W-2011 Q.1

Quantum Theory Of Diamagnetism

OR

The Hamiltonian For An Electron In A Magnetic field

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

$$F = -eE - \left(\frac{e}{c}\right) v \times H \quad \cdots\cdots(1)$$

Introducing the vector potential, A by means of the relation $H = \text{curl } A$. Thus, the hamiltonian is given by -

$$H = KE + PE$$

$$= \frac{1}{2}mv^2 + V$$

(Here, the spin of the e^- will be neglected)

let,

$$p = -i\hbar \nabla$$

and

$$\nabla = \hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}$$

Thus,

$$H = \frac{(-i\hbar\nabla)^2}{2m} + V$$

$$= -\frac{\hbar^2\nabla^2}{2m} + V$$

In the absence of the magnetic field, $\vec{p}$ i.e the momentum is given by -

$$\vec{p} = m\vec{v}$$

and in the presence of magnetic field

$$\vec{p} = m\vec{v} + \frac{Q}{c} \cdot \vec{A}$$

$$m\vec{v} = \vec{p} - \frac{Q}{c} \vec{A}$$

$$m\vec{v} = \left[-i\hbar \nabla + \frac{e}{c} \vec{A} \right]$$

Therefore,

$$H = \frac{1}{2m} \left[-i\hbar \nabla + \frac{e}{c} \vec{A} \right]^2 + V$$

$$H = \frac{1}{2m} \left[-\hbar^2 \nabla^2 + \frac{e^2}{c^2} A^2 - \frac{ie\hbar}{c} \left[\nabla \cdot \vec{A} + \vec{A} \cdot \nabla \right] \right] + V$$

$$H = \frac{-\hbar^2}{2m} \nabla^2 + \frac{e^2 A^2}{2mc^2} - \frac{ie\hbar}{2mc} \left[\nabla \cdot \vec{A} + \vec{A} \cdot \nabla \right] + V$$

$$H = -\frac{\hbar^2}{2m} \nabla^2 \underbrace{- \frac{ie\hbar}{2mc} \left[\nabla \cdot \vec{A} + \vec{A} \cdot \nabla \right]}_{\text{paramagnetic contribution}} + \underbrace{\frac{e^2}{2mc^2} A^2}_{\text{Diamagnetic contribution}} + V \quad \ldots (2)$$

where, V is the potential energy. Thus, if we take -

* $A_x = -\frac{1}{2} yH$, $A_y = \frac{1}{2} xH$ and $A_z = 0$

then,

$$H_x = H_y = 0 \quad \text{and} \quad H = H_z$$

Thus,

$$\nabla \times \bar{A} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ \partial/\partial x & \partial/\partial y & \partial/\partial z \\ -yH/2 & xH/2 & 0 \end{vmatrix} = H$$

Now solving for-

$$\nabla \cdot \vec{A} + \vec{A} \cdot \nabla = -\frac{y}{2} H \frac{\partial}{\partial x} + \frac{x}{2} H \frac{\partial}{\partial y}$$

$$= \frac{H}{2}\left[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right]$$

$$= \frac{Hi}{2\hbar}\left[xp_y - yp_x\right]$$

since,

$$p = -i\hbar\nabla$$

Therefore,

$$p_x = -i\hbar\frac{\partial}{\partial x}$$

and

$$p_y = -i\hbar\frac{\partial}{\partial y}$$

$$\Rightarrow \frac{\partial}{\partial x} = \frac{i}{\hbar} p_x$$

and

$$\frac{\partial}{\partial y} = \frac{i}{\hbar} p_y$$

Therefore, for a magnetic field in a z-direc^n becomes-

$$H = -\frac{\hbar^2}{2m}\nabla^2 + \frac{eH}{4mc}(xp_y - yp_x) + \frac{e^2}{2mc^2}A^2 + V \quad \cdots (3)$$

From this we draw two important conclusions First, if the electron motion were associated with a permanent magnetic dipole moment μ which give rise to a term $-\mu H = -\frac{\mu_z H}{2}$ in the hamiltonian. Thus, the Second term on the right may be identified with $-\mu_z H$, so that -

$$\mu_z = -\left(e/2mc\right)(xp_y - yp_x)$$

From the definition of the angular momentum, we have -

$$L = r \times p$$

that is related to the z-component of the angular momentum.

$$xp_y - yp_z = L_z$$

Thus, equ^n (3) becomes -

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{H}{2}\mu_z + \frac{e^2}{2mc^2}A^2 + V$$

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{1}{2}\vec{\mu}\cdot\vec{H} + \frac{e^2}{2mc^2}A^2 + V$$

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

Now, considering the third term -

$$\frac{e^2}{2mc^2}A^2 = \frac{e^2}{2mc^2}(A_x^2 + A_y^2) \quad \because A_x = -\frac{yH}{2}$$

$$A_y = \frac{xH}{2}$$

$$= \frac{e^2}{2mc^2}\left[\langle x^2\rangle + \langle y^2\rangle\right]\frac{H^2}{4}$$

$$= \frac{e^2}{2mc^2}\left[\langle \rho^2\rangle\right]\frac{H^2}{4} \quad \because \langle \rho^2\rangle = \frac{2}{3}\langle r^2\rangle$$

$$= \frac{e^2}{2mc^2}\left[\langle r^2\rangle\frac{2}{3}\right]\frac{H^2}{4}$$

$$= \frac{e^2H^2}{12mc^2}\langle r^2\rangle NZ$$

This term is equivalent to - $\boxed{-\frac{1}{2}\chi H^2}$

Thus,

$$\chi = \frac{-e^2}{6mc^2}NZ\langle r^2\rangle$$

where, $\langle r^2\rangle$ represents the mean square distance of the electron relative to the nucleus.