclusion principle:~ (பௌலியின் தவிர்க்கைத் தத்துவம்)

Statement:~ No two $\bar{e}$s in an atom exist in the same Quantum state. The quantum numbers n, l, m_l, m_s. The principle may be stated as "No two $\bar{e}$s in an isolated atom may have the same 4 quantum numbers.

Explanation:~

Two $\bar{e}$s have all their quantum numbers identical, then one of those two $\bar{e}$s would be excluded from entering into the Constitution of the atom. Hence the name "exclusion principle".

Application:~

To calculate the no. of. $\bar{e}$s that can occupy a given Subshell:

(i) The K-Shell with $n=1$, $l=0$ and $m_l=0$, $S=1/2$ $m_s=\pm 1/2$. Hence, the K-shell can have 2 $\bar{e}$s: $\bar{e}$ 1 with Quantum numbers $n=1$, $l=0$, $m_l=0$, $m_s=1/2$ and $\bar{e}$ 2 with Quantum numbers $n=1$, $l=0$, $m_l=0$, $m_s=-1/2$.

If there were a 3$\bar{e}$, its Q.numbers will be identical with those of the Ist (or) IInd $\bar{e}$, which is against Pauli's exclusion principle. The K-shell is therefore Completed (or) closed with 2$\bar{e}$s.

(ii) The L-shell, $n=2$, and $l=0$ (or) 1.

* Subshell $n=2$, $l=0$, $m_l=0$, $m_s=\pm 1/2$. Hence there can be only 2$\bar{e}$s in this subshell.
* For the Subshell $n=2$, $l=1$, m_l can have 3 values $+1, 0, -1$. For each of these 3 values of m_l, m_s may be either $+1/2$ or $-1/2$. 6 possible set of values for the Q.numbers characterizing the $\bar{e}$'s. Maximum no. of. $\bar{e}$'s in this subshell is 6. The L-Shell with two Subshells [$(n=2, l=0)$ and $(n=2, l=1)$] is, therefore, Completed when it Contains $2+6=8\bar{e}$'s.

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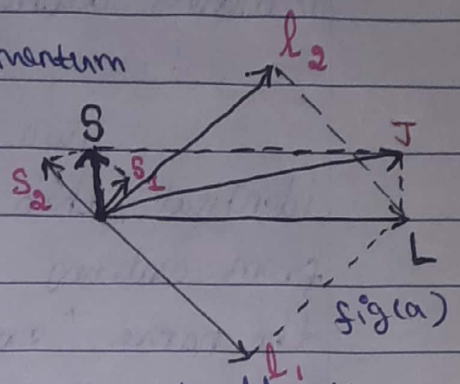
L-S Coupling :- (L-S இணைப்பு)

The Other name was Russel-Saunders Coupling (or) Normal Coupling.

$J = L + S$ → spin angular momentum.

J → Total angular Momentum.

L → Orbital angular momentum



fig(a)

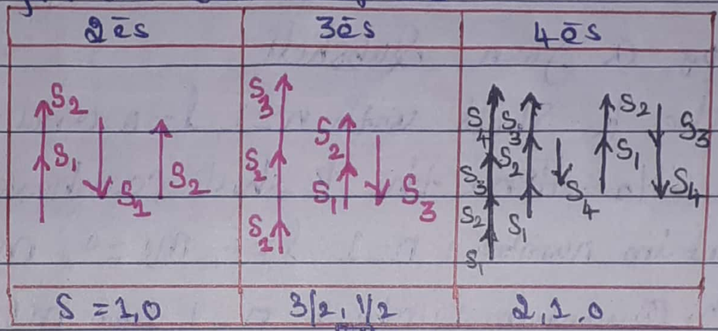
This scheme Summarised as,

$L = \sum l_i$

$S = \sum s_i$

L → always integer including zero.

S → integer for an even no. of $\bar{e}$'s and odd multiple of ½ for an odd no. of $\bar{e}$'s.



fig(b)

Fig (b) J must be integer, S is an integer, J must be odd multiple of ½ if S is an odd multiple of ½.

(i) $L > S$, J can have $(2S+1)$ Values.

(ii) $L < S$, J can have $(2L+1)$ Values.

(iii) Particular, if $L = 0$, J can have only one value namely $J = S$.

j-j Coupling :- (j-j இணைப்பு முறை)

The Orbital and Spin angular momenta of each $\bar{e}$ in the atom are added to obtain the resultant angular momentum of the electron, in fig (a).

Thus,

$$\vec{j_i} = \vec{l_i} + \vec{S_i}$$

Where $l_i = l_1, l_2 \ldots$; $j_i = j_1, j_2 \ldots$

$S_i = S_1, S_2 \ldots$

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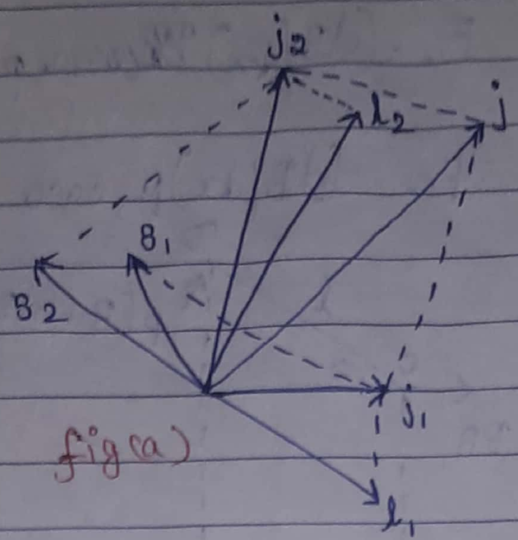


fig (a)

The Vectors sum of all the individual j vectors gives the total angular momentum J of the atom.

Thus, $J = \sum j_i$.

This type of coupling exists mainly in heavy atoms.

— x —

Stern Gerlach Experiment :-

(ஸ்டெர்ன்-கெர்லாக் சோதனை)

Direct evidence for the existence of Magnetic moments of atoms and their space Quantisation is provided by the experiments of Stern and Gerlach.

Principle & Theory:-

The magnetic field is homogeneous is straight line path without any deviation. In an inhomogeneous mag. field, it will be deviated away from its rectilinear path.

Let the mag. field along the X-direction, field gradient is dB/dx is +ve. CD atomic magnet the axis inclined at an angle θ to the field direction. Hence the forces on the 2 poles are pB and $p\left(B + \frac{dB}{dx} l \cos\theta\right)$.

Hence the atomic Magnet experiences not only a torque but also a translatory force.

$F_x = (dB/dx)$ ~~Pl cosθ~~ $pl\cos\theta$

$\therefore \quad F_x = (dB/dx)\mu_s \cos\theta. \longrightarrow (1)$

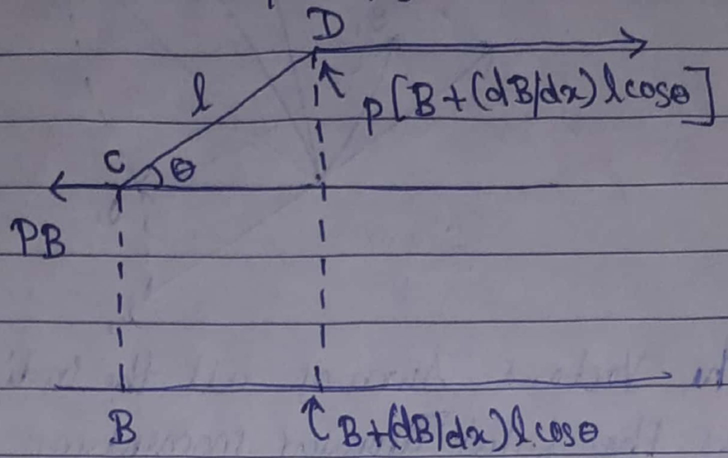


fig (a)

Let, V → velocity, m → mass, L → length, t → time.
The translatory force F_x is F_x/m.
On emerging out of the field is,

$$\alpha = \frac{1}{2}\left(\frac{F_x}{m}\right)t^2 = \frac{1}{2}\frac{F_x}{m}\frac{L^2}{V^2}$$

$$= \frac{1}{2}\frac{dB}{dx}\frac{\mu_s\cos\theta}{m}\frac{L^2}{V^2} \longrightarrow (2)$$

μ → is resolved component of the mag. moment in the field direction,

$$\mu = \mu_s \cos\theta \longrightarrow (3)$$

equ (3) sub in equ (2) we get

$$\alpha = \frac{1}{2}\, dB/dx\, \frac{\mu}{m} \cdot L^2/V^2 \longrightarrow (4)$$

Experimental arrangement:~

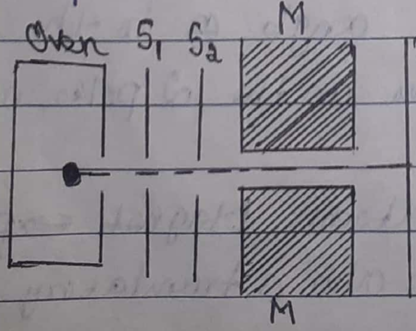


fig (a)

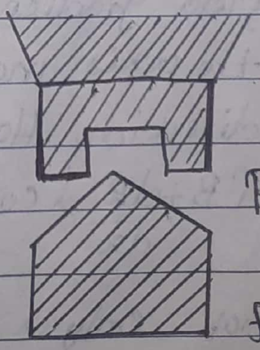
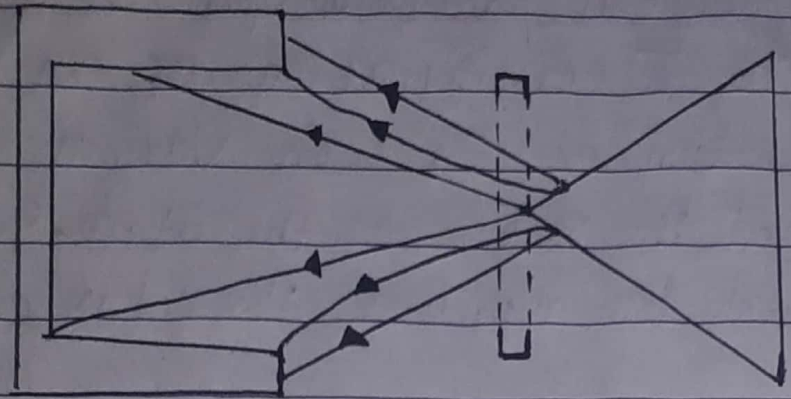
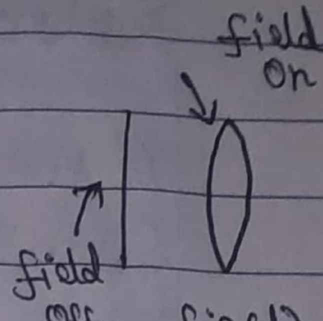


fig (b)



fig(a)



fig(d)

Silver is boiled in an Oven. fig(a). Slits S_1 & S_2; Pass through a very inhomogeneous mag field between the shaped poles of a magnet MM. One of the pole pieces of a powerful electromagnet a knife-edge Shape and the other plat fig(b). These lines close together Knife edge fig(c). Finally the atoms fall on a photographic plate P. The whole arrangement is enclosed in an evacuated chamber.

Results:-

On applying the inhomogeneous equal intensity mag. field, it was found that the stream of silver atoms splits into two separate lines fig(d). Knowing dB/dx, L, V, and α, μ was calculated.

It was found that each silver atom had a mag. moment of one Bohr magnetron in the direction of the field.

— x —

Electron Configuration :- ([illegible])

The $\bar{e}$ configuration of an atom is the distribution of $\bar{e}$'s in various subshells around the nucleus of the atom. Small letters are used to represent the values of l as follows:-

$l = 0, 1, 2, 3, 4, 5 \ldots$

$s, p, d, f, g, h \ldots$

When $l=0$, it is called s electron.

$l=1$, a p electron and so on.

Principal Quantum number n is written as a prefix to the representing its l value.

For eg:- $n=2$, $l=0$ is a 2s - state

$n=4$, $l=2$ is a 4d state

The no. of $\bar{e}$'s having the same n and l values is indicated by an index written at the upper right of the letter representing their l value. Thus the 11 $\bar{e}$'s of Sodium in the normal state are designated as follows: $1s^2 2s^2 2p^6 3s$. ie; there are two $1s$ $\bar{e}$'s, two $2s$ $\bar{e}$'s, six $2p$ $\bar{e}$'s, and one $3s$ $\bar{e}$. We shall now consider $\bar{e}$ configuration of a few elements.

(i) Hydrogen ($z=1$):-

Quantum numbers, $n=1$, $l=0$, $m_l=0$, and $m_s = \pm 1/2$. The symbolic representation is $1s$. The K shell requires one more $\bar{e}$ to be completed. Hence atomic hydrogen is very active chemically.

(ii) Helium ($z=2$):-

It has both its $\bar{e}$'s in shell $n=1$, $l=0$, $m_s = 1/2$ for one $\bar{e}$ and $-1/2$ for the second $\bar{e}$. The symbolic representation is $\boxed{1s^2}$. The shell is now Completed (or) closed. The rectangular enclosure indicates that the $\bar{e}$s are interlocked in a closed shell. It is a very stable and the inert gases.

(iii) Lithium (Z=3): It has $3\bar{e}$'s. First $2\bar{e}$ in K shell, and third $\bar{e}$ L shell. It has represented by $1s^2 2s$.

(iv) Beryllium (Z=4):~

It has two electrons in the Completed K-Shell (n=1); It has two additional electrons in the (n=2, l=0) Subshell. It is represented by $1s^2 2s^2$. Beryllium is one of the alkaline earth elements with a Valance of 2.

ll'y the electronic configuration from boron (Z=5) to neon (Z=10) are:~

(v) Boron (Z=5): $1s^2 2s^2 2p$

(vi) Carbon (Z=6): $1s^2 2s^2 2p^2$

(vii) Nitrogen (Z=7): $1s^2 2s^2 2p^3$

(viii) Oxygen (Z=8): $1s^2 2s^2 2p^4$

(ix) Flourine (Z=9): $1s^2 2s^2 2p^5$

(x) Neon (Z=10): $1s^2 2s^2 2p^6$

(xi) Sodium (Z=11):~ $\boxed{1s^2 2s^2 2p^6}$ 3s. Sodium has an $\bar{e}$ (3s) outside closed shell. The single $\bar{e}$, like that Li, is easily ionised; the valance is 1; the spectrum is that of one-electron atom.

(xii) Magnesium (Z=12):~ $\boxed{1s^2 2s^2 2p^6}$ $3s^2$. The $2\bar{e}$ in the outermost incomplete M-shell (n=3) are the Valence $\bar{e}$'s making Mg divalent.

(xiii) Aluminium (Z=13):~ $\boxed{1s^2 2s^2 2p^6}$ $3s^2$ 3p. Al is trivalent.

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Periodic Classification Of Elements:-

(தனிம அட்டவணை)

The periodic table:-

The periodic table is arrangement of different elements that exist in nature, based on their chemical properties and atomic numbers.

Elements with similar properties from the group shown as vertical columns in the table. Thus group I consists of hydrogen plus the alkali metals, all of which are extremely active chemically and have valence of +1. Group VII consists of the halogens that have of -1. Group VIII consists of the inert gases which are chemically inactive.

The horizontal rows are called periods. Left to right in the same period, the chemical and physical properties of the elements vary gradually as the atomic number increases.

We have already seen the arrangement of electrons in an atom by applying Pauli's exclusion principle. The total orbital and spin angular momenta of the electrons in a closed subshell are zero. The electrons in a closed shell are all very tightly bound, since the +ve nuclear charge is large relative to the -ve charge of the inner shielding electrons. Since an atom containing only closed shells has no dipole moment, it doesn't attract other electrons, and its $\bar{e}$'s cannot be readily detached.

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It is clear that the chemical and physical properties of an atom are determined by the number and arrangement of the electrons in the Outermost - shell and not by the total number of electrons in the atom. In this manner the similarities of the members of the Various groups of the periodic table may be accounted for.

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Salient features of Vector Atom Model :-

(i) Bohr's theory was able to explain Only the Series spectra Of the hydrogen atom. It Could not explain the multiple Structure of Spectral lines in the simplest hydrogen atom.

(ii) Sommerfeld's theory was able to given an explanation of the fine Structure of the Spectral lines Of Hydrogen. However, Sommerfeld's theory Could not predict the Correct number of the fine Structure lines. More over, it gave no information about the relative intensities Of the lines.

(iii) These Older theories were inadequate to explain new discoveries like Zeeman effect and Stark effect in which the spectral lines could be Split up under the influence of Magnetic and electric fields.

(iv) Another Drawback of the Bohr Model was that it could not explain how the Orbital electrons in an atom were distributed around the nucleus.

In order to explain the complex spectra of atoms and their relation to atomic Structure, the Vector atom model was introduced. The two distinct features of the vector atom model are:-

1.) The conception Of Spatial quantisation.

2.) The spinning electron hypothesis.

(1.) Spatial Quantisation:-

According to Quantum theory, the direction (or) Orientation of the orbits in space also should be quantised. This reference line is Chosen as the direction of an external mag. field that is applied to the atom.

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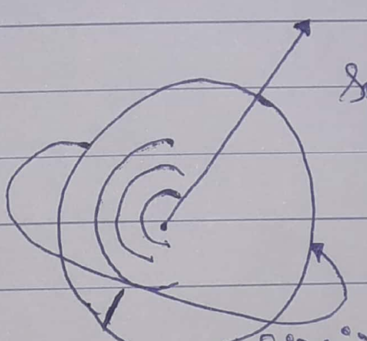
The different permitted orientations of an orbit are determined by the fact that the projections of the quantised orbits on the field direction must themselves be quantised. This is explain for Zeeman effect. The Stern Gerlach experiment provided an excellent proof of the space quantisation of atom.

(2.) Spinning electron:-

Fine Structure of spectral lines and to explain the Anamalous Zeeman effect, the concept of Spinning electron was introduced by Uhlenbeck and Goudsmith in 1926. According to the quantum theory, the spin of the electron also should be quantised. Hence a new Quantum number called the spin quantum number (S) is introduced. Since the orbital and spin motions are both quantised in magnitude and direction according to the idea of spatial quantisation, they are considered as quantised vectors. Hence the atom model based on these quantised vectors is called the "Vector atom Model", to which vector laws apply.



fig(i)

According to the older theories, the electron was supposed to have only orbital motion round the nucleus. Hence, only the orbital angular momentum and orbital magnetic moment were considered.

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The spin of the $\bar{e}$ with spin angular Momentum ($S\hbar$) and spin Magnetic Moment. So,

Total angular Momentum = Orbital angular Momentum + Spin angular Momentum.

$||^{ly}$,

The total Magnetic Moment = Orbital Magnetic Moment + Spin magnetic Moment

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