Quantum Theory of Diamagnetism

The Hamiltonian of $\mathcal{H}$ of an electron changes to $\mathcal{H}+\mathcal{H}'$ in presence of a magnetic induction $\vec{B}$, where $\mathcal{H}'$ represents small perturbation.

Using quantum mechanics we can show that

$$\mathcal{H}' = -\frac{ie\hbar}{2m}\left(\nabla\cdot\vec{A} + 2\vec{A}\cdot\nabla\right) + \frac{e^2}{2m}(A^2) \quad —(1)$$

where $\vec{A}$ is the magnetic vector potential given by

$\vec{B} = \nabla\times\vec{A}$

If $\vec{B}$ is uniform then it can be expressed as

$$\vec{A} = \frac{1}{2}\vec{B}\times\vec{r} = \frac{1}{2}\left[\hat{i}(B_y z - B_z y) + \hat{j}(B_z x - B_x z) + \hat{k}(B_x y - B_y x)\right] \quad —(2).$$

If $\vec{B}$ is along the z direction then $B_x = B_y = 0;\ B_z = B$.

$$\therefore A_x = -\frac{1}{2}yB,\ A_y = \frac{1}{2}xB \ \&\ A_z = 0.$$

Also
$$\nabla\cdot\vec{A} = \frac{\partial A_x}{\partial x} + \frac{\partial A_y}{\partial y} + \frac{\partial A_z}{\partial z} = 0. \quad —(3)$$

and
$$\vec{A}\cdot\nabla = A_x\frac{\partial}{\partial x} + A_y\frac{\partial}{\partial y} + A_z\frac{\partial}{\partial z}$$
$$= \frac{1}{2}B\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \quad —(4).$$

Now eq^n (1) becomes

$$\mathcal{H}' = -\frac{ie\hbar B}{2m}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) + \frac{e^2B^2}{8m}(x^2+y^2) \quad —(5).$$

The quantum mechanical angular momentum operator is

$$\vec{L} = -i\hbar\vec{r}\times\nabla$$

or
$$\hat{i}L_x + \hat{j}L_y + \hat{k}L_z = -i\hbar\left[\hat{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) + \hat{j}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) + \hat{k}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\right] \quad —(6)$$

$$\therefore L_z = \hat{k}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \quad —(7).$$

from eqⁿ (5) & (7) it is clear that the first term on the right hand side of eqⁿ (5) is proportional L_z

If Now N be the number of atoms per unit volume and n' the number of electron in each atom, then the Second term of eqⁿ (5) becomes.

$$\cancel{\frac{Ne^2B^2}{8m}\sum_{i=1}^{n'}(x^2+y_i^2) = \frac{Nn'e^2B^2}{8m}\langle\rho^2\rangle}$$

$$\frac{Ne^2B^2}{8m}\sum_{i=1}^{n'}(x_i^2+y_i^2) = \frac{Nn'e^2B^2}{8m}\langle\rho^2\rangle \quad —(8)$$

where $\langle\rho^2\rangle$ is the mean squared radius of the projection of the orbit on a plane perpendicular to the magnetic field $\vec{B}$, If $\vec{B}$ induces a dipole moment in the specimen, the corresponding energy term should contain B^2, Hence $\frac{Nn'e^2B^2}{8m}\langle\rho^2\rangle$ is the energy term associated with the diamagnetism of the material But the diamagnetic energy is given by

$$\frac{1}{2}\vec{M}\cdot\vec{B} = -\frac{1}{2\mu_0}\chi_{dia}B^2$$

$$\therefore \frac{Nn'e^2B^2}{8m}\langle\rho^2\rangle = -\frac{1}{2\mu_0}\chi_{dia}B^2$$

or

$$\chi_{dia} = -\frac{Nn'\mu_0e^2}{4m}\langle\rho^2\rangle \quad —(9)$$

or

$$\chi_{dia} = \frac{N n' \mu_0 e^2}{6m} \langle r^2 \rangle \quad \text{— (10)}$$

$$\left[\because \langle r^2 \rangle = \frac{3}{2} \langle \rho^2 \rangle \right]$$

Here $\langle r^2 \rangle$ is the mean squared distance of the electron from the nucleous. Determing $\langle r^2 \rangle$ we can calculate the value of χ_{dia} of the material. In quantum mechanical treatment $\langle r^2 \rangle$ has diffrent significance from that in classical treatment.

The experimental value of χ_{dia} agrees fairly with theoritical result specially for light elements and rare gases

for He - atom $\chi_{dia} = -1.9 \times 10^{-6}$

indicating that diamagnetism is very weak effect.