QUANTUM MECHANICAL TREATMENT OF PARAMAGNETISM

The classical theory of paramagnetism is based on the assumption that the permanent magnetic moments of a given atom or ion can rotate freely and possess any orientation with respect to the applied magnetic field. According to quantum theory the magnetic moments are quantized. So the magnetic dipole moment ' $\vec{\mu}$ ' and its component' μ_z ' in the direction of applied field cannot have arbitrary values. There is a direct relation between the magnetic dipole moment ' $\vec{\mu}$ ' of an atom or ion in free space and its angular momentum ' \vec{J} ' given by:

 $\vec{\mu} = -g\mu_{B}'\vec{J}'$ (2.1)

Where $\mu_B = \frac{e\hbar}{2m} =$ Bohr magneton: 'e' is the charge on electron, 'm' is the mass of electron, 'h' is the Plancks constant and 'ħ' is equal to $\frac{\hbar}{2\pi}$ '. 'g' is called the Lande's g factor. 'g' is equal to 2 if the net angular momentum of the dipole is due to electron spin and 1 if it is due to orbital motion only. In general 'g' has mixed origin and is given by:

$$G = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{J(J+1)}$$
(2.2)

Where 'S' and 'L' represent spin and orbital quantum number of the dipole respectively. The orientation of the magnetic moment $(\vec{\mu}')$ with respect to the direction of the applied magnetic field are specified by the rule that the possible components of $(\vec{\mu}')$ along the field direction is given by:

 $\mu_{z} = -g\mu_{B}m_{J}$ (2.3)

Where m_J= -J, -J+1, -J+2,-1, 0, 1, 2,J-1, J

'm_J' is the magnetic quantum number associated with J. For each vaue of 'J', 'm_J' can have 2J+1 integer values, which means that the magnetic moment of the atomic dipole can have 2J+1 orientations with respect to the applied field. The potential energy of such a magnetic dipole in presence of magnetic field \vec{B} is given by:



$$E = -\vec{\mu} \cdot \vec{B} = g\mu_B m_J B \qquad (2.4)$$

According to Maxwell Boltzmann distribution, the number of atoms having a particular value of 'm_j' is proportional to : $e^{-\frac{gm_J\mu_B B}{KT}}$. Considering a unit volume of paramagnetic materials containing 'N' atoms, the magnetization in the field direction is given by:

$$M = N \left\{ \frac{\sum_{m_J=-J}^{m_J=J} -gm_J \mu_B B e^{-\frac{gm_J \mu_B B}{KT}}}{\sum_{m_J=-J}^{m_J=J} e^{-\frac{gm_J \mu_B B}{KT}}} \right\} \dots (2.5)$$

Case I: At normal flux density and ordinary temperature

Substituting (2.7) in (2.6)

$$M = N \frac{(g\mu_B)^2 B^{\underline{J}(J+1)(2J+1)}}{2J+1} = \frac{(g\mu_B)^2 B J(J+1)}{3KT} = \frac{\mu_0 (g\mu_B)^2 H J(J+1)}{3KT}....(2.8)$$

Hence the paramagnetic susceptibility is

$$\chi_{para} = \frac{M}{H} = \frac{\mu_0 (g\mu_B)^2 J(J+1)}{3KT}$$
Or
$$\chi_{para} = \frac{\mu_0 (\mu_B)^2 P_{eff}^2}{3KT}$$

Where $\mathsf{P}_{\mathsf{eff}}$ is the effective number of Bohr magnetons and is given by

.....
$$P_{eff} = g\sqrt{J(J+1)}$$
 2.11)

Equation (2.10) is identical to the classical expression for paramagnetic susceptibility ($\chi = \frac{\mu_0 N \mu^2}{3 KT}$)

with ' μ^2 ' replaced by $(\mu_B)^2 P_{eff}^2$. The **Curie law** can also be deduced by replacing $\frac{\mu_0(\mu_B)^2 P_{eff}^2}{3K}$ by a constant 'C' giving: $\chi_{para} = \frac{C}{3KT}$ (2.12) (Curie Law)

Case II: At low temperatures and strong magnetic field

In this case $gm_J \mu_B B \gg KT$, i.e. $\frac{gm_J \mu_B B}{KT}$ >>1.

$$M = N \left\{ \frac{\sum_{m_{J}=-J}^{m_{J}=J} - gm_{J}\mu_{B}Be^{-\frac{gm_{J}\mu_{B}B}{KT}}}{\sum_{m_{J}=-J}^{m_{J}=J}e^{-\frac{gm_{J}\mu_{B}B}{KT}}} \right\} = \frac{-N g\mu_{B}B \sum_{m_{J}=-J}^{m_{J}=J}m_{J}e^{-\frac{gm_{J}\mu_{B}B}{KT}}}{\sum_{m_{J}=-J}^{m_{J}=J}e^{-\frac{gm_{J}\mu_{B}B}{KT}}}....(2.13)$$

When equation (2.13) is evaluated the value of magnetization becomes:

 $M = NgJ\mu_BB_J(x)$ (2.14)

Where $x = \frac{gJ\mu_B B}{KT}$(2.15)

And $B_J(x)$ is the Brillouin function defined as

$$B_{J}(x) = \frac{2J+1}{2J} \operatorname{Coth}\left(\frac{2J+1}{2J}\right) x - \frac{1}{2J} \operatorname{Coth}\left(\frac{x}{2J}\right) \qquad (2.16)$$

As $\frac{gJ\mu_BB}{KT}$ >>1 hence 'x' is >> 1, 1.e. at low temperature and strong magnetic field

Substituting equation (2.17) in (2.16):

Again Substituting equation (2.18) in (2.14):

 $M = NgJ\mu_B = constant$ (2.19)

Since magnetization is constant it implies the state of Magnetic Saturation, i.e all the dipoles get aligned along the direction of Magnetic induction 'B'. Thus in this limit, the expression (2.14) is analogous to the Langevin expression, with the difference that the Langevin expression is applicable to free rotating dipoles only. For $J \rightarrow \infty$, i.e. for a very large number of allowed orientations, of a magnetic dipole:

$$\operatorname{Coth}\left(\frac{x}{2J}\right) = \frac{2J}{x} \qquad (2.20)$$
$$\operatorname{Coth}\left(\frac{2J+1}{2J}\right) x = \operatorname{Coth}(x)$$

And

Which gives $B_{J}(x) = Coth(x - \frac{1}{x}) = L(x)$ (2.21)

Thus at low temperature and high magnetic field, the Quantum result approaches the classical one. At room temperature the paramagnetic susceptibility is as low as 10⁻⁷, while at very low temperatures at about 1K, the susceptibility increases by more than hundred times.

Ferromagnetism

Like paramagnets, the ferromagnetic materials also contain permanent magnetic dipoles. But in this case the dipoles are not randomly arranged. On the contrary, the dipole moments of adjacent dipoles are aligned in a particular direction even in absence of a magnetic field. Thus a ferromagnet exhibits a magnetic moment even in absence of a magnetic field. The magnetization



The magnetization existing in а ferromagnetic material in absence of an applied magneticfild is called spontaneous magnetization. It exists below a certain critical temperature called the Curie temperature T_c. The alignment of the magnetic dipoles below the Curie temperature is due to exchange interaction between the magnetic ions. Above the Curie temperature, the thermal effects upset the directional alignment of the atomic dipoles and randomness sets in. So the ferromagnetic substance behaves as paramagnetic material.

Even in presence of a weak magnetic field, a ferromagnetic material acquires a high magnetisation and subsequently a high susceptibility.

The susceptibility is not constant but varies with the strength of the applied field. The variation of magnetisation with field strength exhibits the well known Hysteresis curve.

Weiss Domain Theory of Ferromagnetism

The theory of Ferromagnetism put forward by Weiss is based on the following hypotheses:

1. A specimen of ferromagnetic material contains a number of small regions called **domains**, which are spontaneously magnetized. The magnitude of the spontaneous magnetisation of the specimen as a whole is determined by the vector sum of the magnetic moment of individual domains.



2. The spontaneous magnetization of each domain is due to the presence of an exchange field B_E, which tends to produce a parallel alignment of the atomic dipoles. The field B_E is assumed to be proportional to the magnetization 'M' of each domain.

 $B_E = \lambda M$ (2.22)

Where λ is the constant of proportionality called the Curie Weiss constant. B_E and M are the average values of exchange field and magnetization for a domain. B_E is called the molecular **field** or the Weiss field. This field is quite strong as compared (of the order of $\approx 10^3$ Tesla) to the applied magnetic field B. Hence in presence of an applied magnetic field B the total effective field non an atom or ion is:

 $B_{eff} = B + B_E = B + \lambda M$ (2.23)

Weiss originally used the classical Langevin approach to develop the theory of Ferromagnetism but in is more convenient to apply quantum approach to Weiss assumptions

Quantum theory of ferromagnetism:

Let a ferromagnetic specimen be considered with 'N' atoms per unit volume, each having a total angular momentum number J. From equation (8.14) the expression for the magnetization can be written as :

 $M = NgJ\mu_BB_J(x)$ (2.24)

Where $B_J(x) = \frac{2J+1}{2J} \operatorname{Coth}\left(\frac{2J+1}{2J}\right) x - \frac{1}{2J} \operatorname{Coth}\left(\frac{x}{2J}\right)$(2.25)

And
$$x = \frac{gm_J \mu_B B_{eff}}{KT} = \frac{gm_J \mu_B}{KT} (B + \lambda M)$$
....(2.26)

In case of spontaneous magnetization in absence of external field, B = 0, which gives

$$x = \frac{g J \mu_B \lambda M}{KT} \qquad (2.27)$$

and $M(T) = \frac{xKT}{\lambda g J \mu_B}$ (2.28)

At very low temperature: $T \rightarrow 0$. Hence $x \rightarrow \infty$

(01.4)

$$B_{J}(x) = \frac{2J+1}{2J} \frac{\operatorname{Cosh}\left(\frac{2J+1}{2J}\right)x}{\sinh\left(\frac{2J+1}{2J}\right)x} - \frac{1}{2J} \frac{\operatorname{Cosh}\left(\frac{x}{2J}\right)}{\sinh\left(\frac{x}{2J}\right)} = \frac{2J+1}{2J} \left(\frac{e^{\omega} + e^{-\omega}}{e^{\omega} - e^{-\omega}}\right) - \frac{1}{2J} \left(\frac{e^{\omega} + e^{-\omega}}{e^{\omega} - e^{-\omega}}\right) = \frac{2J+1}{2J} - \frac{1}{2J} = 1 \dots (2.29)$$



Fig. 2.3: Magnetic saturation.



$$M_{S}(0) = NgJ\mu_{B}$$
 (2.30)

From equation (2.28) and (2.30):

$$\frac{M(T)}{M_{S}(0)} = \frac{xKT}{\lambda Ng^{2} I^{2} \mu R^{2}} \dots (2.31)$$

Also equations 92.24) and (2.30) generate:

$$\frac{M(T)}{M_{S}(0)} = B_{J}(x) \qquad(2.32)$$

The magnetization M(T) given at a temperature is obtained by solving eqns.(2.31) and (2.32). Equation (2.31) represents a straight line passing through the origin, with a slope directly proportional to the absolute temperature 'T'. The graph of Brillouin function is a curved line. At the critical temperature the straight line represented by equation (2.31) is a tangent to the Brillouin function at the origin. The intersection of the two plots at the origin represents a positive solution. But at this



Fig: 2.4. Graphical solution of the simultaneous eqns.(2.31) and (2.32). 'P', the point of intersection determines the spontaneous magnetization $M_s(T)$ at a given temperature.



point magnetization is unstable. Another point of intersection occurs at the point 'p' for T<T_C, which indicates a non zero value of 'M' even for no external field. This point corresponds to spontaneous magnetization. The plots also reveal that spontaneous magnetization decreases with increase of temperature and vanishes beyond the critical temperature. This temperature is called the Ferromagnetic Curie temperature. Fig. (2.5) shows the variation of spontaneous magnetization, with temperature. It is maximum at OK when the moments of all the atoms in all the domains align themselves in a particular direction under the influence of exchange field.

At T = T_c the spontaneous magnetization disappears and $M_s(T)$ becomes zero.Based on this variation one can classify the paramagnetic to ferromagnetic transition and vice versa as a second order phase transition characterized by order parameter M_s , which is non zero only above curie temperature.

The Paramagnetic Region

Let a temperature zone be considered well above Curie temperature. Spontaneous magnetization is absent in this region. Hence to produce some magnetization an external field is necessary. This field however should be weak enough to avoid the saturation state. Now from equation (2.27):

$$x = \frac{gm_J \mu_B B_{eff}}{KT} = \frac{gm_J \mu_B}{KT} (B + \lambda M)$$

Substituting M = 0

$$x = \frac{gm_J B\mu_B}{KT}$$
(2.33)

For T>> T_C, x is << 1, which gives

For very small value of ' θ ' : Coth(θ) = $\frac{1}{\theta} + \frac{\theta}{3}$ (2.35)

Hence for x<<1, $\left(\frac{2J+1}{2J}\right)x \ll 1$ and $\left(\frac{x}{2J}\right)$ << 1., which gives

$$B_J(x) = \left(\frac{J+1}{3J}\right)x$$
(2.36)

Substituting in equation (2.24):

$$M = NgJ\mu B_J(x) = NgJ\mu \left(\frac{J+1}{3J}\right)$$
(2.37)

Substituting the value of 'x' from (2.33):

$$M = \frac{Ng^{2}\mu_{B}^{2}J(J+1)(B+\lambda M)}{3KT}$$
Or
$$M - \frac{Ng^{2}\mu_{B}^{2}J(J+1)(\lambda M)}{3KT} = \frac{Ng^{2}\mu_{B}^{2}J(J+1)B}{3KT}$$
Or
$$M = \frac{\frac{Ng^{2}\mu_{B}^{2}J(J+1)B}{3KT}}{\left\{1 - \frac{Ng^{2}\mu_{B}^{2}J(J+1)\lambda}{3KT}\right\}}$$

$$= \frac{Ng^{2}\mu_{B}^{2}J(J+1)B}{\left\{3KT - Ng^{2}\mu_{B}^{2}J(J+1)\lambda\right\}}$$

$$= \frac{\left(\frac{Ng^{2}\mu_{B}^{2}J(J+1)B}{3K}\right)}{\left\{T - \frac{Ng^{2}\mu_{B}^{2}J(J+1)\lambda}{3KT}\right\}}$$
Or
$$M = \frac{\left(\frac{Ng^{2}\mu_{B}^{2}J(J+1)B}{3K}\right)}{\left\{T - \frac{Ng^{2}\mu_{B}^{2}J(J+1)B}{3K}\right\}} = \frac{\left(\frac{T_{C}}{\lambda}\right)}{T - T_{C}}$$
(2.38)

Where $T_{C} = \frac{Ng^{2}\mu_{B}^{2}J(J+1)\lambda}{3K}$ (2.39)

Paramagnetic susceptibility :

$$\chi = \frac{\mu_0 M}{B}$$

$$= \frac{\left(\frac{\mu_0 T_C}{\lambda}\right)}{\{T - T_C\}}$$
Or
$$\chi = \frac{C}{T - T_C}$$
Where
$$C = \frac{\mu_0 T_C}{\lambda}$$
(2.41)

Equation (2.40) gives the Mathematical form of **Curie** –**Weiss Law.** This law satisfactorily explains the temperature dependence of susceptibility in the paramagnetic region where the temperature is well above Curie temperature. For $T >> T_c$, The denominator of equation 92,40) is much higher than the numerator and susceptibility has a small positive value.

Nature and origin of Weiss Molecular field: Exchange interaction

Weiss theory of ferromagnetism is based on the concept of ferromagnetic domains, wherethe spontaneous magnetization of each domain is due to the presence of an exchange field $B_{E,C}$ alled the Weiss field or exchange field, which tends to produce a parallel alignment of the atomic dipoles. But the nature and origin of the exchange field is not obtainable from Weiss theory. Magnetic dipole-dipole interaction generates fields of the order of 10^{3} Gauss whereas the actual field strength is observed to be quite high $\approx 10^{7}$ Gauss. This points out that the exchange field is not merely due to dipole-dipole interaction. The concept of Weiss field was first proposed by Heisenberg in 1928 from quantum mechanical exchange interaction between the atoms of the ferromagnetic sample. He proposed that the interaction arises due to the Pauli Exclusion Principle. This principle concludes that any change in the relative orientation of the two spin states of atoms would disturb the spatial distribution of charge. This perturbation leads to an interaction between the atoms. The strength of interaction between the adjacent atoms depend on the extent of overlapping of their wave functions as well as on the relative orientation of their electron spins but is independent on the spin magnetic moments. Thus the exchange interaction is an electrostatic interaction, not a magnetic one.

Heitler-London theory of chemical bonding shows that the total energy of a system of two atoms 'I' and 'j' contains an exchange interaction term given by

Where $\vec{S_1}$ and $\vec{S_j}$ represent the spins of the two atoms and J_e is the exchange integral which is assumed to be same for any pair of atoms of the specimen.



The value of J_e depends on the extent of overlapping of the charge distribution of the two atoms which is related to the inter-atomic distance. Je is positive for large inter-atomic distance and negative for smaller ones. The expression (2.42) is known as Heisenberg model of exchange energy.IfJe is positive , the parallel alignment of spin exhibits lower energy and hence is more stable than the anti parallel arrangement, thereby producing a magnetization in the material even in absence of external field. Consequently negative value of Je does not favour magnetization.

Fig. (2.6) shows a plot of J_e vs. ratio of inter-atomic separation(r_{ij}) between the atoms 'I' and 'j' to radius of the unfilled 3d orbit(r_{3d}). The exchange integral is positive for $\frac{r_{ij}}{r_{3d}}$ is slightly greater

than 3. From the figure it is evident that Iron, cobalt, nickel and gadolinium favours ferromagnetism, while manganese and chromium does not.

Deduction of the relation between the exchange field ' B_{E}^{\prime} and the magnetization 'M' : Stoner's process

Assuming that interaction occurs only between the nearest neighbor atoms and exchange integral J_e to be constant for all the neighbouring pairs the total exchange energy for 'i^{th'} atom is given by:

 $U_i = \sum_j U_{ij} = -2J_e \sum_j (\vec{S_i}, \vec{S_j})$ (2.43) Summing over all the nearest neighbours of 'i^{th'} atom

Stoner replaced the instantaneous values of the neighbouring spins by their average values. If 'Z' be the total number of nearest neighbours then equation (2.43) can be written as:

$$U_{i} = -2ZJ_{e} \left(\sum_{j} S_{xi} < S_{xj} > + S_{yi} < S_{yj} > + S_{zi} < S_{zj} > \right) \quad (2.44)$$

For magnetization along Z axis, we have for 'N' atoms per unit volume: $< S_{xj} > = < S_{yj} > = 0 = < S_{zj} > = \frac{M}{gN\mu_B}$ (2.45)

From equations (2.44) and (2.45) :

 $U_i = -\frac{2ZJ_e S_{zi}M}{gN\mu_B}$ (2.46)

Where $B_E = \frac{2ZJ_eM}{g^2 N\mu B^2}$(2.48)

The factor $\frac{2ZJ_e}{g^2N\mu_B{}^2}$ is a constant $% J_{\mu}^{2}$ and J_{μ}^{2} and J_{μ}^{2} and J_{μ}^{2} is a constant J_{μ}^{2} and J_{μ}^{2} and J_{\mu}^{2} and J_{μ}^{2} and J

$$\lambda = \frac{2ZJ_{e}}{g^{2}N\mu_{B}^{2}} \quad(2.49)$$

This gives:

 $B_E = \lambda M$ (2.50)

Concept of domains and Hysteresis

According to Weiss theory the exchange interaction between adjacent atomic dipoles generate an exchange field B_E , which aligns the magnetic dipoles in a particular direction, thus producing a net magnetisation even in absence of an external field. But in actual practice it has been found that ferromagnetic materials like iron exhibit magnetic behaviour only in presence of an external magnetic field.Weiss explained this by introducing the concept of ferromagnetic domains. According to this concept, a single crystal of a ferromagnetic solid can be assumed to be divided into a number of small regions called **domains**, which are spontaneously magnetized by the exchange field. The magnetization vectors of different domains are randomly oriented so that no net magnetization is produced in the material as a whole. In the presence of an external field the domains pointing in the direction of the field grow at the expense of those pointing in other directions. This results in a net non zero magnetization.



Fig, 2.7: Magnetisation by domain growth

According to Neel, the domain structure of a ferromagnetic solid owes its origin to the minimization of total energy of the material. The total energy of the solid comprises of

- 1. Exchange energy
- 2. Magnetic field energy
- 3. Anisotropy energy
- 4. Domain wall energy
- 5. Magnetostriction energy

Fr examplethe presence of free magnetic poles at the ends of a magnetized ferromagnetic sample generates a magnetic field \vec{H} which interacts with the external magnetic field \vec{B} giving rise to magneticenergy $\frac{1}{2}\vec{H}$. \vec{B} . This energy can be minimized by reducing the size of the domains by dividing them to subdomains which in turn reduces the value of \vec{H} and hence the magnetic energy. But such a subdivision of domains can not continue indefinitely, as the formation of new domain walls require additional energy. Hence by making a compromise between all types of energies a ferromagnetic structure should contain that number of domains which correspond to a state of minimum energy.

All ferromagnetic materials exhibit the phenomenon of hysteresis, the phenomenon being described in the form of curve in Fig. (2.8). From the relation:

$$M = \frac{Ng^2 \mu_B^2 J(J+1)(B+\lambda M)}{3KT}....(2.51)$$

The value of M obtained is:

Where x = $\frac{\text{gm}_{\text{J}}\text{B}\mu_{\text{B}}}{\text{KT}}$(2.53)



Also	it	has	been	shown	that	:
$\frac{M(T)}{M_{s}(0)}$	= B」((x)			.(2.54)	

A plot of the curves represented by equations (2.52) and (2.54) on the same scale, below the Curie temperature shows two points of intersection pointing out to two solutions for M which trace the boundary of the hysteresis curve. He physical cause of the hysteresis curve follows from the concept of domains. The magnetization produced in a ferromagnetic sample in presence of an external field may be due to:

- Growth in size of the domains having favourable orientation with respect to the external magnetic field at the expense of those having unfavourable orientaions
- 2. Rotation of the direction of magnetization of various domains along the field direction.

Fig. 2.8: Two fundamental processes of Magnetisation

When a ferromagnetic solid is subjected to a small magnetic field, the domains with favourable orientation with respect to the external magnetic field starts growing at the expense of those having unfavourable orientaions.

This results in a small magnetization as indicated by the initial portion OA of the M-H curve. Such small displacements of the domain boundary are usually reversible and the specimen becomes unmagnetised as soon as the external field is removed. So, the portion OA of the curve is reversible. As the external field is increased, growth of favourable domains continues with their magnetization vectors still pointing along the **easy directions** as shown in the second picture of Fig. 2.8.Thisresults in a large increase in magnetization. This is represented by the portion AB of the curve. The boundary displacements in this region. are large and irreversible. Domain growth continues till the favourable domains grow to their maximum size. As external field is further increased the domains rotate from their easy direction to the direction of the applied field. The magnetization increases slowly and reaches a saturation value(portion BC) when all the domains point along the direction of the applied field. The path from B to C being irreversible, Magnetisation does not decrease along the same path if the applied field is reduced.





This is because the aligned domains do not regain their random orientation easily. Even after the applied field is completely removed, the magnetization does not become zero. The residual magnetism left in the solid called is remnant magnetization or remnence denoted by $'M_{R}'$ To reduce the magnetization to zero a reverse magnetic field (H_{c}) is required which is called coercive field or coercivity. A similar variation in the reverse magnetization is exhibited if the reverse field is first increase and then decreased. The closed loop CEFKC is called the Hystesesis loop. A similar loop is obtained by plotting magnetic induction 'B' in the solid vs. 'H'.except tht the line CI in the B-H curve is never parallel to the 'H' axis. The study of hysteresis curves of ferromagnetic materials are important as they allow us to determine the quality of the material and select the right material for a particular material.