ECE230: Poster Day Presentation Topic: Quantum Theory of Paramagnetism

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Bohr–Van Leeuwen Theorem

- The Bohr–Van Leeuwen theorem states that when statistical mechanics and classical mechanics are applied consistently, the thermal average of the magnetization is always zero.
- This makes magnetism in solids solely a quantum mechanical effect.
- Classical physics cannot account for paramagnetism, diamagnetism and ferromagnetism.

Lagrangian and Hamiltonian of a Charged Particle in an Electromagnetic Field

Particle of mass m and charge q.

$$\bar{F} = q(\bar{E} + \bar{v} \times \bar{B}) \quad \text{Lorentz Force}$$

$$\bar{E} = -\nabla\phi - \frac{\partial \bar{A}}{\partial t} \qquad \bar{B} = \bar{\nabla} \times \bar{A}$$

$$\bar{F} = q\left[\left(-\bar{\nabla}\phi - \frac{\partial \bar{A}}{\partial t}\right) + \bar{v} \times (\bar{\nabla} \times \bar{A})\right]$$

$$\Rightarrow \bar{F} = q\left[-\nabla\phi - \frac{\partial \bar{A}}{\partial t} + \bar{\nabla}(\bar{v}\cdot\bar{A}) - (\bar{v}\cdot\bar{\nabla})\bar{A}\right]$$

$$\Rightarrow \bar{F} = q\left[-\nabla\phi - \left\{\frac{\partial \bar{A}}{\partial t} + (\bar{v}\cdot\bar{\nabla})\bar{A}\right\} + \bar{\nabla}(\bar{v}\cdot\bar{A})\right] \quad \text{— (1)}$$

Let $\bar{A}(r,t) = \bar{A}(x,y,z,t)$

$$\frac{d\bar{A}}{dt} = \frac{\partial \bar{A}}{\partial x}\frac{dx}{dt} + \frac{\partial \bar{A}}{\partial y}\frac{dy}{dt} + \frac{\partial \bar{A}}{\partial z}\frac{dz}{dt} + \frac{\partial \bar{A}}{\partial t}\frac{dt}{dt}$$

$$= v_x \frac{\partial \bar{A}}{\partial x} + v_y \frac{\partial \bar{A}}{\partial y} + v_z \frac{\partial \bar{A}}{\partial z} + \frac{\partial \bar{A}}{\partial t}$$

$$= \frac{\partial \bar{A}}{\partial t} + \left(v_x \frac{\partial}{\partial x} + v_y \frac{\partial}{\partial y} + v_z \frac{\partial}{\partial z}\right)\bar{A}$$

$$\frac{d\bar{A}}{dt} = \frac{\partial \bar{A}}{\partial t} + (\bar{v}\cdot\nabla)\bar{A} \quad \text{— (2)}$$

Put (2) in (1)

$$\bar{F} = q\left[-\bar{\nabla}\phi - \frac{d\bar{A}}{dt} + \nabla(\bar{v}\cdot\bar{A})\right]$$

$$\Rightarrow \boxed{\bar{F} = q\left[-\bar{\nabla}(\phi - \bar{v}\cdot\bar{A}) - \frac{d\bar{A}}{dt}\right]}$$

We know,

$$\bar{F} = \frac{d}{dt}(m\bar{v})$$

$$\Rightarrow \frac{d}{dt}(m\bar{v}) = q\left[-\bar{\nabla}(\phi - \bar{v}\cdot\bar{A}) - \frac{d\bar{A}}{dt}\right]$$

$$\Rightarrow \frac{d}{dt}(m\bar{v} + q\bar{A}) = -q\bar{\nabla}(\phi - \bar{v}\cdot\bar{A}) \quad \text{— (3)}$$

Lagrange's Equation

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}_k}\right) = \frac{\partial L}{\partial x_k} \quad \text{— (4)}$$

Comparing (3) & (4)

$$\frac{\partial L}{\partial \dot{x}_k} = mv_k + qA_k \quad \text{— (5)} \qquad \{\dot{x}_k = v_k\}$$

$$\frac{\partial L}{\partial x_k} = \frac{\partial}{\partial x_k}\left[-q(\phi - v_k A_k)\right] \quad \text{— (6)}$$

But $\frac{\partial L}{\partial \dot{x}_k} = p_k = k^{th}$ component of generalized momentum

$$\Rightarrow p_k = mv_k + qA_k$$

$$\Rightarrow \boxed{\bar{p} = m\bar{v} + q\bar{A}} \Rightarrow \boxed{m\bar{v} = \bar{p} - q\bar{A}}$$

Integrating (5).

$$\int \partial L = m\int v_k\, \partial v_k + qA_k \int \partial v_k$$

$$\Rightarrow L = \frac{1}{2}mv_k^2 + qA_k v_k + C_1 \qquad \{C_1 \neq f(v_k)\}$$

$$\Rightarrow L = \frac{1}{2}m|v|^2 + q(\bar{v}\cdot\bar{A}) + C_1'$$

Integrating (6)

$$L = q(\bar{v}\cdot\bar{A}) - q\phi + C_2 \qquad \{C_2 \neq f(x_k)\}$$

C_1 may be a function of x_k and C_2 may be a function of v_k.

$$\Rightarrow L = \frac{1}{2}m|v|^2 + q(\bar{v}\cdot\bar{A}) - q\phi$$

$$\Rightarrow \boxed{L = \frac{1}{2}mv^2 - q(\phi - \bar{v}\cdot\bar{A})}$$

$$L = T - V \Rightarrow T = \frac{1}{2}mv^2 = KE$$

$$V = q(\phi - \bar{v}\cdot\bar{A}) = PE$$

Hamiltonian

$$H = \sum_k p_k \dot{q}_k - L$$

$$= \sum_k p_k \dot{x}_k - L$$

$$= (m\bar{v} + q\bar{A})\cdot\bar{v} - \left[\frac{1}{2}mv^2 - q(\phi - \bar{v}\cdot\bar{A})\right]$$

$$= mv^2 + \cancel{q(\bar{v}\cdot\bar{A})} - \frac{1}{2}mv^2 + q\phi - \cancel{q(\bar{v}\cdot\bar{A})}$$

$$= \frac{1}{2}mv^2 + q\phi$$

$$= \frac{(m|\bar{v}|)^2}{2m} + q\phi$$

We proved earlier

$$m|\bar{v}| = \bar{P} - q\bar{A}$$

$$\boxed{H = \frac{(\bar{P} - q\bar{A})^2}{2m} + q\phi}$$

Origin of Paramagnetism

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Just as dielectric polarization is established by an electric field, magnetization is produced in a magnetic material by an applied magnetic field.

Magnetism mainly arises from e^- in atoms & molecules.

No classical way to explain magnetism.

Magnetic spin → Quantum mechanical degree of freedom.

How is magnetic moment produced in an e^-?

→ orbital motion ⇒ Current carrying loop in an applied magnetic field.

→ spin

orbital angular momentum (l)
spin angular momentum (s)
total angular momentum (j)

TISE of an e^- in an applied uniform static magnetic field :

$H\psi = E\psi$

$\bar{p} \to \bar{p} - e\bar{A}$ in electromagnetic field.

$\bar{p} = -i\hbar\bar{\nabla}$

$\bar{B} = B_0\hat{z}$

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

$$H\psi = \left\{\frac{(\bar{p}-e\bar{A})^2}{2m} + V\right\}\psi$$

$$= \left\{\frac{(-i\hbar\bar{\nabla}-e\bar{A})^2}{2m} + V\right\}\psi$$

$$= \left\{\frac{-\hbar^2\nabla^2}{2m} + \frac{e^2|A|^2}{2m} + \frac{ie\hbar}{2m}(\overset{0}{\cancel{\bar{\nabla}\cdot\bar{A}}} + \bar{A}\cdot\bar{\nabla}) + V\right\}\psi$$

We choose $\bar{\nabla}\cdot\bar{A} = 0$ Gauge freedom

Symmetric gauge : $\bar{A} = \frac{-1}{2}(\bar{r}\times\bar{B})$

$\bar{r}$: 2D position vector (x_0, y_0)

$$\bar{A} = \frac{-1}{2}(\bar{r}\times\bar{B}) = \frac{-B_0y_0}{2}\hat{x} + \frac{B_0x_0}{2}\hat{y}$$

$$|A|^2 = \frac{B_0^2}{4}(x_0^2+y_0^2)$$

$$\bar{A}\cdot\bar{\nabla} = A_x\frac{\partial}{\partial x} + A_y\frac{\partial}{\partial y}$$

$$= \frac{-B_0y_0}{2}\frac{\partial}{\partial x} + \frac{B_0x_0}{2}\frac{\partial}{\partial y}$$

$$= \frac{B_0}{2}\left(x_0\frac{\partial}{\partial y} - y_0\frac{\partial}{\partial x}\right)$$

We know $\bar{L} = \bar{r}\times\bar{p}$

$\bar{L}$ → angular momentum, $\bar{r}$ → position vector, $\bar{p}$ → linear momentum.

$$L_z = \left(x_0\frac{\partial}{\partial y} - y_0\frac{\partial}{\partial x}\right)(-i\hbar)$$

$$H\psi = \left\{\underbrace{\frac{-\hbar^2\nabla^2}{2m}}_{KE} + \underbrace{\frac{e^2}{2m}\cdot\frac{B_0^2}{4}(x_0^2+y_0^2) - \frac{e}{2m}\cdot\frac{B_0}{2}L_z + V}_{PE}\right\}\psi$$

$\mu = \frac{-\partial H}{\partial B}$ change in energy of the system wrt applied magnetic field.

magnetic moment opposes applied $\bar{B}$ {Lenz's law}

$$\mu_1 = -\frac{e^2}{4m}B_0(x_0^2+y_0^2) \quad \text{Diamagnetic.}$$

$$\mu_2 = \frac{e}{4m}L_z \quad \text{Paramagnetic.}$$

μ_1 → antiparallel to $\bar{B}$

μ_1 → universal, exists in all materials in p^nce of $\bar{B}$

μ_2 → parallel to $\bar{B}$

μ_2 → exists only in materials with non-zero L_z, ie. unpaired e^-.

$\mu \propto \frac{1}{M}$ ⇒ μ of protons & neutrons is negligible.

Spatial Quantization and Brillouin Function

All orientations, $\theta = 0 \to \pi$ are not allowed
Only certain quantised orientations are

$S = 1/2$

$m = \pm \frac{1}{2} \Rightarrow \uparrow$ or $\downarrow$

$m_S \to 2S+1$ possible orientations
$\downarrow$
$-S$ to $+S$

net average magnetic moment

$$\langle \mu \rangle = \frac{\sum_{M_J=-J}^{+J} g_J \mu_B M_J \, e^{\left(\frac{g_J \mu_B B M_J}{k_B T}\right)}}{\sum_{-J}^{+J} e^{\left(\frac{g_J \mu_B M_J B}{k_B T}\right)}}$$

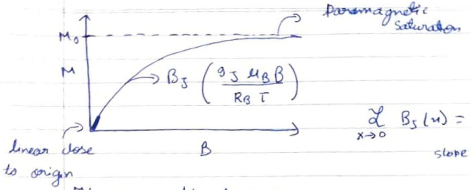
let $x = \dfrac{g_J \mu_B B}{k_B T}$

$$\langle \mu \rangle = g_J \mu_B \underbrace{B_J(x)}_{\text{Brillouin function}} . J$$

$$B_J(x) = \left(\frac{2J+1}{2J}\right) \coth\left[\left(\frac{2J+1}{2J}\right) x\right] - \frac{1}{2J} \coth\left[\frac{x}{2J}\right]$$

$$M = N\langle \mu \rangle = M_0 B_J(x)$$

M_0: Saturation value
when all the N spins are $\parallel^{el}$ to applied magnetic field



$$\lim_{x \to 0} B_J(x) = \left(\frac{J+1}{3}\right) x$$

slope

The curve depends on x, specifically on B & T.

$$\chi_m = N \frac{g_J^2 J(J+1) \mu_B^2}{3 k_B T} \leftarrow \text{in the linear region}$$

$$= \frac{N \mu_{eff}^2}{3 k_B T} = 0.1241 \, p_{eff}^2$$

p_{eff}: effective Bohr magneton number

paramagnetic susceptibility $\propto \frac{1}{T}$

$$\mu_{eff}^2 = g_J^2 J(J+1) \mu_B^2$$

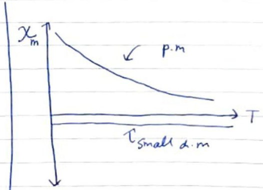
$$\mu_{eff} = g_J \sqrt{J(J+1)} \mu_B$$

$$\lim_{x \to \infty} B_J(x) = 1$$

$$M = M_0$$

$$\chi = \frac{C}{T}$$

C: curie const.



Sources

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