Diamagnetism

Langevin Diamagnetic Equation (Classical theory):

Langevin formula for the volume susceptibility of core electrons:

$$\chi = -\left(\frac{Ze^2N}{6m_e}\right) < r^2 > \qquad \text{.....(1)}$$

Where

N - Number of atoms per unit volume

$< r^2 >$ - Average mean square distance of electrons from the nucleus

Z - Atomic number

m_e - Mass of electron

Quantum theory of diamagnetism:

Hamiltonian for an electron in a magnetic field

Starting from Lorentz equation for the force on an electron moving in a combined electric and magnetic field

$$F = -e\boldsymbol{E} - \left(\frac{e}{c}\right)\boldsymbol{v} \times \boldsymbol{H} \qquad .....(2)$$

Introducing the vector potential, **A** by means of the relation $\boldsymbol{H} = \nabla \times \boldsymbol{A}$

Thus the Hamiltonian is given by –

$$\boldsymbol{\mathcal{H}} = K.E. + P.E = \frac{1}{2}mv^2 + V \qquad .....(3)$$

Here, the spin of the electron will be neglected.

Let $\boldsymbol{p} = -i\,\hbar\boldsymbol{\nabla}$ and $\nabla = \hat{\imath}\,\frac{\partial}{\partial x} + \hat{\jmath}\,\frac{\partial}{\partial y} + \hat{k}\,\frac{\partial}{\partial z}$

$$\boldsymbol{\mathcal{H}} = \frac{(-\,i\,\hbar\nabla)^2}{2m} + V = -\frac{(\hbar\nabla)^2}{2m} + \mathrm{V} \qquad \ldots..(4)$$

In the absence of the magnetic field moment $\boldsymbol{p}$ is given by $\boldsymbol{p} = m\boldsymbol{v}$ and in the presence

$$\boldsymbol{p} = m\boldsymbol{v} + \frac{Q}{C}\boldsymbol{A} \qquad \ldots..(5)$$

$$m\boldsymbol{v} = \boldsymbol{p} - \frac{Q}{C}\boldsymbol{A} = [-\,i\,\hbar\boldsymbol{\nabla} + \frac{e}{C}\boldsymbol{A}] \qquad \ldots..(6)$$

$$\boldsymbol{\mathcal{H}} = \frac{1}{2m}\{\left[\frac{e}{C}\boldsymbol{A}\right]^2 + h^2\boldsymbol{\nabla}^2 - i\,\hbar\frac{e}{C}[\boldsymbol{A}.\boldsymbol{\nabla} + \boldsymbol{\nabla}.\mathbf{A}]\} + V \qquad \ldots..(7)$$

$$\boldsymbol{\mathcal{H}} = -\frac{h^2\boldsymbol{\nabla}^2}{\mathbf{2m}} - \frac{i\hbar e}{2mC}[\boldsymbol{A}.\boldsymbol{\nabla} + \boldsymbol{\nabla}.\mathbf{A}] + \frac{1}{2m}\left[\frac{e}{C}\boldsymbol{A}\right]^2 + V \qquad \ldots..(8)$$

Paramagnetic Contribution Diamagnetic Contribution

Where V is the potential energy, thus if we take:

$$A_x = -\frac{1}{2}yH,\ A_y = \frac{1}{2}xH \ and \ A_z = 0 \qquad \text{.....(9)}$$

Then

$$H_x = H_y = 0 \ and \ H = H_z \qquad \text{.....(10)}$$

$$H = \begin{vmatrix} \hat{\imath} & \hat{\jmath} & \hat{k} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ \frac{1}{2}yH & \frac{1}{2}xH & 0 \end{vmatrix} = H_z \qquad \text{.....(11)}$$

Now solving for –

$$\boldsymbol{A}.\boldsymbol{\nabla} + \boldsymbol{\nabla}.\mathbf{A} = -\frac{1}{2}yH\frac{\partial}{\partial x} + \frac{1}{2}xH\frac{\partial}{\partial y} \qquad \text{.....(12)}$$

Since $\boldsymbol{p} = -i\,\hbar\boldsymbol{\nabla}$ and $\nabla = \hat{\imath}\,\frac{\partial}{\partial x} + \hat{\jmath}\,\frac{\partial}{\partial y} + \hat{k}\,\frac{\partial}{\partial z}$

Therefore,

$$\boldsymbol{p_x} = -i\,\hbar\frac{\partial}{\partial x} \quad \text{and} \quad \boldsymbol{p_y} = -i\,\hbar\frac{\partial}{\partial y} \qquad \text{.....(13)}$$

$$\boldsymbol{A}.\boldsymbol{\nabla} + \boldsymbol{\nabla}.\mathbf{A} = \frac{\mathrm{Hi}}{2\hbar}(xp_y - yp_x) \qquad \text{.....(14)}$$

Therefore, for a magnetic field in z direction Hamiltonian becomes

$$\boldsymbol{\mathcal{H}} = -\frac{h^2\boldsymbol{\nabla}^2}{\mathbf{2m}} + \frac{eH}{4mC}(xp_y - yp_x) + \frac{1}{2m}\left[\frac{e}{C}\boldsymbol{A}\right]^2 + V \qquad \text{.....(15)}$$

Rom the definition of angular momentum –

$$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$$

$$L_z = xp_y - yp_x$$

and $\mu_z = -\frac{e}{2mc} L_z = -\frac{e}{2mc}(xp_y - yp_x)$ .....(16)

$$\boldsymbol{\mathcal{H}} = -\frac{h^2}{\mathbf{2}\mathrm{m}}\boldsymbol{\nabla}^2 - \frac{1}{2}H\mu_z + \frac{e^2}{2mc^2}A^2 + V \qquad .....(17)$$

$$\boldsymbol{\mathcal{H}} = -\frac{h^2}{2\mathrm{m}}\boldsymbol{\nabla}^2 - \frac{1}{2}\boldsymbol{\mu}.\boldsymbol{H} + \frac{e^2}{2mc^2}A^2 + V \qquad .....(18)$$

The second term contributes to the permanent dipole i.e. paramagnetic contribution.

Now, considering the third term –

$$\frac{e^2}{2mc^2}A^2 = \frac{e^2}{2mc^2}({A_x}^2 + {A_y}^2) \qquad .....(19)$$

Substitution the values of A_x and A_y in this from equation (9)-

$$\frac{e^2}{2mc^2}A^2 = \frac{e^2}{2mc^2}(< x^2 > + < y^2 >)\frac{H^2}{4} \qquad .....(20)$$

$$\frac{e^2}{2mc^2}A^2 = \frac{e^2}{2mc^2}(< \rho^2 >)\frac{H^2}{4} \quad \text{.....(21)}$$

$$< \rho^2 > = \frac{2}{3} < r^2 > \quad \text{.....(22)}$$

Suppose we had written the H for the electrons associated with unit volume of substance containing N atoms and each atom containing Z electrons.

$$\frac{e^2}{2mc^2}A^2NZ = \frac{e^2H^2}{12mc^2} < r^2 > NZ \quad \text{.....(23)}$$

Now if the magnetic field induces a dipole moment in the material, the corresponding energy term should be quadratic in H. This equation (23) may be considered the energy term associated with the diamagnetism of solid.

$$-\frac{1}{2}\chi H^2 = \frac{e^2H^2}{12mc^2} < r^2 > NZ \quad \text{.....(24)}$$

$$\chi_{dia} = -\frac{e^2H^2}{6mc^2} < r^2 > NZ \qquad \text{.....(25)}$$

Where $< r^2 >$ represents the mean square distance of the electrons relative to the nucleus.