

Quantum theory of Paramagnetism

In classical theory, we assume that the permanent magnetic moment of a given atom or ion rotates freely and can possess any orientation with respect to the applied magnetic field. According to quantum theory, since these magnetic moments are quantized, the magnetic dipole moment μ and its component μ_z in the direction of the applied magnetic field can not have arbitrary values. We have, in general, a direct relation between the magnetic dipole moment μ of an atom or ion in free space and its angular momentum J as $\mu = -g\mu_B J$

The quantity μ_B is called the Bohr magneton and is equal to $\frac{eh}{2m}$ in SI system; g is known as Lande's g-factor and 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, it has mixed origin and is obtained from the expression: $g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$

where S and L represent the spin and orbital quantum numbers of the dipole respectively. The orientations of the magnetic moment μ with respect to the direction of the applied magnetic field are specified by the rule that the possible components of μ along the field direction are given by

$\mu_z = -g\mu_B m_j$; where $m_j = -J, -J + 1, \dots, J - 1, J$ is the magnetic quantum number associated with J . For each value of J , m_j can have $(2J+1)$ values which means that the magnetic moment of the atom can have $(2J+1)$ different orientations relative to the applied magnetic field.

The potential energy of such a magnetic dipole in the presence of a magnetic field is, therefore, given by

$$E = -\mu \cdot B = gm_j \mu_B B$$

According to the M-B distribution, the number of atoms having a particular value of m_j is thus proportional to $\exp\left(-\frac{gm_j \mu_B B}{k_B T}\right)$

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

$M = N \times$ (Statistical average of the magnetic moment component per atom along *magnetic field direction*)

$$= N \sum_{m_j=-J}^{+J} \frac{-m_j g \mu_B \exp\left(-\frac{m_j g \mu_B B}{k_B T}\right)}{\exp\left(-\frac{m_j g \mu_B B}{k_B T}\right)}$$

We consider following two cases:

Case I: At normal flux densities and ordinary temperature

$$i.e \frac{m_j g \mu_B B}{kT} \ll 1$$

Therefore,

$$M = N \frac{g\mu_B \sum_{m_j=-j}^j -m_j \left(1 - \frac{m_j g \mu_B B}{kT}\right)}{\sum_{m_j=-j}^j \left(1 - \frac{m_j g \mu_B B}{kT}\right)}$$

Now,

$$\sum_{m_j=-j}^j m_j = 0$$

$$\sum_{m_j=-j}^j 1 = (2j + 1)$$

and $\sum_{m_j=-j}^j m_j^2 = 2 \sum_{m_j=0}^j m_j^2 = 2\{1^2 + 2^2 + 3^2 + \dots + j^2\} = 2 \frac{j(j+1)(2j+1)}{6} = \frac{j(j+1)(2j+1)}{3}$

$$\therefore M = N \frac{\frac{g^2 \mu_B^2 B}{kT} \frac{j(j+1)(2j+1)}{3}}{(2j+1)} = N \frac{g^2 \mu_B^2 B}{3kT} j(j+1)$$

$$\therefore \chi_{para} = \frac{\mu_0 M}{B} = \frac{\mu_0 N \mu_B^2}{3kT} g^2 j(j+1) = \frac{\mu_0 N p_{eff}^2 \mu_B^2}{3kT} = \frac{C}{T},$$

where $C = \frac{\mu_0 N p_{eff}^2 \mu_B^2}{3k}$ is Curie constant.

and $p_{eff} = g\sqrt{j(j+1)}$ is effective Bohr magneton number.

Case II: At low temperature and strong magnetic fields, $\frac{m_j g \mu_B B}{kT}$ is not smaller than unity and it is not possible to make a series expansion of the exponential terms present in the equation of magnetization. After some algebraic manipulations*we get, $M = Ngj\mu_B B_j(x)$

Where $x = \frac{gj\mu_B B}{kT}$ and $B_j(x)$ is the Brillouin function defined as,

$$B_j(x) = \frac{2j+1}{2j} \coth\left(\frac{2j+1}{2j}x\right) - \frac{1}{2j} \coth\left(\frac{x}{2j}\right)$$

For $x \gg 1$ i.e. at low temperature and strong magnetic fields,

$$\text{Coth } x \cong 1 \text{ and hence } B_j(x) \cong 1$$

Therefore, $M = Ngj\mu_B B_j(x)$ becomes $M = Ngj\mu_B$

This result implies the state of magnetic saturation, i.e., all the dipoles get aligned along the magnetic induction \mathbf{B} . Thus, in this limit, the expression is analogous to the Langevin expression with the difference that the latter is applicable to freely rotating dipoles only. In fact, for $j \rightarrow \infty$, i.e., for a large number of allowed orientations of a magnetic dipole, we have

$$\coth\left(\frac{x}{2j}\right) \rightarrow \frac{2j}{x}$$

And $\coth\left(1 + \frac{1}{2j}\right)x \rightarrow \coth x$

$$B_j(x) \rightarrow \coth x - \frac{1}{x} \text{ or } L(x)$$

Thus, the quantum results approach the classical ones. This is what is expected as the classical theory allows all conceivable orientations. For other values of j , however, the two results differ considerably.

For $x \ll 1$, i.e., at weak magnetic field and high temperature, we have

$$\coth x \cong \frac{1}{x} + \frac{x}{3}$$

$$B_j(x) \cong \frac{x(j+1)}{3j}$$

∴

Thus, the susceptibility becomes

$$\chi_{para} = \frac{\mu_0 M}{B} = \frac{\mu_0 N \mu_B^2}{3k} g^2 j(j+1) = \frac{\mu_0 N p_{eff}^2 \mu_B^2}{3kT} = \frac{C}{T}, \text{ (same as we got earlier)}$$

where $C = \frac{\mu_0 N p_{eff}^2 \mu_B^2}{3k}$ is Curie constant

Thus, we see that Curie law is valid again. The above equation is successfully employed to predict the values of susceptibility for various paramagnetic crystals particularly rare earth ions. The value of j is determined by applying the Hund's rules.

Hund's rules state that, for the ground state of atoms with incompletely filled shells,

(i) the electron spins add up to give the maximum possible S consistent with the Pauli's exclusion principle.

(ii) the orbital momenta combine to give the maximum value for L that is consistent with (i)

(iii) the value of J is given by

$$J = |L - S| \text{ if a shell is less than half-filled}$$

$$J = |L + S| \text{ if a shell is more than half-filled.}$$

If the shell is just half-filled, $L=0$ and, therefore, $J = S$

However, equation of paramagnetic susceptibility written above is unable to account for the experimental observations of susceptibility for the ions of the iron group. This is because of the presence of crystal field due to other ions which cannot be neglected in comparison with the externally applied field.

In case of iron group ions, it is found that different J-multiplets are very close together so that orbital and spin momenta are quantized separately. In such a case, p_{eff} should be given by the expression $p_{eff} = \sqrt{L(L+1) + 4S(S+1)}$. However, experiments show that p_{eff} of these elements is given by $p_{eff} = \sqrt{4S(S+1)}$. D.M. Bose and Stoner explained this by suggesting orbital quenching due to crystal field of these ions. According to them the orbital motion for these ions are not manifested in the determination of magnetic moment and hence we get only the contribution of spin. Thus, for iron group elements such as Ni^{2+} , Co^{2+} , Mn^{2+} , ($3d$ configuration) the p_{eff} will be given by $\sqrt{4S(S+1)}$.

Example 1:

Dy^{3+} has outer electron configuration of $4f^9 6s^0$. Calculate magnetic susceptibility for a salt containing one kg mole of Dy^{3+} ions at 300 K.

Ans:

number of unpaired electron = 5

for f state ($L=3$)

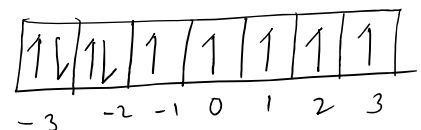
Applying Hund's rule

$$S = 5 \times \frac{1}{2} = \frac{5}{2}$$

$$L = 3 + 2 + 1 + 0 - 1 = 5$$

$$J = |L + S| = \frac{5}{2} + \frac{5}{2} = \frac{15}{2}$$

$$\chi = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} = 1.33$$



$$\text{Now, } \chi_{\text{para}} = \frac{\mu_0 N \mu_B^2}{3kT} g^2 J(J+1)$$

For 1 kg mole of salt $N = 6.023 \times 10^{26}$

$$\begin{aligned} \text{Therefore, } \chi_{\text{para}} &= \frac{4\pi \times 10^{-7} \times 6.023 \times 10^{26} \times (9.27 \times 10^{-24})^2}{3 \times 1.38 \times 10^{-23} \times 300} \times (1.33)^2 \times \frac{15}{2} \left(\frac{15}{2} + 1\right) \\ &= 5.9 \times 10^{-4} \end{aligned}$$

Example 2:

The electronic configuration of a Cr^{2+} ion is $3d^4 4s^0$. Calculate the magnetic susceptibility for a salt containing 1 kg mole of Cr^{2+} ions at 300 K.

Ans: Here, number of unpaired electron = 4

$$\text{therefore, } S = 4 \times \frac{1}{2} = 2$$

Here Cr^{2+} is iron-group ion and due to orbital quenching

$$P_{\text{eff}}^2 = 4S(S+1) = 4 \times 2(2+1) = 24$$

$$\begin{aligned} \chi_{\text{para}} &= \frac{\mu_0 N \mu_B^2}{3kT} P_{\text{eff}}^2 \\ &= \frac{4\pi \times 10^{-7} \times 6.023 \times 10^{26} \times (9.27 \times 10^{-24})^2}{3 \times 1.38 \times 10^{-23} \times 300} \times 24 \end{aligned}$$

$$\therefore \chi_{\text{para}} = 1.25 \times 10^{-4}$$

$$\begin{aligned} \text{for d state} \\ L = 2 \\ \hline (2+1) \\ = 5 \text{ state} \end{aligned}$$