of $\bar{e}$
must be continuous

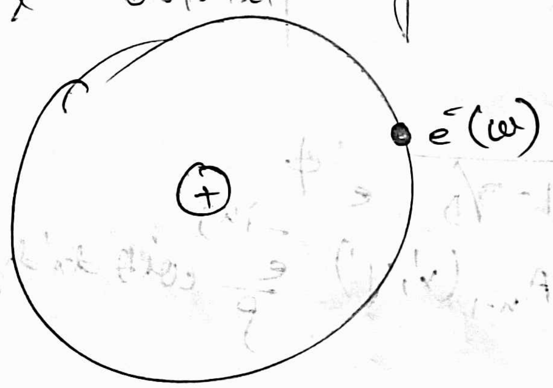
16/1/25 [Mag & CC]

Orbital & spin L momentum.

orbital motion of $\bar{e}$ around the nucleus is known as orbital L momentum.

$l \to$ orbital L momentum quantum no.

$m_l \to$ orbital magnetic moment quantum no.



$\hbar L = \vec{r} \times \vec{p}$

$= -i\hbar(\vec{r} \times \nabla)$.

$\hbar L_z = i\hbar\left[\hat{i}\frac{\partial}{\partial x} - \hat{j}\frac{\partial}{\partial y}\right]$.

$= -i\hbar \frac{\partial}{\partial \phi}$.

$\hbar L_z|\psi\rangle = -i\hbar \frac{\partial}{\partial \phi} \hbar e^{im_l\phi} = m_l \hbar e^{im_l\phi}$

$\hbar L^2|l, m_l\rangle = \hbar^2 l(l+1)|l, m_l\rangle$

$= \left\{\hbar\sqrt{l(l+1)}\right\}^2 |l, m_l\rangle$.

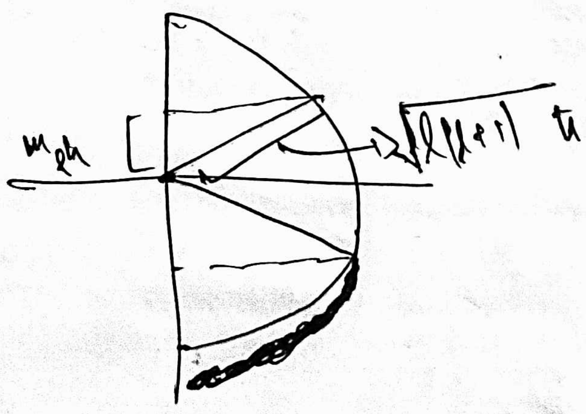
$\hbar L_z|l, m_l\rangle = m_l \hbar|l, m_l\rangle$

$\boxed{\text{P}}$

$L_\pm = L_x \pm iL_y$.

$L_\pm|l, m_l\rangle$

$= \sqrt{l(l+1) - m_l(m_l \pm 1)}\,|l, m_l \pm 1\rangle$



$\vec{\mu} = \gamma \vec{L}$ $\qquad$ $\vec{\mu}$ & $\vec{L}$ should be ∥.

$(\mu_L)_z = \gamma L_z$: (projection along z (direc^n of $\vec{B}$)).

$= \gamma m_l \hbar$.

$= \left(\frac{e}{2m}\hbar\right) m_l$

$= m_l$ (Bohr magneton) $\boxed{m_l \mu_B}$

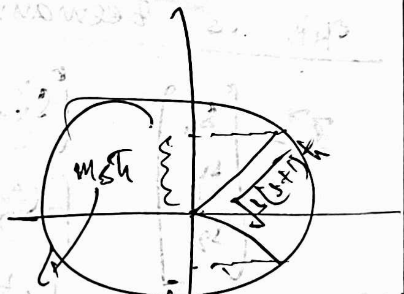
Total μ_z^L (mag dipole moment):

$\vec{\mu}_L = \gamma \sqrt{l(l+1)}\,\hbar$

$= \left(\frac{e\hbar}{2m}\right)\sqrt{l(l+1)} = \sqrt{l(l+1)}\,\mu_B$

Spin L momentum.

Intrinsic L momentum is called SPIN.



For spin 1/2 (e^-)

$+\hbar/2$, $-\hbar/2$

$s^2|s, m_s\rangle = \hbar^2 s(s+1)|s, m_s\rangle$

$s_z|s, m_s\rangle = m_s\hbar|s, m_s\rangle$

component of $\vec{s}$ along field axis.

Magnitude of total $\mu_s = \hbar\sqrt{s(s+1)}$.

$(\mu_s)_z = \gamma g m_s \hbar$.

$= \left(\frac{e\hbar g}{2m}\right) m_s = -g\mu_B m_s$ $\quad$ landé g factor.

$g = 2\left(1 + \frac{\alpha}{2\pi} + \dots\right)$

α [fine struct const] $= \frac{e^2}{4\pi\epsilon_0 \hbar c}$

$\boxed{g = 2.0023}$

Zeemann Splitting

$(\mu_s)_z = -g\mu_B m_s$

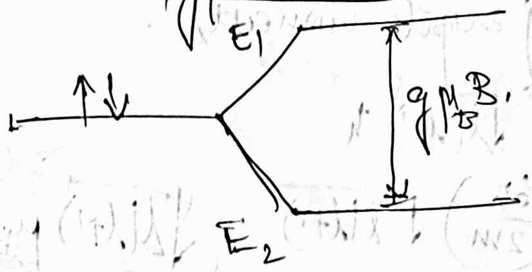
$\vec{B}$ along z : Energy $= -(\mu_s \cdot B)$

$= -(\mu_s)_z \cdot B$

$= \boxed{g\mu_B m_s \cdot B}$

$E_1 = \frac{g\mu_B B}{2}$

$E_2 = -\frac{g\mu_B B}{2}$



This is Zeemann splitting.

$\vec{S} = \begin{bmatrix} S_x \\ S_y \\ S_z \end{bmatrix}$

$[\vec{S_x}, \vec{S_y}] = i\vec{S_y}$

$[S^2, S_z] = 0$

$[S^2, S_\pm] = 0$

$[S_+, S_-] = 2S_z$

$[S_z, S_\pm] = \pm S_\pm$

$\hat{S}_x = \hbar/2\, \hat{\sigma}_x$

$\hat{S}_i = \hbar/2\, \sigma_i$

$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$ $\sigma_z \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$

$\sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$

An Atom in a magnetic field.

[magnetization & susceptibility]

$$\hat{H}_0 = \sum_{i=1}^{Z} \left(\frac{p_i^2}{2m_e} + V_i \right)$$

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

canonical

let's assume that the interac^n b/w ions or b/w moment & their env are completely ignored.

electron momentum ⟷ canonical momentum

$\tilde{p}_i = p_i + e\vec{A}(r)$. | $T_0 = \frac{p_i^2}{2m_e}$

λ for unperturbed, $KE = \frac{\tilde{p}_i^2}{2m_e} = \frac{(p_i + eA)^2}{2m_e}$

In the presence of magnetic field.

$$\hat{H} = \sum_{i}^{2} \left\{ \frac{[p_i + eA(r)]^2}{2} + V_i \right\} = H_0 + \Delta H_{perturbed}.$$

$\hat{p} = -i\hbar\nabla = -i\hbar\left(\frac{\partial}{\partial x}\hat{i} + \frac{\partial}{\partial y}\hat{j} + \frac{\partial}{\partial z}\hat{k}\right)$.

$-i\hbar\nabla A f = -i\hbar(\nabla\cdot A)f - i\hbar A\cdot\nabla f = \boxed{-i\hbar A\cdot\nabla\cdot f}$.

$\nabla\cdot A \to 0$

$(p_i + eA)^2 = p_i^2 + e^2A^2 + (p_i\cdot A)e + (A\cdot p_i)e$.

$= p_i^2 + e^2A^2 + 2(A\cdot p_i)e \xrightarrow{\text{PTO}}$

CHOOSE a gauge such that. $A(r) = \overrightarrow{\frac{B\times r}{2}}$

$\vec{A} = A_x\hat{i} + A_y\hat{j} + A_z\hat{k}$.

let B be along $\hat{k}$.

$$A = \frac{1}{2}\begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ 0 & 0 & B \\ x & y & z \end{vmatrix} = \frac{B}{2}\left[x\hat{j} - y\hat{i}\right].$$

$$B = \nabla\times A = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ \partial/\partial x & \partial/\partial y & \partial/\partial z \\ -\frac{By}{2} & \frac{Bx}{2} & 0 \end{vmatrix}$$

$A_x = -\frac{By}{2}$.

$A_y = +\frac{Bx}{2}$.

$A \leftrightarrow \overrightarrow{\frac{B\times r}{2}}$.

(gauge invariant choice)

gauge choice,

$B_x = \left(\frac{\partial}{\partial z}\frac{Bx}{2}\right) = 0$.

proof

$B_y = \frac{\partial}{\partial z}\frac{By}{2} = 0$.

$B_z = \frac{\partial}{\partial x}\frac{Bx}{2} + \frac{\partial}{\partial y}\frac{By}{2} = B \to$ for $A = \frac{B\times r}{2}$

$\vec{A}\cdot\vec{p}$ (for our gauge)

$= i\hbar\left(A_x \frac{\partial}{\partial x}\hat{i} + A_y \frac{\partial}{\partial y}\hat{j} + A_z \frac{\partial}{\partial z}\hat{k}\right)$,

$= i\hbar\left(-\frac{B}{2}\left\{y\frac{\partial}{\partial x}\hat{i} - x\frac{\partial}{\partial y}\hat{j}\right\}\right)$,

$= \left(-\hbar\right)\left(\frac{B}{2}\right)\left[y\frac{\partial}{\partial x}\hat{i} + x\frac{\partial}{\partial y}\hat{j}\right]$

$\to L_z$,

$= \frac{B}{2}L_z$,

$\hat{\mathcal{H}} = \mathcal{H}_0 + \sum_1^Z \frac{e^2A^2}{2m_e} + \frac{e}{m_e}\frac{\hbar}{2}\,\vec{L\cdot B}$,

$\hat{\mathcal{H}} = \mathcal{H}_0 + \left(\frac{e\hbar}{2m_e}\right)\vec{L}\cdot\vec{B} + \frac{e^2}{8m_e}\sum_i (B\times r_i)^2$.

$= \mathcal{H}_0 + \frac{e\hbar}{2m_e}(\vec{L}\cdot\vec{B}) + \frac{e^2B^2}{8m_e}\sum_i^Z (x_i^2+y_i^2)$.

If spin is considered,

$\mathcal{H} = \mathcal{H}_0 + \underbrace{\frac{e\hbar}{2m_e}}_{\mu_B}(L+gS)\vec{B} + \boxed{\frac{e^2B^2}{8m_e}\sum_1^Z (x_i^2+y_i^2)}$.

This is the effect of atoms own magnetic moment.

motion.

paramagnetic term.

Diamagnetic term.

The energy shift produced by the above eqn is quite small

$E_n = E_n + \Delta E_n.$

$$\Delta E_n = \langle n | \Delta H_B | n \rangle + \sum_{n'} \frac{|\langle n | \Delta H_B | n' \rangle|^2}{E_n - E_{n'}}$$

$\rightarrow$ PM

$$= \mu_B B \langle n | L + gS | n \rangle \text{ --- --- } \rightarrow \text{PM}$$

$$+ \frac{e^2 B^2}{8 m_e} \langle n | \sum_i (x_i^2 + y_i^2) | n \rangle \text{ --- --- } \rightarrow \text{DM.}$$

$$+ \mu_B^2 B^2 \frac{|\langle n | (L + gS) | n' \rangle|^2}{E_n - E_{n'}}.$$

1st (Largest contribution) 2nd

$$= \mu_B B \langle n | L + g s | n \rangle + \frac{e^2 B^2}{8 m_e} \langle n | \sum_{i=1}^{Z} (x_i^2 + y_i^2) | n \rangle$$

(PM) (DM)

3rd (higher order term)

$$+ \frac{|\langle n | \mu_B B (L + g s) | n' \rangle|^2}{E_n - E_{n'}}$$

Van-Vleck Term

Date: 17/01/2025

$$\Delta E_n = \mu_B B \cdot \langle n | L + g s | n \rangle + \frac{e^2 B^2}{8 m_e} \langle n | \sum_{i=1}^{Z} (x_i^2 + y_i^2) | n \rangle$$

PM

$$+ \frac{|\langle n | \mu_B B (L + g s) | n' \rangle|^2}{E_n - E_{n'}}$$

Dominating Term, linear in B, is going to be much larger than the other 2 terms

$$\mu_B B \langle n | L + g s | n \rangle \approx O(\mu_B B)$$

$$\mu_B = \frac{e\hbar}{2 m_e} \qquad \sim \frac{\hbar e B}{2 m_e} \sim \hbar \omega_c$$

10^{-4} eV when B = 1 tesla

This energy shift is very small

Diamagnetic Term →

$$\frac{e^2B^2}{8me}\langle n|\sum_i (x_i^2+y_i^2)|n\rangle$$

$$\sim \frac{\cancel{e^2B^2}}{\cancel{8me}}\left(\frac{eB}{me}\right)^2 \cdot me^2 \cdot a_0^2$$

$\because a_0$ = atomic radius

$= 5\mathring{A}$

This term is smaller than the linear in B term, by a factor of 10^{-5} (smaller than the linear term) even for B = 1 tesla.

☆ Inert gas
{ He → $\sum l_i = l = 0$
Ne $\sum s_i = S = 0$
Ar
⋮ }

Diamagnetic contribution (only contribution)

☆ Van-Vleck Term

↓

Also very small (com

$$\frac{\hbar\omega_c}{\Delta}$$

$n \neq n'$

☆

Na^+ → no unfilled shell → Fully filled shell

• Pure diamagnetic Term —

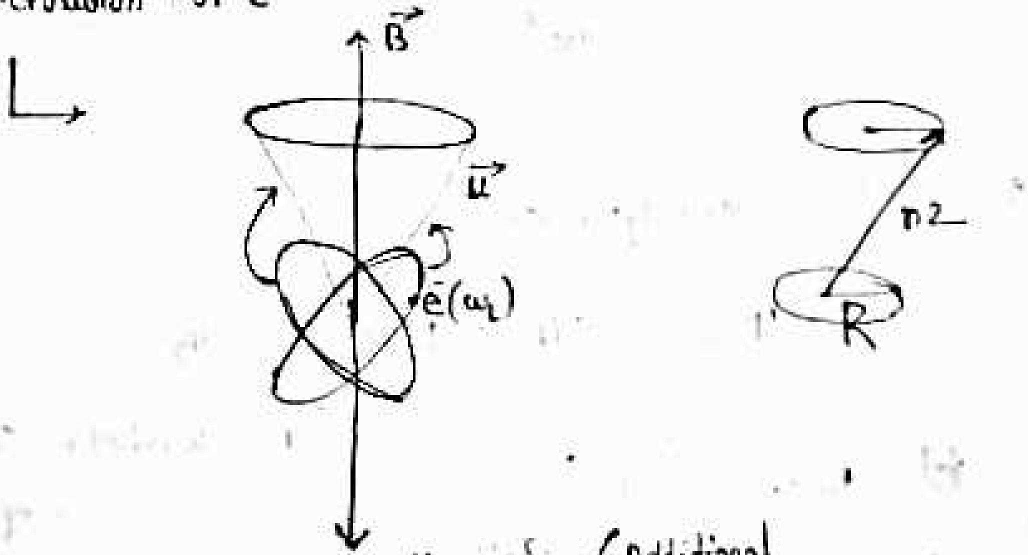
☆ PM = 0. Only Diamagnetic term —

First order shift in the ground state energy due to diamagnetic term —

$$\Delta E_0 = \frac{e^2 B^2}{8mc} \sum_{i=1}^{z} \langle 0 | x_i^2 + y_i^2 | 0 \rangle \quad \text{--- (1)}$$

where, $|0\rangle \rightarrow$ ground state wave function.

☆ electronic orbit
↳ revolution of e^-



μ precision (Additional motion in opposite direction)

origin of diamagnetism ← Lentz's law

$$\mu_{precision} = \text{Diamagnetic moment} = -\frac{e\omega_L \langle R^2 \rangle}{2}$$

$\chi = -ve$

If we assume spherically symmetric atom —

$$\langle x_i^2 \rangle = \langle y_i^2 \rangle = \langle z_i^2 \rangle = \frac{1}{3} \langle r_i^2 \rangle$$

$$x_i^2 + y_i^2 + z_i^2 = r_i^2 .$$

$$\therefore \langle 0 | x_i^2 | 0 \rangle + \langle 0 | y_i^2 | 0 \rangle = \langle 0 | r_i^2 | 0 \rangle$$

$\therefore$ from eq^n 1 $\longrightarrow$

$$\Delta E_0 = \frac{e^2 B^2}{8me^2} \sum_{i=1}^{z} \frac{2}{3} \langle 0 | r_i^2 | 0 \rangle$$

From the Thermodynamics —

$$dF = - SdT - PdV - MdB$$

F = Helmholtz free energy

$$M = -\left(\frac{\partial F}{\partial B}\right)_{T,V}$$

Diamagnetic magnetization

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,B}$$

$$\chi = M/H$$

$$\frac{\partial M}{\partial H} = - \mu_0 \frac{\partial^2 F}{\partial B^2}$$

- Consider a solid composed of N ions each with χ electron of mass m_e) in volume V with all shell filled —

$$M = -\frac{\partial F}{\partial B} = -\frac{N}{V} \cdot \frac{\partial}{\partial B}(\Delta E_0)$$

$$= -\frac{N}{V} \cdot \frac{e^2 B}{6m_e} \sum_{i=1}^{\chi} \langle r_i^2 \rangle$$

at ground state

$$\chi_{dia} = M/H = \mu_0 M/B \qquad \left[\begin{array}{l} \text{as } B = \mu_0 H \\ H = B/\mu_0 \end{array}\right]$$

$$= -\frac{\mu_0 N}{V} \cdot \frac{e^2}{6m_e} \cdot \sum_{i=1}^{\chi} \langle r_i^2 \rangle$$

In S.I. → unitless

In C.G.S $\quad \chi_{dia} = -\dfrac{N e^2}{c^2 6m_e V} \displaystyle\sum_{i=1}^{\chi} \langle r_i^2 \rangle$

- $\chi_{dia} = -ve$ in sign
  - → Temp independent
  - → Property of All matter

$\chi_{dia} \propto \langle r_i^2 \rangle$

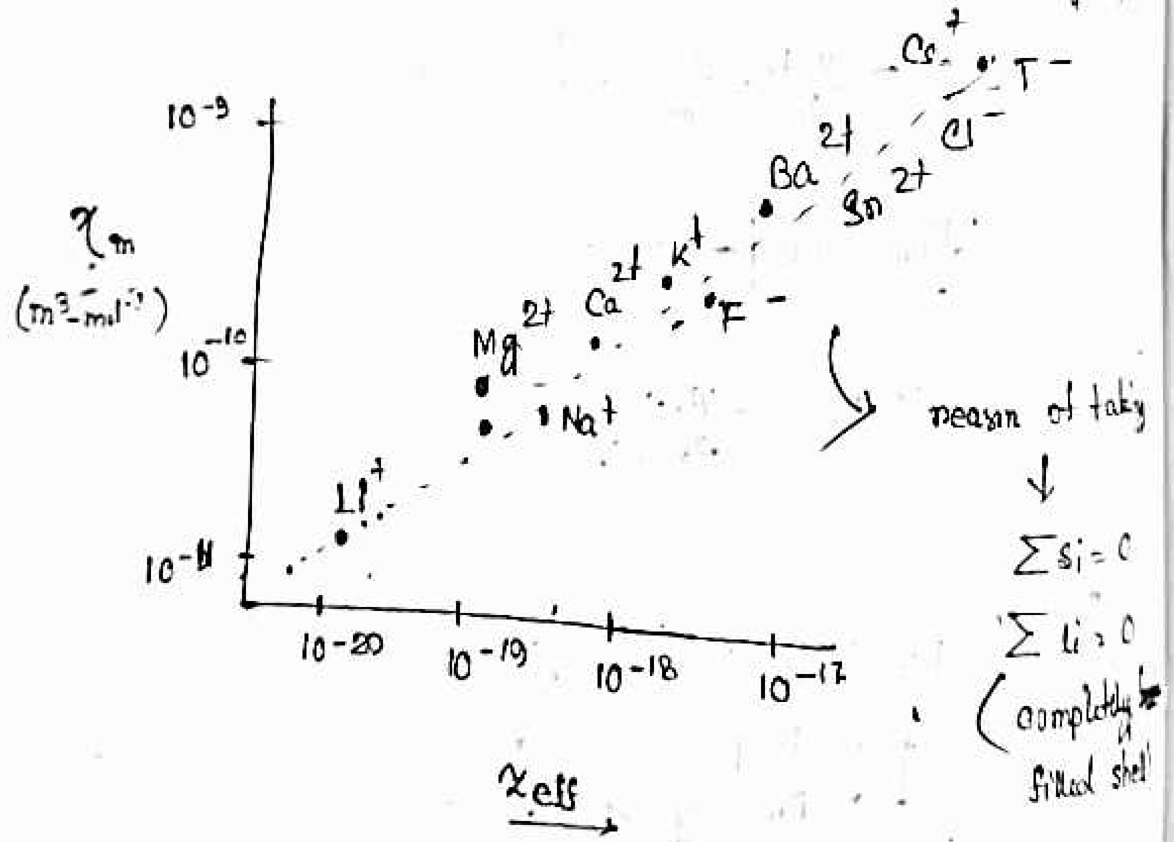
$\langle r_i^2 \rangle$ → mean square of electron distance from nucleus

If Z_{eff} = no. of electron in the outer shell of an ~~atom~~ ion and r = measured ionic radius,

All the electron in the outer shell of the ion have roughly, same value of $\langle r_i^2 \rangle$

$$\sum_{i=1}^{Z_{eff}} \langle r_i^2 \rangle \sim Z_{eff}\, r^2$$

$\therefore \quad \chi_{dia} \propto Z_{eff} \times r^2$) Diamagnetic)



Larmour Diamagnetic Calculation.

- Not all electrons in an atom ion have same $\langle r^2 \rangle$ but the agreement is quite impressive.

Measured diamagnetic susceptibility ——

$$\chi_m \propto z_{eff} \cdot r^2 \quad \left[\text{plot shows linearity}\right]$$

For Ne,

$$z = 10 \quad , \quad k = 2 \quad L = 8$$

$$\langle r_i^2 \rangle \approx (10^{-8})^2 \ cm^2 = 10^{-16} \ cm^2$$

$$N = 5 \times 10^{22} \ cm^{-3}$$

$$\chi = 10^{-6} \qquad J|0\rangle = L|0\rangle = S|0\rangle = 0$$

- Larmour Diamagnets

  Solid composed of atoms with all electron shell filled.

Negative Ions

Elements	Susceptibility (molar susceptibility)
F^-	-9.4×10^{-6} cm^3/mol
Cl^-	-24.2×10^{-6}
Br^-	-34.5×10^{-6}
I^-	-50.6×10^{-6}

Positive Ions	Li^+	-6.7×10^{-6}	cm^3/mol
	Na^+	-6.1×10^{-6}	
	K^+	-14.6×10^{-6}	
	Rb^+	-22.0×10^{-6}	
	Co^{2+}	-35.1×10^{-6}	

Inert gas	He	-1.9×10^{-6}	radius
	Ne	-7.2×10^{-6}	
	Ar	-19.4×10^{-6}	
	Kr	-28.0×10^{-6}	
	Xe	-43.0×10^{-6}	

- density: 2220 kg/m3

$\sqrt{(n^2)}\ m$