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B. Sc. IV Semester
Elements of Modern Physics.
Paper II

Vector — Model of Atom

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Chapter 10 :- Vector-Model of Atom.

Drawback's of Old Quantum Theory :- The quantum theory based on Planck's idea, Bohr's quantum condition and Wilson-Sommerfeld quantisation rule for periodic system is known as old quantum theory. It was found to be adequate in explaining certain limited problems such as energy states of hydrogen atom, particle in a box, harmonic oscillator, rigid rotator etc. However, it suffered from following drawbacks:

(a) The observed splitting of the H_α line did not agree (quantitatively) with the expected splitting even when the selection rules were applied — the wavelength differences between the split components were found to be different from those expected from Sommerfeld's theory.

(b) In the case of complex atoms, Bohr-Sommerfeld theory failed to calculate the energy of the system and frequencies of radiation emitted in case of two electron atom.

(c) Both the atomic models could not explain the distribution of electrons in atoms.

(d) It does not throw any rules ~~suggestion~~ on the intensities of spectral lines.

(e) It could not explain Zeeman effect etc.

In order to provide a satisfactory explanation of these above facts, the vector model of atom was formulated which are based on experiments as well as on empirical methods.

Vector Atom Model :- Vector atom model is based on quantum theory and the result of the works of Bohr, Sommerfeld, Uhlenbeck, Pauli, Lande and Stern-Gerlach. It is an extension of Bohr-Sommerfeld model on new lines in which new ideas were introduced to interpret complex spectral phenomenon and their relation to atomic structure. The two essential features of the vector atom model are (i) The concept of space quantization and (ii) hypothesis of spinning electron.

Space Quantization :- In Bohr-Sommerfeld model the magnitude of orbits (i.e. their shape and form) is quantised but in vector atom model, the magnitude and direction (i.e. orientation in space) both are quantised. In this way the orbits are made vector quantities. A preferred direction with respect to which orbits receive their orientation in space may be obtained by application of very weak external magnetic field which tends to zero, causing negligible interaction. Thus, when the atom is placed in a magnetic field, there are restrictions on the orientation of the electron orbits because of which they are said to be space quantized.

Thus as a general case, the motion of electrons is three dimensional (as against Sommerfeld's model in which motion of single electron is two dimensional) and so there should be three quantum numbers to describe the each or single energy state. The third quantum number does not change the size or shape of the electron orbit but simply determines the orientation with respect to certain direction in space.

Spinning Electron :- This hypothesis was given by Uhlenbeck and Goudsmit to explain the fine structure of spectral lines. According to which electron revolves round the nucleus but also revolves about an axis of its own like planet in the solar system. Orbital and spin motion are all quantized vectors and the atom model built on such considerations is correctly called vector atom model to which vector laws apply.

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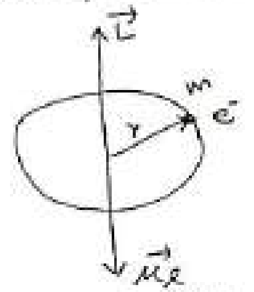
Orbital Magnetic Moment of Electron :- It is well known that a current carrying loop produces magnetic field around it. Similarly an electron revolving in an orbit will also be treated as a current loop, so the magnetic field will be produced. Consider a charged particle of mass 'm' having a charge $-e$ revolving round the nucleus of an atom in a circular orbit of radius r with a velocity v.



The charge circulating in a loop is equivalent to current

$$I = \frac{\text{charge}}{\text{Time taken to once complete the orbit}}$$

$v = r\omega = r \cdot \frac{2\pi}{T}$, or $T = \frac{2\pi r}{v}$

$$= -\frac{e}{T} = \frac{-e}{2\pi r/v} = -\frac{ev}{2\pi r}$$

The magnitude of the dipole magnetic moment of the rotating charged particle, which is equivalent to a current loop.

$\therefore$ orbital magnetic moment of the electron

$$\mu_l = \text{current} \times \text{Area} = IA = -\frac{ev}{2\pi r}\pi r^2 = -\frac{evr}{2} \quad \text{---(1)}$$

where A is the area of the loop.

The magnitude of the angular momentum of the charged particle of mass m rotating with a velocity v in a circular path of radius r is given by, $L = mvr$

multiplying and dividing by m, ~~we obtain~~ in Eq(1), we have

$$\mu_l = -\frac{emvr}{2m} = -\frac{e}{2m}L$$

In vector notation

$$\vec{\mu}_l = \frac{-e}{2m}\vec{L} \quad \text{----(2)}$$

The negative sign shows that the direction of the orbital magnetic moment is opposite to that of the orbital angular momentum.

Ratio of orbital magnetic moment to angular momentum :- From above Eq(2), we have

$$\frac{\text{orbital magnetic moment}}{\text{orbital angular momentum}} = \frac{\vec{\mu}_l}{\vec{L}} = -\frac{e}{2m} \quad \text{---(3)}$$

Magnetic moment of the atom :- Generally Eq^n (2) can be written as

$$\vec{\mu}_l = -g_l \frac{e}{2m}\vec{L}$$

where $\vec{g}_l = 1$ and is called orbital - g-factor of the electron.

According to quantum mechanics

$$\vec{L} = \sqrt{l(l+1)} \cdot \hbar$$

where l is the orbital quantum number, having values $0, 1, 2, \ldots$ etc.

$$\therefore \quad \vec{\mu}_l = -g_l \frac{e}{2m}\sqrt{l(l+1)}\,\hbar = -\frac{e\hbar}{2m}\sqrt{l(l+1)} \quad \text{---(4)}$$

For $l = 0$, $\mu_l = 0$; For $l = 1$, $\mu_l = \sqrt{2}\,\frac{e\hbar}{2m}$; For $l = 2$, $\mu_l = \sqrt{6}\,\frac{e\hbar}{2m}$

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produces current ... field the orbit of ...

Z-component of orbital magnetic moment :- The z-component of orbital angular momentum, $\vec{L} = L_z = m_\ell \hbar$ where m_ℓ is the orbital magnetic quantum number. For a given value of ℓ

$$m_\ell = \ell, (\ell-1), \ldots 0, 1, \ldots (-\ell+1), -\ell$$

The z-component of orbital magnetic moment.

$$(\mu_\ell)_z = -\frac{e}{2m} L_z = -\frac{e\hbar}{2m} m_\ell$$

For $m_\ell = 1$, $(\mu_\ell)_z = -\frac{e}{2m}\hbar$

~~Bohr magneton~~

Quantisation of magnetic moment :- The presence of smallest unit of magnetic moment equal to one Bohr magneton $= \frac{e\hbar}{2m}$ shows that the magnetic moment of the atom, like charge, mass etc. is quantised.

The z-component of orbital magnetic moment

$$(\mu_\ell)_z = -\frac{e\hbar}{2m} m_\ell$$

where $-\frac{e\hbar}{2m}$ is the smallest unit of magnetic moment known as a Bohr magneton and m_ℓ is an integral number given by $m_\ell = \ell, (\ell-1), \ldots (-\ell+1), -\ell$

Thus the magnetic moment is always an integral multiple of the smallest unit Bohr magneton. This shows the quantisation of magnetic moment.

The orbital quantum number ℓ determines the magnitude L of the electron's angular momentum $\vec{L}$. However, angular momentum, like linear momentum, is a vector quantity, and to describe it completely means that its direction be specified as well as its magnitude (The vector $\vec{L}$ is perpendicular to the plane in which the rotational motion takes place, and its sense is given by the right-hand rule. When the fingers of the right hand point in the direction of the motion, the thumb is in the direction of $\vec{L}$. This rule is shown in figure.

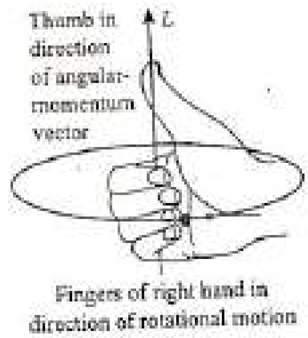

Fig. The right-hand rule angular momentum.

Larmor Precession :-

We have seen that an electron moving around a nucleus produces current and ultimately a magnetic dipole moment. When this system is placed in an external magnetic field the orbit of electron precesses about the magnetic field direction as the axis. This precession is known as Larmor precession and frequency of precession is known as Larmor frequency.

Refer Figure in which the electron orbit is placed in external magnetic field $\vec{B}$. The orbit of electron precesses about the magnetic field direction as the axis.

Let the angular momentum of electron makes an angle θ with the applied magnetic field, and the orbital dipole moment $\vec{\mu}_l$ of the electron is given by :

$$\vec{\mu}_l = -\frac{e}{2m}\vec{L}$$

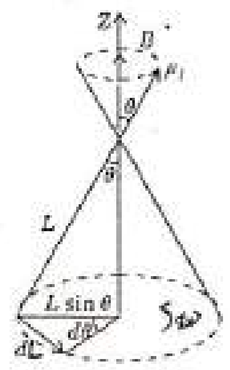

Fig: . .

An electron with an orbital magnetic moment $\vec{\mu}_l$ will experience a torque $\vec{\tau}$ given by

$$\vec{\tau} = \vec{\mu}_l \times \vec{B} = -\frac{e}{2m}\vec{L}\times\vec{B}$$

The torque $\vec{\tau}$ is always perpendicular to the angular momentum $\vec{L}$. This torque will cause a change in angular momentum given by

$$\vec{\tau} = \frac{d\vec{L}}{dt} = -\frac{e}{2m}\vec{L}\times\vec{B} = -\mu_l B \sin\theta$$

Hence, $\frac{d\vec{L}}{dt}$ $(=\vec{\tau})$ is perpendicular to μ_l, $\vec{L}$ and $\vec{B}$. In other words the change in angular momentum $d\vec{L}$ is also in the direction to τ. To produce the change in angular momentum its direction will change, as the magnitude of $\vec{L}$ remains constant. Hence, the change in angular momentum $d\vec{L}$ requires the precession of the vector $\vec{L}$ about the applied magnetic field $\vec{B}$. Vectors $\vec{\mu}_l$ and $\vec{L}$ are antiparallel, so both, $\vec{\mu}_l$ and $\vec{L}$ precess about the magnetic field $\vec{B}$.
This precession is known as Larmor precession. ~~and~~

The Larmor ~~frequency~~ velocity ω_L is given as :

$$\omega_L = \frac{d\theta}{dt} = \frac{1}{L\sin\theta}\cdot\frac{dL}{dt}$$

$$= \frac{1}{L\sin\theta}\,\mu_l B \sin\theta = \frac{\mu_l B}{L}$$

Angle $= \frac{\text{arc}}{\text{radius}}$

$\omega\, dt = \frac{d\vec{L}}{|L|\sin\theta}$.

$$|\omega_L| = \frac{e}{2m}B$$

or

$$f = \frac{\omega}{2\pi} = \frac{e}{4\pi m}B$$

Q:- An atom is placed in a magnetic field of strength 0.1 Tesla. Calculate the rate of precession. Given $m = 9\times10^{-31}$ kg.

Ans:- Rate of precession, $\omega_L = \frac{eB}{2m} = \frac{1.6\times10^{-19}\times0.1}{4\pi\times9\times10^{-31}}$ sec^{-1} $= 14.14\times10^{8}$ sec^{-1}

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Space Quantization :— The space quantization introduces the idea of selecting from continuous manifold orbits in space, a selected number of orbits which satisfy the quantum conditions. Thus, the orbits are made vector quantities whose magnitude and direction in space, both, are quantized. A very-very weak magnetic field is applied on atom to provide the direction with respect to which orbits receive orientation.

When an atom is placed in an external magnetic field ($\vec{B}$), which is in z-direction, the electron orbit precesses about the field direction as axis. The orbital angular momentum vector of electron (i.e. $\vec{L}$) traces a cone around $\vec{B}$, which is in z-direction. The component of $\vec{L}$ along $\vec{B}$ is;

$$\vec{L}_z = |L| \cos\theta \quad \text{or} \quad \cos\theta = \frac{\vec{L}_z}{|L|} \qquad \text{—— (1)}$$

where θ is the angle between $\vec{L}$ and the z-axis.

Quantum mechanically, it has been proved that the angular momentum $\vec{L}$ and its z-component are quantized, and the conditions are given as

$$|\vec{L}| = \sqrt{l(l+1)}\,\frac{h}{2\pi} \qquad \text{—— (2)}$$

and

$$L_z = m_l \frac{h}{2\pi} \qquad \text{—— (3)}$$

where l and m_l are the orbital and magnetic quantum numbers.

For the given value of n (principal quantum number), the possible values of l are from 0 to $n-1$ (i.e., n values 0, 1, 2, 3, --- , $n-1$), and for a given value of l the possible values of m_l are from $-l$ to $+l$ (including 0), i.e. there are $(2l+1)$ values of the m_l.

Using Eqn (1), (2) & (3), we have

$$\cos\theta = \frac{L_z}{L} = \frac{m_l \frac{h}{2\pi}}{\sqrt{l(l+1)}\,\frac{h}{2\pi}} = \frac{m_l}{\sqrt{l(l+1)}} \qquad \text{—— (4)}$$

From above relation we can say that the $\cos\theta$ has $(2l+1)$ discrete values, or the angular momentum $\vec{L}$ can have $(2l+1)$ discrete orientation with respect to the magnetic field $\vec{B}$. The angular momentum $\vec{L}$ in space cannot have random orientation, it should have only fixed orientations. This quantization of the orientation of angular momentum of deny in space is termed as "Space Quantization".

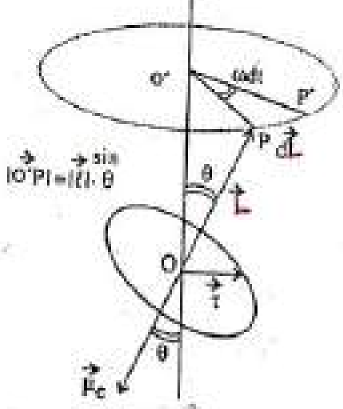

Fig.

215

Figure is showing the space quantization of the angular momentum for $l = 2$.
For $l = 2$, the possible values of m_l are $m_l = 0, \pm 1, \pm 2$.
The z-component of $\vec{L}$ will be

$$\vec{L}_z = 0, \pm \frac{h}{2\pi}, \pm 2\frac{h}{2\pi}$$

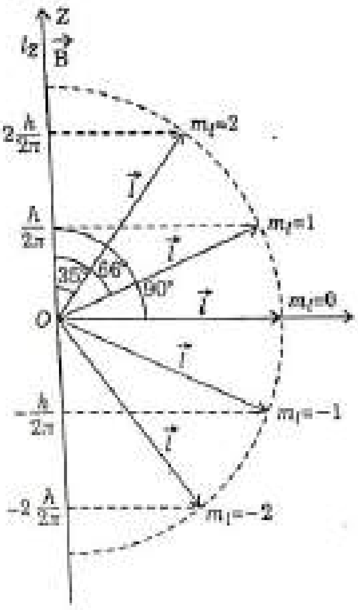

Fig. 6

From Eqn.

$$\cos\theta = \frac{L_z}{L} = \frac{m_l \frac{h}{2\pi}}{\sqrt{l(l+1)}\frac{h}{2\pi}} = \frac{m_l}{\sqrt{l(l+1)}}$$

the orientation θ of $\vec{L}$ with respect to the field are given as

$$\cos\theta = \frac{m_l}{\sqrt{l(l+1)}} = 0, \pm\frac{1}{\sqrt{6}}, \pm\frac{2}{\sqrt{6}}$$

The approximate values of θ are 35°, 66°, 90°, 114°, 135°.

Spin of Electron and spin angular momentum :- To overcome the drawbacks of Sommerfeld's quantum theory. The hypothesis of spinning electron was put forward by Uhlenbeck and Goudsmit in 1925 for explaining satisfactorily the fine structure of spectral lines and Zeeman effect (splitting of spectral lines under the influence of strong magnetic field). They assumed that while revolving around the nucleus the electron also rotates (spin) about its own axis. Thus, this motion of charged particle about its own axis, also creates intrinsic (spin) angular momentum and intrinsic (spin) magnetic moment. The spin angular momentum and spin magnetic moment are denoted as $\vec{S}$ and $\vec{\mu_s}$ respectively.
The spin motion has also to be quantised just like orbital motion. this introduces another quantum number as spin quantum number which is denoted by s and has a magnitude $\frac{1}{2}$.
The ~~spin~~ magnitude of the spin angular momentum is

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

where $\vec{s}$ is spin quantum number. It has only one value as $s = \frac{1}{2}$.
Thus

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

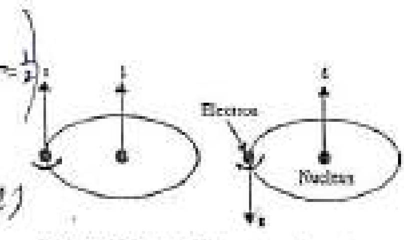

Fig. The possible orientations of the spin momentum vector s, with respect to orbital angular momentum vector l.

The component of $\vec{S}$ along z-axis (direction of magnetic field) will be

$$S_z = m_s \frac{h}{2\pi}$$

where m_s is the spin magnetic quantum number. It can take $2s+1 = 2$ values i.e. $m_s = +s$ and $-s$

or

$$m_s = \pm\frac{1}{2}$$

Thus

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

The electron spin magnetic moment $\vec{\mu_s}$ and spin angular momentum $\vec{S}$ are related as:

$$\vec{\mu}_s = -\frac{e}{m}\vec{S}$$

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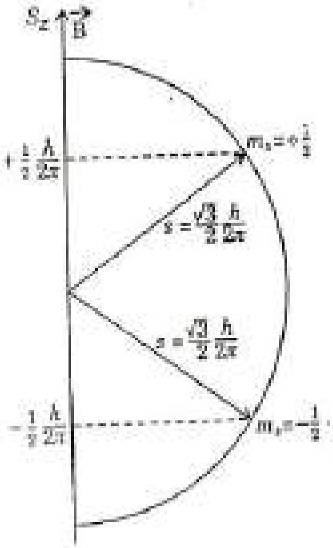
The gyromagnetic ratio for electron spin, $\frac{|\vec{\mu}_s|}{|\vec{S}|}$ is twice the corresponding electron orbital motion.

We have also seen that the possible values of m_s or S_z are

$$S_z = +\frac{1}{2}\frac{h}{2\pi}$$

and

$$S_z = -\frac{1}{2}\frac{h}{2\pi}$$



The magnitude of spin magnetic moment will be:

$$\mu_s = \frac{e}{m} S$$

$$= \frac{e}{m}\frac{\sqrt{3}}{2}\frac{h}{2\pi}$$

$$= \sqrt{3}\frac{eh}{4\pi m} = \sqrt{3}\,\mu_B$$

where $\mu_B = \frac{eh}{4\pi m}$ is the Bohr-magneton.

Importance of concept of electron spin :- (1) It explained fine structure (2) Explained anomalous Zeeman effect (3) Explained other atomic phenomenon also.

The postulate of electron spin was put on theoretical formulation by Dirac. The practical evidence of its existence was offered by Stern-Gerlach experiment.

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• **Spin-Orbit Coupling** :- The total angular momentum of an atom is the combination of orbital and spin angular momenta of its electrons. Since these are vector quantities, the resultant angular momentum is given by

$$\vec{J} = \vec{L} + \vec{S}$$

where $\vec{J}$ is known as total angular momentum vector.

The combination of orbital and spin angular momentum vectors $\vec{L}$ and $\vec{S}$ to form a single total angular momentum vector $\vec{J}$ is known as spin-orbit coupling.

In case of one electron atom, $|\vec{L}| = \sqrt{l(l+1)}\,\hbar$ and its z-component is given as $l_z = m_l \hbar$. Similarly, the spin angular momentum is given as $|\vec{S}| = \sqrt{s(s+1)}\,\frac{h}{2\pi}$ and its z-component is $S_z = m_s \hbar$ (where m_s has values $\pm\frac{1}{2} = \pm s$).

The total angular momentum $\vec{J}$ and $|\vec{J}|$ is then

$$\vec{J} = \vec{L} + \vec{S}$$

and $$|\vec{J}| = \sqrt{j(j+1)}\,\hbar$$, where j is the total angular momentum quantum number.

and its z-component is given as:

$$j_z = m_j \hbar$$

where m_j is called Total angular magnetic Quantum number.

m_j has values lying between $-j$ to $+j$. ~~[illegible]~~

We can also write $j_z = l_z \pm s_z$

and $m_j = m_l \pm m_s$

The possible values of m_l range from $+l$ through 0 to $-l$ and those of m_s are $\pm s$ where $s = \frac{1}{2}$.

The quantum number l is always an integer or 0. Therefore, m_j is always half integral and its possible values range from $+j$ to $-j$ in integral steps.

$$j = l \pm s$$

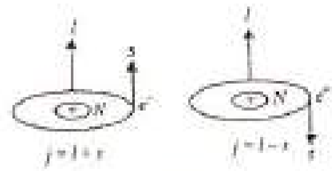


Fig.

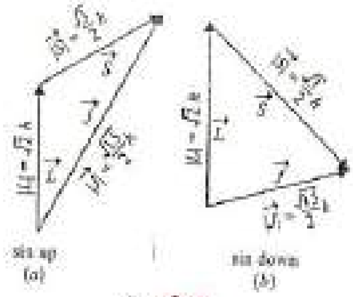
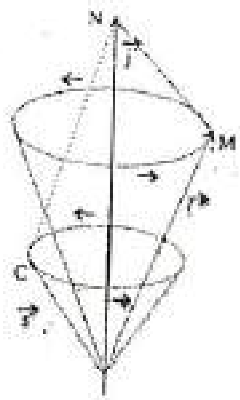


Fig.

The magnetic interaction of $\vec{s}$ and $\vec{l}$ is known as spin-orbit interaction. They exert internal torque on each other as a result of which magnitude of $\vec{l}$ and $\vec{s}$ doesnot change but they precess uniformly about j. In absence of external magnetic field, $\vec{J}$ is conserved and angle between $\vec{l}$ and $\vec{s}$ also doesnot change.



From $\square$ OMNC :

$$j^2 = l^2 + s^2 + 2ls\cos(\vec{l}, \vec{s})$$

or

$$\cos(\vec{l}, \vec{s}) = \frac{j^2 - l^2 - s^2}{2ls} = \frac{j(j+1) - l(l+1) - s(s+1)}{2\sqrt{l(l+1)}\sqrt{s(s+1)}}$$

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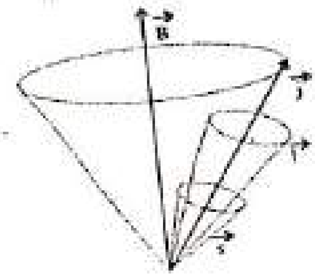
<u>Atom placed in external magnetic field ($\vec{B}$)</u>:- The $\vec{L}$ and $\vec{S}$ continue processing about the direction of $\vec{B}$. The discrete orientations of $\vec{J}$ with respect to $\vec{B}$ involve slightly different energies. This explains anomalous Zeeman effect.

However, atomic nuclei also have small spin angular momenta and magnetic moments. These vectors along with the atomic model explain observed hyperfine structure.



<u>Notation for an atom</u>:- In an atom with many electrons, the orbital angular momenta vectors $\vec{l_1}, \vec{l_2}, ---$ of individual electrons couple among themselves giving resultant orbital angular momenta for atom, the $\vec{L}$. Similarly, the spin angular momenta of each combine to give $\vec{S}$. Resultant orbital angular momentum has magnitude $\sqrt{L(L+1)}\,\hbar$ and resultant spin angular momentum is $\sqrt{S(S+1)}\,\hbar$ where L and S are orbital and spin quantum number respectively for the atom. The $\vec{L}$ and $\vec{S}$ finally couple to give $\vec{J}$, the total angular momentum of atom with magnitude $\sqrt{J(J+1)}\,\hbar$.

The states of atom are described quite as of one electron atom but with capital letters (i.e. L, S, J etc.)

Q:- Find the possible values of j and m_j for states in which $l=3$ and $s=\frac{1}{2}$.

Ans:- Given $l=3$, $s=\frac{1}{2}$

$\therefore j = l+s = 3+\frac{1}{2} = \frac{7}{2}$

and $j = l-s = 3-\frac{1}{2} = \frac{5}{2}$

For $j=\frac{7}{2}$, $m_j = \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}, -\frac{5}{2}$ and $-\frac{7}{2}$

For $j=\frac{5}{2}$, $m_j = \frac{5}{2}, \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}, -\frac{5}{2}$.

Q:- What are the possible z-component of the vector L which represents the orbital angular momentum of the state with $l=1$. Calculate the length of the vector L. Also find the possible orientations of the vector L with respect to the z-axis.

Ans:- The possible z-components are $m\hbar$, where $m=1,0,-1$.

The length of the vector L is $\sqrt{l(l+1)}\,\hbar = \sqrt{2}\,\hbar$

The number of possible orientations are three, corresponding to the m values $1, 0, -1$.

If θ is the angle from z-axis.

$$\cos\theta = \frac{L_z}{|\vec{L}|} = \frac{m}{\sqrt{l(l+1)}}$$

For $m=1$, $\cos\theta_1 = \frac{1}{\sqrt{2}} \Rightarrow \theta_1 = 45^\circ$

For $m=0$, $\cos\theta_2 = \frac{0}{\sqrt{2}} \Rightarrow \theta_2 = 90^\circ$

For $m=-1$, $\cos\theta_2 = -\frac{1}{\sqrt{2}} \Rightarrow \theta_3 = 135^\circ$

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Landé's Vector Model of the Atom :-

The magnitude $\vec{L}$ of the orbital angular momentum L of an atomic electron is given by

$$L = \sqrt{l(l+1)}\,\hbar$$

Where l is the orbital quantum number. The magnetic moment due to the orbital motion of the electron is given by

$$\mu_l = \frac{e}{2m_e} L$$

As the charge on the electron is negative, the direction of the orbital magnetic moment vector is opposite to that of the angular momentum vector.

The spin angular momentum $\vec{S}$ has a magnitude S given by

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

where s is the spin quantum number. The magnetic moment due to the spin of the electron is given by

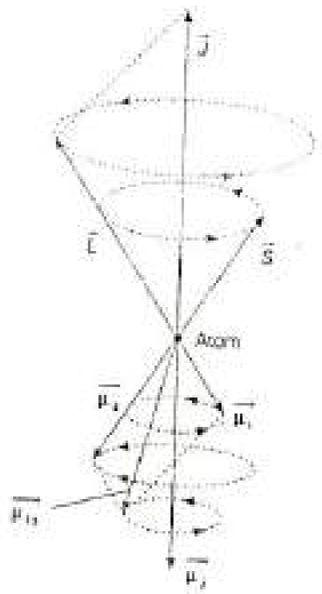
$$\mu_s = 2\left(\frac{e}{2m}\right) S$$

The spin magnetic moment vector is opposite in direction to the spin angular momentum.

The orbital angular momentum $\vec{L}$ and the spin angular momentum $\vec{S}$ combine vectorially to yield the resultant $\vec{J}$ i.e.

$$\vec{J} = \vec{L} + \vec{S}$$

When an external magnetic field is introduced $\vec{L}$ will tend to precess round it at the Larmor precession frequency. $\vec{S}$ will also tend to precess round the field direction but at twice the Larmor frequency. If the ~~magnitude~~ magnetic field is not very strong, the coupling between $\vec{L}$ and $\vec{S}$ will be strong enough to maintain a resultant $\vec{J}$. The resultant $\vec{J}$ will precess around the field direction with a compromise frequency. To calculate the resultant magnetic moment μ_j of the atom consider the vector model of the atom shown in figure.



As $\vec{L}, \vec{S}, \mu_l, \mu_s$ all precess round $\vec{J}$ their components normal to $\vec{J}$ will average to zero. Hence the resultant magnetic moment will be the sum of the components of μ_l and μ_s parallel to $\vec{J}$.

Component of μ_l along $\vec{J} = \vec{L}\left(\frac{e}{2m_e}\right)\cos(\vec{L},\vec{J})$

Where $(\vec{L},\vec{J})$ is the angle between $\vec{L}$ and $\vec{J}$. Similarly, component of μ_s along $\vec{J}$

$$= S \cdot 2\left(\frac{e}{2m_e}\right)\cos(\vec{S},\vec{J})$$

Therefore resultant magnetic moment

$$\mu_j = \left[L\cos(\vec{L},\vec{J}) + 2S\cos(\vec{S},\vec{J})\right]\frac{e}{2m_e}$$

Applying the cosine law to the vector model

$$S^2 = L^2 + J^2 - 2LJ\cos(\vec{L},\vec{J})$$

$$\therefore \quad L\cos(\vec{L},\vec{J}) = \frac{J^2 + L^2 - S^2}{2J}$$

Similarly

$$S\cos(\vec{S},\vec{J}) = \frac{J^2 + S^2 - L^2}{2J}$$

Making these substitutions in above eq, we get

$$\mu_j = \left[(J^2 + L^2 - S^2)/2J + 2(J^2 + S^2 - L^2)/2J\right]\frac{e}{2m_e}$$

$$= \left[1 + (J^2 - L^2 + S^2)/2J^2\right]\frac{Je}{2m_e}$$

According to quantum mechanics $L^2 = l(l+1)$, $S^2 = s(s+1)$, $J^2 = j(j+1)$ and $J = \sqrt{j(j+1)}\,\hbar$

Hence

$$\mu_j = \left[1 + \{j(j+1) + s(s+1) - l(l+1)\}/2j(j+1)\right]\sqrt{j(j+1)}\,\frac{eh}{4\pi m_e}$$

Here the quantity within the brackets is called Landé's g-factor and is denoted by 'g', thus

$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

we know that $\frac{eh}{4\pi m}$ is the Bohr magneton.

The magnetic moment of the atom is therefore given by $\boxed{\mu_j = g\left[j(j+1)\right]^{\frac{1}{2}} \cdot \text{Bohr magnetons}}$

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Quantum numbers associated with vector atom model :- The quantum numbers associated with vector atom model are (1) Principal quantum number (n) (2) orbital quantum number (l) (3) Spin quantum number (s) (4) Total angular momentum quantum number (j) (5) Magnetic orbital quantum number (m_l) (6) Magnetic spin quantum number (m_s) (7) Magnetic total angular momentum quantum number (m_j).

(1) Principal quantum number (n) :- This refers to principal orbit or shell in which electron lies and is same to one used in Bohr-Sommerfeld's model. According to Bohr-Sommerfeld's model it can be an integral value only i.e. $n = 1, 2, 3, ---$. The value of $n = 1, 2, 3, ---$ corresponds to first orbit (K-shell), second orbit (L-shell), third orbit (M-shell) --- respectively. The value of n also explain the size, energy and number of electron in the shell as $r_n = .529/n^2$ °A, $E_n = -313/n^2$ kcal and $2n^2$ respectively.

(2) Orbital Quantum Number :- It gives the orbital angular momentum of the electron and also defines the shape of the orbital occupied by the electron. The orbital angular momentum L due to orbital motion of electron is given as:

$$\vec{L} = \sqrt{l(l+1)}\,\hbar$$

For a given principal quantum number n, l takes any integral value from 0 to $(n-1)$ and each value of l refers to subenergy level or subshell. For $l = 0, 1, 2, ---$, the subshells are known as s, p, d, f, --- etc. respectively.

Example : For $n = 4$ the permitted l value are $l = 0$ (the s-orbital), $l = 1$ (p-orbital), $l = 2$ (d-orbital) and $l = 3$ (f-orbital).

(3) Spin Quantum Number :- The electron revolve around the nucleus and simultaneous rotates around its own axis i.e. it has spin also. The electron's spin angular momentum $\vec{S}$ is also quantized and is given as

$$\vec{S} = \sqrt{s(s+1)}\,\hbar$$

where s is the spin quantum number, its magnitude is $\frac{1}{2}$.

(4) Total angular momentum Quantum Number :- It refers to the resultant angular momentum of the electron due to both orbital and spin motions and is numerically equal to vector sum of $\vec{l}$ and $\vec{s}$ i.e. $\vec{j} = \vec{l} \pm \vec{s} = \vec{l} \pm \frac{1}{2}$, + refer to l vector parallel to s vector and −ve refers to l vector antiparallel s vector.

$$\vec{J} = \sqrt{j(j+1)}\,\hbar$$

Thus for a given value of orbital quantum number l for an electron in a one electron atom two values of total angular momentum quantum number j are possible.

To explain the splitting of spectral lines in a magnetic field there are three more quantum numbers known as magnetic orbital quantum number (m_l), magnetic spin quantum number (m_s) and magnetic total angular momentum quantum number (m_j).

(5) Magnetic Orbital Quantum Number (m_l) :- Quantum mechanically, it has been shown that in presence of external magnetic field, electron rotation plane has definite orientation i.e. known as space-quantization. It is the numerical value of the projection of $\vec{l}$ upon the field direction i.e. $m_l = l\cos\theta$. The value of $\cos\theta$ lies between −1 to +1, so values of m_l lie between $-l$ to $+l$ and total values of m_l are thus $(2l+1)$ including 0.

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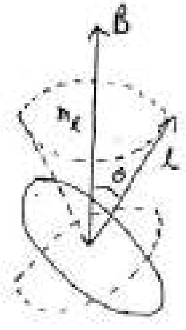
Example: According to the wave mechanics, the vector l can assume only such orientations for which its projection on the field direction is an integer. If the vector l is inclined to the field direction is $m_l = l\cos\theta$ as shown in figure. As m_l is an integer and $\cos\theta$ cannot be greater than unity, the possible values of m_l are $l, (l-1), (l-2), \ldots 0, -1, -2, \ldots -(l-1), -l$. If $l = 2$, the possible values of m_l are $+2, +1, 0, -1, -2$ as shown in figure.



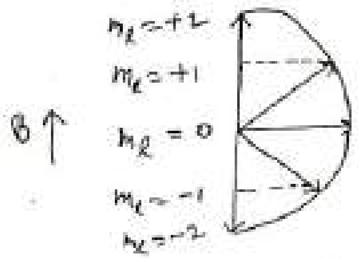


Fig: Possible values of m_l for $l = 2$

(6) Magnetic Spin Quantum Number (m_s): It is the numerical value of the projection of the spin vectors on the field direction. It is also space quantised and is given by

$$S_z = m_s \hbar = \pm \frac{1}{2}\hbar$$

where m_s is the magnetic spin quantum number. It has two values $m_s = \pm S$.

(7) Magnetic total Angular Momentum Quantum Number (m_j): The numerical value of the projection of the total angular momentum vector j on the magnetic field direction is referred to as the magnetic total angular momentum quantum number and is denoted by m_j. In the case of a single electron the vector j can have only odd half-integral values, since $j = l \pm \frac{1}{2}$ and therefore m_j must also assume only odd half-integral values. The possible values of m_j are $(2j+1)$ from $+j$ to $-j$ excluding zero in integral steps. Figure shows the possible values of m_j for $j = \frac{3}{2}$.

The quantum number m_j is effective in ordinary magnetic fields, but when the magnetic field is so strong that the coupling between vectors s and l is broken then m_l and m_s come into play.

It may be pointed out that the term space quantization is usually applied to the above restriction imposed on the vectors $\vec{l}, \vec{s}, \vec{j}$ in the presence of a magnetic field.

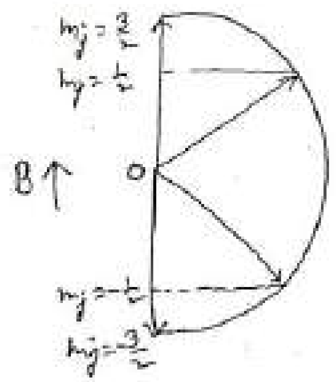


Fig: Possible values of m_j for $j = \frac{3}{2}$

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System of notation or Spectroscopic Terms :- The following system of notation is employed in designating the state of an electron or atom.

The orbital angular momentum of electron denoted by $l =$	0	1	2	3	4	5	6	7
The state of the electron denoted by	s	p	d	f	g	h	i	j
The corresponding state of the atom denoted by	S	P	D	F	G	H	I	J

The state of an electron is more completely designated by putting the principal quantum number n before the letter specifying the value of the vector l of the orbit. Thus a 2s electron is one for which $n=2, l=0$. The corresponding states of the atom are designated by capital letters, e.g. an electron in 2p state will be an atom in a 2P state, but provided only a single electron is involved in energy level changes (e.g. in the case of hydrogen or alkali metals).

→ For each value of l, other than zero, two values of j given by $l+\frac{1}{2}$ and $l-\frac{1}{2}$ and corresponding two energy level terms arise. Therefore a electron which was formerly considered to be pay, in an energy level denoted by 2p ($n=2, l=1$) can exist in two energy levels close together which give rise to the observed doublet in the spectrum on transition. In the case of 2p state thus

$n=2,\ l=1,\ j=1-\frac{1}{2}=\frac{1}{2}$

or $\quad n=2,\ l=1,\ j=1+\frac{1}{2}=\frac{3}{2}$

The state of an electron is thus denoted by modified notation. For example the 2p electron is designated either by $2p_{\frac{1}{2}}$ or $2p_{3/2}$. The abbreviated notation for these states is $2^2P_{\frac{1}{2}}$ denoting the multiplicity of the level as 2.

The s level is single but for uniformity 2 is also written before s, e.g., $3^2S_{\frac{1}{2}}$.

The transition between various energy levels of the atom are restricted by the selection rules that l can only change by ±1 i.e. $\Delta l = \pm 1$ while j can change by 0 or ±1 i.e. $\Delta j = 0$ or ± 1. Only those transitions will be allowed, for which $\Delta S = 0$.

The well known sodium lines of wavelength 5890°A and 5896°A are explained as arising from the transition of the atom states which are written in the form: $3P_{\frac{1}{2}} \rightarrow 3S_{\frac{1}{2}}$ which gives rise to the line of wavelength 5896°A and $3P_{3/2} \rightarrow 3S_{\frac{1}{2}}$ which gives rise to the line of wavelength 5890°A.

Intensity Rules :- (1) If spectral lines are changing with same J and $\vec{L}$ values, then the spectral line, which has transition from higher J value will be more intense.

(2) If change in L value ΔL is not same to the change in J value i.e. ΔJ, ($\Delta L \neq \Delta J$), then intensity of spectral line will be faint.

(3) For $\Delta L = -1$ the spectral line will be more intense than $\Delta L = +1$.

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2213

Multiplicity of Energy levels :- The multiplicity of energy state expresses the possible values of $\vec{J}$ for different possible orientations of $\vec{L}$ and $\vec{S}$. It is denoted by r. For L-S coupling we have already discussed that if $L>S$ the possible values of J are $(2S+1)$, then multiplicity r will be $(2S+1)$. If $L<S$, then the possible values of J are $2L+1$, so multiplicity r will be $2L+1$.

For $L=0$, i.e. ground state, $r=1$. Ground state is always singlet, and $J=L$.

If $S=\frac{1}{2}$, then $r=2S+1=2$, the state will be doublet and $J=L\pm\frac{1}{2}$.

If $S=1$, then $r=2S+1=3$, the state will be triplet and $L=L-1, L, L+1$.

For one electron atom:

$$S=s=\tfrac{1}{2},\ r=2 \text{ doublets}$$

For two electron atom:

$$s_1=\tfrac{1}{2},\ s_2=\tfrac{1}{2}$$

$$S=|s_1-s_2|, |s_1-s_2|+1, \ldots, |s_1+s_2|$$

$$=0,1$$

$$r=2S+1=1,3, \text{ i.e. singlet and triplet states.}$$

For three electron atom:

$$s_1=\tfrac{1}{2},\ s_2=\tfrac{1}{2} \text{ and } s_3=\tfrac{1}{2}$$

In such cases, first we combine any two spins, and obtain a resultant S', this resultant S' is then combined with the third spin, to get the final result S.

Let s_1 and s_2 are combined first, then

$$S'=0,1$$

Now, S will be obtained by combining $S'(=0)$, with $s_3=\frac{1}{2}$ and then $S'(=1)$ and with $s_3=\frac{1}{2}$ i.e we have

$$S=\tfrac{1}{2} \text{ (from first set)}$$

$$S=\tfrac{1}{2}, \tfrac{3}{2} \text{ (from second set)}$$

$$S=\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{3}{2} \Rightarrow$$

Hence, multiplicity will be, two doublets (for $S=\frac{1}{2}$) and one set of quartets.

$2\cdot\frac{1}{2}+1=2$

$2S+1=2\cdot\frac{3}{2}+1=4$

4 — Quartets

5 → Quincet

L-S and j-j coupling :- The addition of angular momenta for orbital motion and for spin motion of an electron system is much simpler than a many electron system. For many electron systems only the electrons outside the closed shell contribute to the angular momentum. On the basis of outer sub-shell electrons, atoms are divided into two categories, namely one-electron atom and many electron system. In one-electron atom there is only one electron in outer sub-shell of atom e.g. H, Li, Na, K etc. In many electron atoms there are more than one electron in outer sub-shell e.g. Mg, Ca, Sr etc. As there are more than one electron contributing to angular momentum and spin angular momentum, their momenta can be added by two methods known as L-S coupling and j-j coupling. Atoms with low to moderate atomic numbers are dealt with L-S coupling or Russel-Saunders coupling on the other hand for heavy atoms j-j coupling is applicable.

(a) L-S Coupling :- In L-S coupling, angular and spin momentum of electrons are added separately, thus we get resultant angular momentum $\vec{L}$ and resultant spin angular momentum $\vec{S}$, the values of $\vec{L}$ and $\vec{S}$ provide total angular momentum $\vec{J}$. If angular momentum of optical electrons (outer sub-shell electron) are $\vec{l}_1, \vec{l}_2, \vec{l}_3, ---$ and spin angular momentum are $\vec{s}_1, \vec{s}_2, \vec{s}_3, ---$ then

$$\vec{L} = \vec{l}_1 + \vec{l}_2 + \vec{l}_3 + \cdots$$

and

$$\vec{S} = \vec{s}_1 + \vec{s}_2 + \vec{s}_3 + \cdots$$

$\mu = g\sqrt{J(J+1)}$ Lande splitting factor

The total angular momentum of atom, will be

$$\vec{J} = \vec{L} + \vec{S}$$
$$= (\vec{l}_1 + \vec{l}_2 + \vec{l}_3 + \cdots) + (\vec{s}_1 + \vec{s}_2 + \vec{s}_3 + \cdots)$$

This is known as L-S coupling. The magnitude of vectors $\vec{L}$, $\vec{S}$ and $\vec{J}$ are $|\vec{L}|$, $|\vec{S}|$ and $|\vec{J}|$ respectively, they are quantized:

$$|\vec{L}| = \sqrt{L(L+1)}\,\hbar$$
$$|\vec{S}| = \sqrt{S(S+1)}\,\hbar$$
$$|\vec{J}| = \sqrt{J(J+1)}\,\hbar$$

The rules for different quantum numbers are:

(1) The magnitude of quantum number L is always integer or zero i.e. L = 0, 1, 2, 3, 4, ---- For L = 0, 1, 2, 3 ... the names of different energy states are said as S, P, D, F ----

(2) For a double electron atom, magnitude of L will be $(l_1 - l_2), (l_1 - l_2)+1, --- (l_1 + l_2)$. Considering the case $l_1 = 1$ and $l_2 = 2$. In this condition L will be 1, 2 and 3 i.e. atom will be in states P, D, F. For $l_1 = 0$ and $l_2 = 1$, L will be 0, 1, and 2 i.e. atom will be in state S, P, D.

(3) The magnitude of spin quantum number S depends on the number of electrons in atom and their direction of spin vector. It may be integer or half integer. For even electron atom magnitude of S is zero or integer while for odd electron atom it is half or odd multiple of half.

(4) For even electron atom the magnitude of J is either 0 or integer. For odd electron atom J is odd multiple of half.

(5) If L > S, the possible values of J are (2S+1), and if L < S, the possible values of J are (2L+1).

(b) j-j coupling :- This is applicable for heavy atoms. In this coupling, the orbital angular momentum $\vec{l}$ and spin angular momentum $\vec{s}$ of the outer electrons of many atom are added with vector addition and so electron's total angular momentum j is obtained, i.e. $\vec{l} + \vec{s} = \vec{j}$.

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Magnetic field 7 Tesla

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These total angular momentum of the electrons are then added, and the total angular momentum of atom is obtained.

$$\vec{l_1}+\vec{s_1}=\vec{j_1}$$
$$\vec{l_2}+\vec{s_2}=\vec{j_2}$$
$$\vec{l_3}+\vec{s_3}=\vec{j_3}$$
$$\vec{J}=\vec{j_1}+\vec{j_2}+\vec{j_3}$$

The magnitude of $\vec{J}$ is quantized, which is

$$\vec{J}=\sqrt{J(J+1)}\,\hbar$$

J is known as total angular momentum quantum number.

Pauli's Exclusion Principle:- In 1925 Pauli's exclusion principle "no two electrons in an atom can have the same set of four identical quantum numbers". This can be explained as follows:

(a) Considering the $n=1$ state i.e. k-shell of an atom. For k-shell $n=1$, $l=0$ (as possible values are 0 to $(n-1)$) and $m_l=0$ and $m_s=+\frac{1}{2},-\frac{1}{2}$. The set of four quantum numbers are $(1,0,0,\frac{1}{2})$ and $(1,0,0,-\frac{1}{2})$. The two possibilities also says that the maximum number of electrons in K-shell is two.

(b) Similarly considering L-shell. For L-shell, $n=2$, $l=0,1$ (0 to $n-1$) and $m_l=0$, (if $l=0$), $m_l=-1,0,1$, (if $l=1$)

For each m_l, the values of m_s are $+\frac{1}{2}$ or $-\frac{1}{2}$. Hence, the possible combinations are $(2,0,0,+\frac{1}{2})$, $(2,0,0,-\frac{1}{2})$, $(2,1,-1,+\frac{1}{2})$, $(2,1,-1,-\frac{1}{2})$, $(2,1,0,+\frac{1}{2})$, $(2,1,0,-\frac{1}{2})$, $(2,1,1,+\frac{1}{2})$, $(2,1,1,-\frac{1}{2})$

Here we can see that 8 combinations are possible i.e. in L-shell maximum number of electrons is 8.

With similar calculation we can see that for M-shell i.e for $n=3$. Possible combinations are 18, i.e, M-shell contains 18 electrons in all.

Thus, we can see that for a shell with $l=0,1,2,3,---$ there are s, p, d, f, --- sub-shells and for a given value of l the values of m_l are $(2l+1)$, and for every m_l are two values of m_s ($+\frac{1}{2}$ and $-\frac{1}{2}$). Combining these two we can say that there can be $2(2l+1)$ electrons in a sub-shell.

The maximum number of electrons in n^{th} shell

$$=\sum_{l=0}^{l=n-1} 2(2l+1)$$

$$=2[1+3+5+---+\{2(n-1)+1\}]$$

$$=2[1+3+5+---+(2n-1)]$$

$$=2n^2.$$

The principle can not be proved directly either experimentally or theoretically, but the deductions from this principle may be experimentally verified.

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Periodic Table and Pauli's Exclusion Principle :- The electron arrangement of atoms form the basis of the periodic table of elements.

In general, we get the two following conclusions from Pauli's Exclusion principle i.e.

(I) In the n^{th} shell there are n sub-shells corresponding to the values 0, 1, 2, 3 ---- (n−1) of l.

The maximum number of electrons in a sub-shell with a given value of l is $2(2l+1)$.

Orbital quantum number (l)	0	1	2	3	4	----
No. of possible electron states	2	6	10	14	18	----
Subshell symbol	s	p	d	f	g	----

(II) The number of electrons that can be accommodated in a shell with principal quantum number n = Sum of the electrons in the constituent n subshells.

$$= \sum_{l=0}^{l=n-1} 2(2l+1) = 2\sum_{l=0}^{l=n-1}(2l+1)$$

$$= 2[1+3+5+7+ \cdots \{2(n-1)+1\}]$$

$$= 2n^2$$

The following table shows the distribution of electrons according to this scheme.

Shell symbol	K	L	M	N	O
Quantum number (n)	1	2	3	4	5
No. of electrons ($2n^2$)	2	8	18	32	50

The distribution of electrons in the various states (shells and sub-shells) according to the exclusion principle is given in the following table.

	n	l $l=(n-1)$	m_l $-l$ to $+l$	m_s	No. of $\bar{e}$ in subshell with spectroscopic notation $2(2l+1)$		Total no. of $\bar{e}$ in shell $=2n^2$
K	1	0 (s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	$1s^2$	2
L	2	0 (s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	$2s^2$	8
	2	p (p)	−1, 0, +1	$+\frac{1}{2}, -\frac{1}{2}$	6	$2p^6$	
M	3	0 (s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	$3s^2$	18
	3	1 (p)	−1, 0, +1	$+\frac{1}{2}, -\frac{1}{2}$	6	$3p^6$	
	3	2 (d)	−2, −1, 0, +1, +2	$+\frac{1}{2}, -\frac{1}{2}$	10	$3d^{10}$	
N	4	0 (s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	$4s^2$	32
	4	1 (p)	−1, 0, +1	$+\frac{1}{2}, -\frac{1}{2}$	6	$4p^6$	
	4	2 (d)	−2, −1, 0, +1, +2	$+\frac{1}{2}, -\frac{1}{2}$	10	$4d^{10}$	
	4	3 (f)	−3, −2, −1, 0, +1, +2, +3	$+\frac{1}{2}, -\frac{1}{2}$	14	$4f^{14}$	

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Electron configurations of few elements :-

Hydrogen $(Z=1)$ $1s$

Helium $(Z=2)$ $1s^2$

Lithium $(Z=3)$ $1s^2 2s$

Beryllium $(Z=4)$ $1s^2 2s^2$

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

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

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

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

Florine $(Z=9)$ $1s^2 2s^2 2p^5$

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

Sodium $(Z=11)$ $1s^2 2s^2 2p^6 3s$,

Magnesium $(Z=12)$ $1s^2 2s^2 2p^6 3s^2$, divalent

Aluminium $(Z=13)$ $1s^2 2s^2 2p^6 3s^2 3p$. , Trivalent

__I-period :-__ It contains $H(Z=1)$, $He(Z=2)$. Their electronic configuration are $1s$ and $1s^2$ respectively.

__II-period :-__ It contains $Li(Z=3)$, $Be(Z=4)$, $B(Z=5)$, $C(Z=6)$, $N(Z=7)$, $O(Z=8)$, $F(Z=9)$ and $Ne(Z=10)$ so on. The electronic configuration of all elements in a period is different and hence the elements of a period exhibit different physical and chemical properties. Their electronic configuration are $1s^2 2s$; $1s^2 2s^2$; $1s^2 2s^2 2p$ ---

__I-Group :-__ It contains $H \to 1s$, $Li \to 1s^2 2s$, $Na \to 1s^2 2s^2 2p^6 3s$, $K \to 1s^2 2s^2 2p^6 3s^2 3p^6 4s$ etc. In each case there exists one electron outside the core which is loosely bound with the core which has a positive charge of one unit. Each has valency of one and this similarity of electronic structure is responsible for their having similar optical and magnetic properties.

__Inert Group :-__ $He \to 1s^2$, $Ne \to 1s^2 2s^2 2p^6$, $Ar \to 1s^2 2s^2 2p^6 3s^2 3p^6$ etc. All the elements have completed subshells and shells with no electrons outside the core. Hence these elements are chemically inert and magnetically neutral and are placed in same group.

__Halogen Group :-__ All the elements here have 7p electron outside the completed subshell and one electron is less in completion of outmost p-subshell. These have similar physico-chemical behaviour.

All the chemical, magnetic, optical and other properties of elements are thus explained in terms of the configuration of electrons in the element.

__Uses :-__ (1) The chief use of the principle lies in the ellucidation of the electronic structure and atomic spectra.

(2) It is very helpful in defining the special quantum property of the closed shells and accounts for the multiplicity of the lines.

(3) The principle is much more universal and fundamental for (a) electrons in molecules (b) conduction electrons (c) constituent particles of the nucleus.

(4) It regulates the vector-atom model.

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Ag − 47 electron +1 nucleus.
1s^1 76

Stern and Gerlach Experiment :- This is an experiment on the deflection of a beam of atomic rays in non-homogeneous magnetic field, was first devised by Stern and Gerlach and was later elaborated by other workers. It has given a very direct and convincing confirmation of

(1) Space quantisation (2) Spin of electron and (3) a quantised atomic magnetic moment (Bohr-Magneton) It is the fundamental unit of atomic and subatomic magnetic moments.

(3) → Magnetic moment of an atom :- The magnetic moment of an atom due to the orbital motion of the electron can be estimated by applying Ampere's theorem. According to this theorem the magnetic moment is given by the current flowing in the orbit due to the motion of the electron, multiplied by the area enclosed by the orbit. $[\mu = IA]$ —(1) The current I equivalent to the charge 'e' on the electron rotating 'f' times per second around the nucleus is given by

$\mu = IA$

$$I = ef \quad \text{—(2)}$$

$q = it = i/n$ $= i/f$

where I is in amperes, provided the charge e is in coulomb. The area of an elliptical orbit is given by

$$A = \frac{1}{2}\int_0^{2\pi} r^2 d\phi$$

$$= \frac{1}{2}\int r^2 \frac{d\phi}{dt}.dt$$

$I = \lambda v = \frac{Q}{2\pi R} v$

$\mu = IA = \frac{Q}{2\pi R} v \pi R^2$

$= \frac{1}{2} QvR$

$= \frac{Q}{2m}(mvR) = \frac{1}{2}\frac{Q}{m}L$

$L = mvR$

$T = \frac{1}{n}$

Now the orbital angular momentum,

$$p_l = m r^2 \frac{d\phi}{dt}$$

$J = I\omega$ $= mr^2\omega$ $= mr^2 \frac{d\phi}{dt}$ $p_l = mr^2\omega$

$v = r\omega$ $= m(r)$

$\mu = \frac{\text{Area of loop} \times \text{current}}{\text{velocity of light}} = \frac{A \cdot I}{V}$

where $\frac{d\phi}{dt}$ is the angular velocity and m_0 is rest mass of electron,

Hence

$$A = \frac{1}{2}\int_0^T \frac{p_l}{m_0} dt = \frac{1}{2} p_l \frac{T}{m_0} = \frac{1}{2}\frac{p_l}{m_0 f} \quad \text{—(3)}$$

$f = \frac{1}{T}$

where T is the time for one rotation of the orbit.

The magnetic moment μ_l due to the orbital motion is therefore given by, (Substituting eq (2) & (3) in eq (1))

$$\mu_l = \frac{IA}{c} = ef \frac{p_l}{2m_0 fc} = p_l \frac{e}{2m_0 c}$$

μ_B · Bohr magneton

9.3×10^{-24} J/Tesla

But according to the quantum theory, $p_l = l \frac{h}{2\pi}$

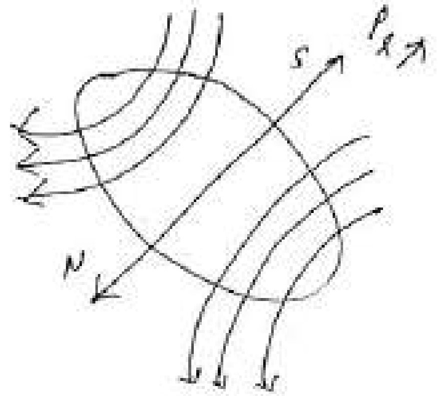
$$\therefore \mu_l = \frac{eh}{4\pi m_0 c} l$$

Since l is an integer, the magnetic moment of the rotating electron is an integral multiple of $\frac{eh}{4\pi m_0 c}$ which depends upon fundamental constants (e, h, π, c and m_0) and is regarded as a fundamental unit of magnetic moment known as Bohr magneton (μ_B)

Thus, the magnetic moment of an electron rotating in any orbit can have only those values

Since an electron has a negative charge, its orbital motion, like that of an electron current in a loop of wire, sets up a magnetic field. The direction of this field is given by the right hand thumb rule.

Since angular momentum is a vector quantity p_l is shown pointing upwards along its axis of rotation. The direction of this mechanical moment is given by the right-handed screw rule.



An orbital electron produces a magnetic field.

The magnetic field produced by the orbital motion of the electron is quite similar to the field around a bar magnet, and is therefore specified as a magnetic dipole moment.

⇒ The ratio $\frac{\mu_l}{p_l} = \frac{e}{2m_0}$

where e and m_0 are the charge and mass of the electron and is called the gyromagnetic ratio. It is the ratio between the magnetic moment and the mechanical moment.

The magnetic moment for a p-electron orbit is one Bohr magneton, for a d-electron it is two Bohr magneton, etc. As s-electron orbit with $l=0$ has no mechanical moment and no magnetic moment.

There is also a magnetic moment associated with spin of an electron about its axis. But as knowledge about the shape of the electron or the manner in which its charge is distributed is not available it is not possible to give a simple consideration of any current corresponding to the electron spin. The most that can be said at this stage is that the magnetic moment due to spin is found to have a value of one Bohr magneton i.e. $eh/4\pi m_0$.

An atom may (therefore) be regarded as an elementary magnet with finite but small dimensions. When this atomic magnet is placed in a magnetic field it will be acted upon by the field. If the field is homogeneous, it will experience a couple tending to bring it in the direction of the field. If such an atomic magnet moves in homogeneous magnetic field in a direction perpendicular to the field, it will trace a straight path without any deviation.

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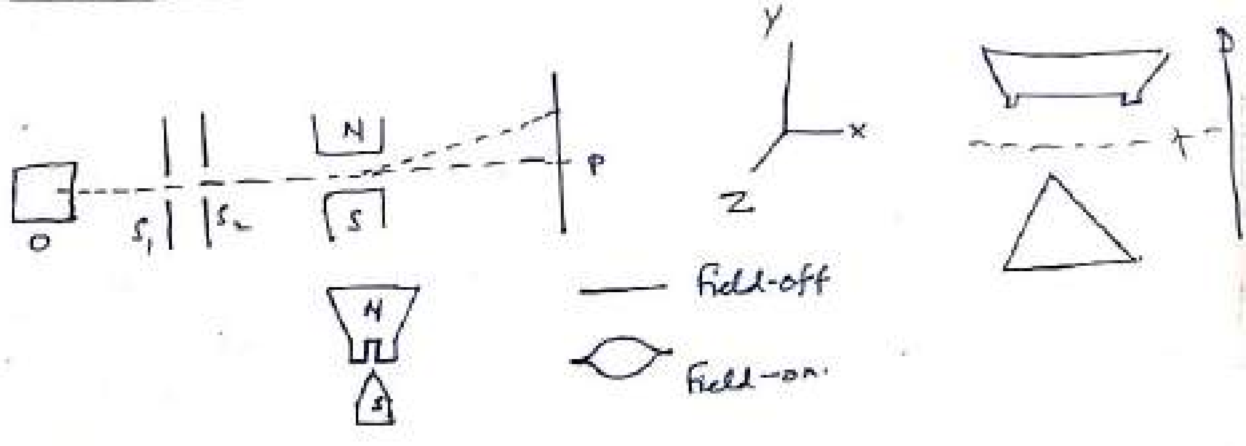
In a non-homogeneous magnetic field, the forces acting on the two poles of the atomic magnet will not be equal and therefore a resultant force over and above the rotating couple will act upon the magnet resulting in a displacement of the atom as a whole. If the atomic magnet moves in such a field, in a direction perpendicular to the field, it will be deviated away from its straight path.

Experimental set-up:- A beam of silver atoms was passed through a highly non-homogeneous magnetic field. The beam was produced by vapourishing silver by heating in a small electric oven 'O' with a slit-shaped exit aperture. The slits S_1 and S_2 produced sharply defined linear beam of silver atoms which then travelled along the x-axis into the space between the specially-designed pole-pieces N, S of the electromagnet. The whole arrangement was placed in a highly evacuated glass chamber in order to avoid collision of silver atoms with gas molecules and to permit volatilisation of silver. The magnetic field was made very intense and non-homogeneous, its lines of force being perpendicular to the beam. It had a large space-rate of variation obtained by taking one pole in the form of a knife-edge and the other in the form of a channel. The magnetic field was thus much more intense near the knife-edge than anywhere else in the gap.

Immediately after emerging from the field, the beam impinged on a glass plate P. When there was no magnetic field, a thin straight line trace was obtained on the glass plate as expected. But with field on, the trace obtained was broken into two lines. The separation between the traces was maximum in the middle where the silver atoms passed through the region of strongest field. This result confirms the existence of electron spin and the postulate of spatial quantisation.

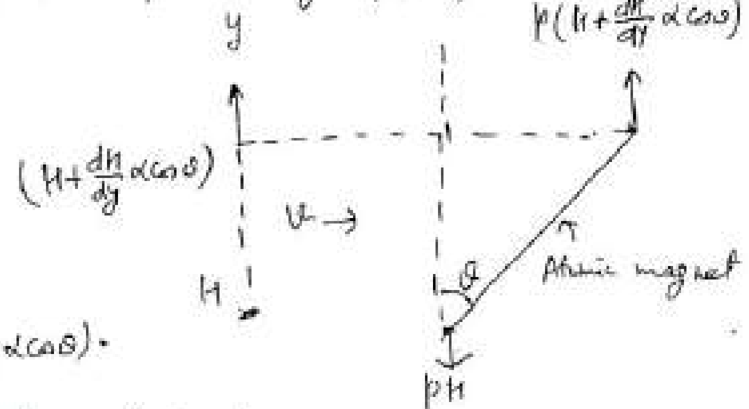


The Spacing between two traces :-

The spacing can be calculated in the following manner :- Let the magnetic field be non-homogeneous along the y-axis so that the field gradient is dH/dy and is positive. Imagine an atomic magnet with pole-strength p, length α and magnetic moment M be placed in such a field with its axis inclined at angle θ to the field direction.

$M = p\alpha$

If H be the strength of the field at one pole then at the other pole it will be $\left(H + \frac{dH}{dy}\alpha\cos\theta\right)$.



The forces acting on the two poles are indicated in the figure. As the two forces are unequal, an extra force $p\frac{dH}{dy}\alpha\cos\theta$ will act on one of the poles, over and above the equal and opposite forces pH constituting the rotating couple. This results in a displacement of the atom as a whole. Let this translatory force be F_y, then

$$F_y = p\frac{dH}{dy}\alpha\cos\theta = M\left(\frac{dH}{dy}\right)\cos\theta$$

$[\because p\alpha = M]$

Now suppose that the atomic magnet moves across the non-homogeneous field at right-angle to the lines of force. It will be displaced from its straight path in the field direction.

Let v be the velocity of the atomic magnet of mass 'm' as it enters the field and let 'L' be the length of its path in the field and 't' the time of flight through the field. The acceleration 'a' imparted to it along the field direction by the translatory force F_y is given by F_y/m. The displacement 'd' of the atom along the field direction at the end of the time t is therefore given by

$F = ma$

$$d = \frac{1}{2}at^2 = \frac{1}{2}\frac{F_y}{m}\left(\frac{L}{v}\right)^2$$

$s = ut + \frac{1}{2}at^2$, $u = 0$

$v = \frac{L}{t}$

$t = \frac{L}{v}$

Putting the value of F_y, we get

$$d = \frac{1}{2}\frac{M\cos\theta}{m}\left(\frac{dH}{dy}\right)\left(\frac{L}{v}\right)^2$$

$$= \frac{1}{2}\frac{\mu_H}{m}\left(\frac{L}{v}\right)^2\frac{dH}{dy} \quad \text{—— (A)}$$

Where $\mu_H = M\cos\theta$, the resolved component of M in the field direction.

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The velocity v of the atom depends upon the oven temperature which may be measured thermoelectrically or optically. The mean velocity of the atoms issuing from the slits is taken to be $v = \sqrt{\frac{3.5kT}{m}}$ where k is the Boltzmann's constant and T is the absolute temperature. On substituting this value of v in above eqn, the expression for d becomes.

$$d = \frac{1}{7} \frac{\mu_H}{kT} L^2 \left(\frac{dH}{dy}\right)$$

The displacement 'd' can be determined from the maximum separation or spacing between the two traces obtained in the experiment, $\left(\frac{dH}{dy}\right)$ can be found, L and T are known, μ_H can therefore be calculated from (A). It is found to be 9×10^{-24} joule/(weber/m^2). Within limits of experimental error this value is in agreement with the value predicted from the silver spectrum. In the normal state of silver $l=0$, as mentioned earlier, so that μ_H, the resolved component of the magnetic moment parallel to the magnetic field, is that due to the spin of the valence electron which is equal to one Bohr magneton, i.e.,

$$\beta = \mu_H = \frac{eh}{4\pi m_e} = 9.27 \times 10^{-24} \text{ joule/(weber/m}^2)$$

The excellent agreement between the experimental results and theoretical predictions is a direct evidence of the postulate of space quantisation and of the existence of electron spin.

The above experiment has been performed using atomic beams of gold, sodium, potassium, lithium, copper etc, all of which have one valence electron in a $S_{\frac{1}{2}}$ state.

Interpretation:-

(1) Spatial Quantization:- According to this theory; only $(2J+1)$ orientation are possible and $(2J+1)$ traces should be obtained. J is total angular quantum numbers. For silver in ground state $l=0, s=\frac{1}{2}$, $J=\frac{1}{2}$. So $(2J+1)=2$. Thus theory of space quantization predicts two orientation and practically two traces are obtained. Thus space quantization is verified.

(2) Spinning Electron:- If it be supposed that spin of electron is absent; then $s=0$, so for silver in ground state $J=l+s=0+0=0$. Thus possible orientation $=(2J+1)=1$, so one trace should be obtained. If spin of electron is considered; then for Ag in ground state, $l=0, s=\frac{1}{2}, J=l+s=0+\frac{1}{2}$; permitted orientation $=2J+1=2$. Two traces should be obtained. Experimentally two traces are obtained. Thus spin of electron must exist.

(3) Atomic and Quantum nature of magnetism:- Stern-Gerlach experiment confirms the general conclusion of classical theory about para and diamagnetism and establish the quantum nature and atomic origin of magnetism. Diamagnetic substances have no atomic magnetic moments ($\mu=0$). Paramagnetic have atoms with one valency electron in ground state. Ferromagnetic have atoms with intermediate incomplete electronic shells and have large value of atomic magnetic moments.

Q:- Sodium doublets are produced by the transition $3^2P_{\frac{1}{2}} \to 3^2S_{\frac{1}{2}}$ (D_1) and $3^2P_{\frac{3}{2}} \to 3^2S_{\frac{1}{2}}$ (D_2). Calculate the Lande g factor for these levels.

233

A:- The formula of Lande-g factor are

$$g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$$

i) For $^2P_{\frac{3}{2}}$ state, $L=1$, $S=\frac{1}{2}$, $J=\frac{3}{2}$

$$\therefore g = 1 + \frac{\frac{3}{2}(\frac{5}{2}) + \frac{1}{2}(\frac{3}{2}) - 2}{2\times\frac{3}{2}\times 5/2} = \frac{4}{3}$$

ii) For $^2P_{\frac{1}{2}}$ state, $L=1$, $S=\frac{1}{2}$, $J=\frac{1}{2}$

$$\therefore g = 1 + \frac{\frac{1}{2}\times\frac{3}{2} + \frac{1}{2}\times\frac{3}{2} - 1\times 2}{2\times\frac{1}{2}\times\frac{3}{2}} = \frac{2}{3}$$

iii) For $^2S_{\frac{1}{2}}$ state, $L=0$, $S=\frac{1}{2}$, $J=\frac{1}{2}$

$$\therefore g = 1 + \frac{\frac{1}{2}\times\frac{3}{2} + \frac{1}{2}\times\frac{3}{2} - 0\times 1}{2\times\frac{1}{2}\times\frac{3}{2}} = 2.$$

Q:- A beam of electrons enters a magnetic field of 1.2 Tesla. Calculate the energy difference between electrons whose spins are parallel and antiparallel to the field.

A:- The spin angular momentum ($\vec{S}$) and spin magnetic dipole moment ($\vec{\mu}_s$) are co-related by

$$\vec{\mu}_s = -g_s \frac{e}{2m} \vec{S}$$

where $g_s = 2$; $|\vec{S}| = \sqrt{S(S+1)}\frac{h}{2\pi}$ and $S=\frac{1}{2}$

If magnetic field $\vec{B}$ is along z-axis, then z-component of magnetic moment is

$$\mu_{sz} = g_s \frac{e}{2m} S_z \quad \text{where } S_z = m_s\frac{h}{2\pi} \text{ with } m_s = \pm\frac{1}{2}$$

then $\mu_{sz} = g_s \frac{e}{2m} m_s \frac{h}{2\pi} = 2\left(\frac{e}{2m}\right)\left(\pm\frac{1}{2}\right)\left(\frac{h}{2\pi}\right) = \pm\frac{eh}{4\pi m}$

The magnetic potential energy of a dipole of moment $\vec{\mu}_s$ in magnetic field $\vec{B}$ is

$$V_m = -\vec{\mu}_s\cdot\vec{B} = -\mu_{sz}B = \pm\frac{eh}{4\pi m}B$$

So, the difference in energy of electrons in parallel and antiparallel spins to the magnetic field

$$\Delta V_m = \frac{ehB}{4\pi m} - \left(-\frac{ehB}{4\pi m}\right) = \frac{ehB}{2\pi m} = \frac{1.6\times10^{-19}\times 6.6\times10^{-34}\times 1.2}{2\times3.14\times 9.1\times10^{-31}}\,J$$

$$= \frac{2.227\times10^{-23}}{1.6\times10^{-19}}\,eV = 1.39\times10^{-4}\,eV.$$

Q:- The quantum numbers of two electrons in the two electrons in the two valence electron which are $n_1=6$, $l_1=3$, $s_1=\frac{1}{2}$; $n_2=5$, $l_2=1$, $s_2=\frac{1}{2}$ (i) assuming L-S coupling find the possible values of L and hence of J (ii) assuming j-j coupling find the possible value of J.

A:- As $l_1=3$ and $l_2=1$, the selection rule are

a) $L = |l_1-l_2|, |l_1-l_2|+1, \ldots (l_1+l_2) = (3-1), (3-1)+1, \ldots (3+1) = 2, 3, 4$

Again as $s_1=\frac{1}{2}$, $s_2=\frac{1}{2}$, so, $S = |s_1-s_2|, |s_1-s_2|+1, \ldots |s_1+s_2| = 0, 1$

So J values are $J = |L-S|, \ldots |L+S|$.

for $S=0$ and $L=2,3,4$; $J=2,3,4$ $\quad \underline{L\pm S}$

for $S=1$ and $L=2,3,4$; $J=1,2,3;\ 2,3,4,5;\ 3,3,4$

b) For $l_1=3$, $s_1=\frac{1}{2}$, we have $j_1 = |l_1-s_1|, |l_1-s_1|+1, \ldots (l_1+s_1)$

$j_1 = (3-\frac{1}{2}), (3+\frac{1}{2}) = \frac{5}{2}, \frac{7}{2}$

again $l_2=1$, $s_2=\frac{1}{2}$ we have $j_2 = |1-\frac{1}{2}|, |1+\frac{1}{2}|$, i.e. $j_2 = \frac{1}{2}, \frac{3}{2}$

The possible j_1-j_2 combinations are $(\frac{1}{2},\frac{5}{2}), (\frac{1}{2},\frac{7}{2}), (\frac{3}{2},\frac{5}{2}), (\frac{3}{2},\frac{7}{2})$

Then for $(\frac{1}{2},\frac{5}{2})$ we have $J=2,3$, for $(\frac{1}{2},\frac{7}{2})$ we have $J=3,4$

for $(\frac{3}{2},\frac{5}{2})$ we have $J=1,2,3,4$ for $(\frac{3}{2},\frac{7}{2})$ we have $J=2,3,4,5$. Ans.

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Q:- What is the total angular momentum of a free electron.

A:- A free electron has no orbital angular momentum. It has only an intrinsic spin angular momentum with spin quantum number $s = \frac{1}{2}$. So its total angular momentum

$$J = S = \sqrt{s(s+1)}\,\hbar = \sqrt{\frac{1}{2}\times\frac{3}{2}}\,\hbar = \frac{\sqrt{3}}{2}\hbar$$

Q:- Find the possible orientations of total angular momentum vector $\vec{J}$ corresponding to $j = \frac{3}{2}$ with respect to a magnetic field along z-axis.

A:- The vector $\vec{J}$ is space quantised with respect to the external magnetic field $\vec{B}$.

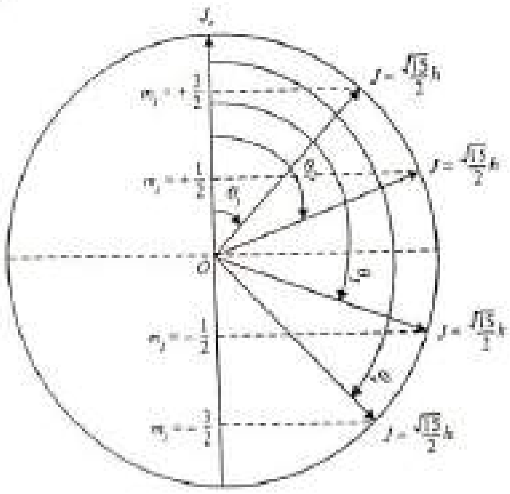
magnitude of $\vec{J} = J = \sqrt{j(j+1)}\,\hbar = \sqrt{\frac{3}{2}\times\frac{5}{2}}\,\hbar = \sqrt{\frac{15}{4}}\,\hbar = \frac{\sqrt{15}}{2}\hbar$.

Where j is total angular momentum quantum number. $\vec{J}$ can have only $(2j+1)$ discrete orientations with respect to the external magnetic field such that $J_z = m_j\hbar$, where m_j is the total angular momentum magnetic quantum number having values

$$m_j = j, (j-1), \ldots, (-j+1), (-j).$$

Also $\frac{J_z}{J} = \cos\theta$, where θ is the angle that vector $\vec{J}$ makes with magnetic field vector $\vec{B}$.

$$\therefore \quad \cos\theta = \frac{J_z}{J} = \frac{m_j\hbar}{\sqrt{j(j+1)}\,\hbar} = \frac{m_j}{\sqrt{j(j+1)}}$$



For $j = \frac{3}{2}$, the values of m_j are $\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}$ and $-\frac{3}{2}$

$$\therefore \cos\theta_1 = \frac{\frac{3}{2}}{\sqrt{\frac{3}{2}\times\frac{5}{2}}} = \frac{3}{\sqrt{15}} = \frac{3}{3.873} = 0.7746$$

or $\theta_1 = 39.2^\circ$

$$\cos\theta_2 = \frac{\frac{1}{2}}{\sqrt{\frac{3}{2}\times\frac{5}{2}}} = \frac{1}{\sqrt{15}} = \frac{1}{3.873} = 0.2582$$

or $\theta_2 = 75^\circ$

Similarly $\theta_3 = 180^\circ - 75^\circ = 105^\circ$ and

$$\theta_4 = 180^\circ - 39.2^\circ = 140.8^\circ$$

So the possible orientations of $\vec{J}$ with respect to $\vec{B}$ are.

$39.2^\circ, 75^\circ, 105^\circ, 140.8^\circ$ as shown in figure.

Q:- Calculate the values of l, s and j and L, S and J for a d-electron in one electron atomic system.

A:- For a d-electron, $l = 2$, and $s = \frac{1}{2}$ as it is one electron atomic system.

$\therefore$ Possible values of j are

$$j = l+s \text{ and } j = l-s$$

or

$$j = 2+\tfrac{1}{2} = \tfrac{5}{2} \text{ and } j = 2-\tfrac{1}{2} = \tfrac{3}{2}$$

$\therefore$ j values are $\frac{5}{2}, \frac{3}{2}$.

Now spin angular momentum $\quad S = \sqrt{s(s+1)}\,\hbar = \sqrt{\frac{1}{2}(\frac{1}{2}+1)}\,\hbar = \frac{\sqrt{3}}{2}\hbar$

orbital angular momentum $\quad L = \sqrt{l(l+1)}\,\hbar = \sqrt{2\times(2+1)}\,\hbar = \sqrt{6}\,\hbar$

Total angular momentum $\quad J = \sqrt{j(j+1)}\,\hbar = \sqrt{\frac{5}{2}\times(\frac{5}{2}+1)}\,\hbar = \frac{\sqrt{35}}{2}\hbar$

and $\quad J = \sqrt{\frac{3}{2}\times(\frac{3}{2}+1)} = \frac{\sqrt{15}}{2}\hbar$

the rule

Q:- Spin-orbit coupling splits all states except S-states into two sub-states. Why are S-states exception to the rule?

A:- The spin-orbit interaction energy is given by $E_{sl} = A[j(j+1) - l(l+1) - s(s+1)]$ where $A = \frac{Ze^2\hbar^2}{16\pi\epsilon_0 m^2c^2r^3}$ = constant

For S-state, $l = 0$, $s = \frac{1}{2}$ and $j = \frac{1}{2}$ $\therefore [j(j+1) - l(l+1) - s(s+1)] = [\frac{1}{2}(\frac{1}{2}+1) - 0 - \frac{1}{2}(\frac{1}{2}+1)] = 0$

Thus the total energy of the atom in the S-state does not change even in the presence of spin-orbit interaction. Hence all S-states remain single.

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Q:- Consider p-electron in one electron atom and calculate the values of L, S and J.

A:- For a p-electron $l=1$ and $s=\frac{1}{2}$

$\therefore$ Possible values of j are $j=l+s$ and $j=l-s$

or $j=1+\frac{1}{2}=\frac{3}{2}$ and $j=1-\frac{1}{2}=\frac{1}{2}$

$\therefore$ j values are $\frac{3}{2}, \frac{1}{2}$.

Now orbital angular momentum, $L=\sqrt{l(l+1)}\hbar=\sqrt{1(1+1)}\hbar=\sqrt{2}\hbar$ (for $l=1$)

Spin-angular momentum, $S=\sqrt{s(s+1)}\hbar=\sqrt{\frac{1}{2}(\frac{1}{2}+1)}\hbar=\frac{\sqrt{3}}{2}\hbar$ (for $s=\frac{1}{2}$)

Total angular momentum, $J=\sqrt{j(j+1)}\hbar=\sqrt{\frac{3}{2}(\frac{3}{2}+1)}\hbar=\frac{\sqrt{15}}{2}\hbar$ (for $j=\frac{3}{2}$)

and $J=\sqrt{\frac{1}{2}(\frac{1}{2}+1)}\hbar=\frac{\sqrt{3}}{2}\hbar$ (for $j=\frac{1}{2}$)

Q:- Calculate Lande's g-factor for a p-electron.

A:- For a p-electron, $l=1$ and $s=\frac{1}{2}$, therefore j has two values $j=1+\frac{1}{2}=\frac{3}{2}$ and $j=1-\frac{1}{2}=\frac{1}{2}$.

(i) For $j=\frac{3}{2}$, $l=1$ and $s=\frac{1}{2}$

$$g=1+\frac{j(j+1)+s(s+1)-l(l+1)}{2j(j+1)}=1+\frac{\frac{3}{2}\times\frac{5}{2}+\frac{1}{2}\times\frac{3}{2}-1\times2}{2\times\frac{3}{2}\times\frac{5}{2}}=1+\frac{1}{3}=\frac{4}{3}$$

(ii) For $j=\frac{1}{2}$, $l=1$ and $s=\frac{1}{2}$

$$g=1+\frac{j(j+1)+s(s+1)-l(l+1)}{2j(j+1)}=1+\frac{\frac{1}{2}\times\frac{3}{2}+\frac{1}{2}\times\frac{3}{2}-1\times2}{2\times\frac{1}{2}\times\frac{3}{2}}=1-\frac{1}{3}=\frac{2}{3}$$

Q:- Calculate Lande's g-factor for $^2D_{\frac{3}{2}}$ state, $^2F_{5/2}$ and $^2P_{\frac{3}{2}}$ state.

A:- For $^2D_{\frac{3}{2}}$ state, $l=2$, $(2s+1)=2$ $\therefore$ $s=\frac{1}{2}$, $j=\frac{3}{2}$

$$\therefore\quad g=1+\frac{j(j+1)+s(s+1)-l(l+1)}{2j(j+1)}=1+\frac{\frac{3}{2}\times\frac{5}{2}+\frac{1}{2}\times\frac{3}{2}-2\times3}{2\times\frac{3}{2}\times\frac{5}{2}}=1-\frac{1}{5}=\frac{4}{5}$$

For $^2P_{\frac{3}{2}}$ state, $l=1$, $(2s+1)=2$ $\therefore$ $s=\frac{1}{2}$, $j=\frac{3}{2}$

$g=\frac{4}{3}$ as above formula used.

For $^2F_{\frac{5}{2}}$ state, $l=3$, $(2s+1)=2$ $\therefore$ $s=\frac{1}{2}$, $j=\frac{5}{2}$

$g=\frac{6}{7}$.

Q:- In Stern-Gerlach experiment silver atoms traverse a distance of 0.1 m through a non-homogeneous field of gradient $60\ Tm^{-1}$. If the separation between the two traces on the collector plate is 0.15 mm, find the velocity of the silver atoms. Mass of silver atom $=1.79\times10^{-25}$ kg, Bohr magneton $=9.27\times10^{-24}\ JT^{-1}$.

Ans:- $$2Z=2\times\frac{1}{2}\times2m_j\,\mu_B\frac{\partial B}{\partial Z}\frac{1}{M}\frac{L^2}{v^2}$$

$$\therefore\quad v^2=\mu_B\frac{\partial B}{\partial Z}\frac{1}{M}\frac{L^2}{2Z}=\frac{9.27\times10^{-24}\times60\times0.1\times0.1}{1.79\times10^{-25}\times0.15\times10^{-3}}=207152$$

or $v=455$ m/sec.