Quantum Mechanical treatment of Para-magnetism :-

In classical theory, it was assumed that permanent mag. moment of a given atom / ion rotates freely and can posses any orientation wrt applied magnetic field. but in qtm. theory, magnetic moments (μ) are quantized, its component μ_z in the direction of magnetic field cannot have arbitrary values and it is related with angular momentum. (J), as

$$\mu = -g \mu_B J \quad \text{—①}$$

μ_B = Bohr magneton $= \frac{e\hbar}{2m}$ — SI units

$= \frac{e\hbar}{2mc}$ — cgs units

g = Lande's g factor

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

S = spin quantum no.

L = orbital quantum no. of the dipoles.

μ_z can have possible components of μ along the field direction are given by

$$\mu_z = -g \cdot \mu_B m_j \quad \text{—— (3)}$$

$\underbrace{m_j}_{\text{range of } m_j \ (-J \text{ to } J)} = -J, -J+1, --- J-1, J$ is the magnetic quantum number associated with J.

For each value of J, mj can have $(2J+1)$ values. $\therefore$ μ can have $(2J+1)$ orientations relative to the field.

The P.E of such a magnetic dipole in the presence of magnetic field B, is given by $E = m_j g \mu_B B$ —— (4) $[\text{as}, E = \mu B]$

Acc to maxwell Boltzman distribution, the number of atom having a particular value of mj is then proportional to

$$e^{-m_j g \mu_B B / K_B T} \qquad [\because e^{-E/K_B T}]$$

Considering a unit volume of paramagnetic material containing a total of ~~volume~~ N atoms, the magnetisation in the direction of the field is given by

$M = N \times$ (statistical average of the magnetic moments component per atom along B)

$$M = N \sum_{m_j=-J}^{+J} \frac{-m_j g \mu_B e^{-m_j g \mu_B B / K_B T}}{e^{-m_j g \mu_B \cdot B / K_B \cdot T}} \quad -(5)$$

Considering two special cases:

(i) <u>At normal flux densities and ordinary temperatures</u> ie

$$\frac{m_j g \mu_B B}{K_B T} << 1$$

eq (5) can be approximated as

$$M = N \frac{g\mu_B \sum_{m_j=-J}^{+J} -m_j \left(1 - \frac{m_j g \mu_B B}{K_B T}\right)}{\sum_{m_j=-J}^{+J} \left(1 - \frac{m_j g \mu_B B}{K_B T}\right)} \qquad \left[\text{using } e^{-x} = 1 - x + \frac{x^2}{2!} - - -\right.$$

$$M = \frac{N g \mu_B \left(\sum_{m_j=-J}^{+J} m_j + \sum_{m_j=-J}^{+J} m_j^2 \frac{g \mu_B B}{K_B T}\right)}{\sum_{m_j=-J}^{+J} 1 - \sum_{m_j=-J}^{+J} m_j \cdot \frac{g \mu_B B}{K_B T}}$$

(4)

Now, $\sum_{m_J=-J}^{+J} m_J = 0$; $\sum_{m_J=-J}^{+J} 1 = (2J+1)$

$$\sum_{m_J=-J}^{+J} m_J^2 = 2\sum_{m_J=0}^{+J} m_J^2 = \frac{J(J+1)(2J+1)}{3}$$

$$\therefore \quad M = N \frac{\frac{g^2\mu_B^2 B}{k_B T}\frac{J(J+1)\cancel{(2J+1)}}{3}}{\cancel{(2J+1)}}$$

$$\boxed{M = \frac{N g^2 \mu_B^2 B\, J(J+1)}{k_B . T}} \quad -(6)$$

$B = \mu_0 H$

$$\chi_{Para} = \frac{M}{H} = \frac{\mu_0 N \mu_B^2 g^2 J(J+1)}{3 k_B T} \quad -(7)$$

~~If we put $\mu_B^2 P_{eff}^2 = \mu^2$~~

Define $P_{eff} = g\sqrt{J(J+1)}$ = effective number of Bohr magnetons

$$\chi_{Para} = \frac{\mu_0 N \mu_B^2 P_{eff}^2}{3 k_B T} \quad -(8)$$

If we put $\mu_B^2 P_{eff}^2 = \mu^2$

$$\boxed{\chi_{Para} = \frac{\mu_0 N \mu^2}{3 k_B T}} \quad -(9)$$

— same as classical Langevin's theory result.

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ii) At low temp and strong magnetic field, $\frac{m_j g \mu_B B}{K_B T} >> 1$

Now,
Series expansion of exponential term is not possible. eq 5 can be written as

$$M = N g J \mu_B B_J(x) \quad \text{—(10)}$$

where, $x = \frac{g J \mu_B B}{K_B T}$ and $B_J(x)$ is called Brillouin f^n.

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}\right)x - \frac{1}{2J}\coth\left(\frac{x}{2J}\right) \quad \text{—(11)}$$

for $x << 1$, $\coth x \simeq \frac{1}{x} + \frac{x}{3}$

$$\therefore \quad B_J(x) = \frac{x(J+1)}{3J}$$

Therefore, Paramagnetic susceptibility

$$\chi_{Para} = \frac{M}{H} = \frac{N g J \mu_B x (J+1)}{H \cdot 3J}$$

Putting the value of x

$$\chi_{Para} = \frac{N g \cancel{J} \mu_B \, g \cdot J \mu_B B \, (J+1)}{H \cdot K_B T \cdot 3\cancel{J}}$$

$B = \mu_0 H$

$$\chi_{Para} = \frac{\mu_0 N g \mu_B^2 J(J+1)}{3 K_B \cdot T}$$

$$\boxed{\chi_{Para} = \frac{\mu_0 N P_{eff}^2 \mu_B^2}{3 K_B T}} \quad \text{—(12)}$$

⑥ which is same as eq ⑧

Now, for $x >> 1$, $\coth x \simeq 1$

$B_J(x) \simeq 1$

eq ⑩ becomes

$$M = NgJ\mu_B$$

This implies, the state of magnetic saturation ie all the dipoles get alligned along the magnetic induction B.

∴ we can infer from eq ⑩ is similar to Langevin's expression with only difference is that in classical Langevin's theory dipoles can be oriented in all possible directions. ie $J \rightarrow \infty$

for large number of allowed orientation of a magnetic dipole, we have

$$\coth\left(\frac{x}{2J}\right) \longrightarrow \frac{2J}{x}$$

and $\coth\left(1+\frac{1}{2J}\right)x \longrightarrow \coth x$

∴ eq ⑪ ie $B_J(x) = \frac{2J+1}{2J}\coth x - \frac{1}{\cancel{2J}}\cdot\frac{\cancel{2J}}{x}$

$$B_J(x) \simeq \coth(x) - \frac{1}{x}$$

$$B_J(x) \sim L(x) - \text{Langevin's function}$$

∴ quantum result approaches the classical ones. χ_{para} of a solid estimated from eq ⑫ at room temp. $\sim 10^{-7}$, which is quite small.