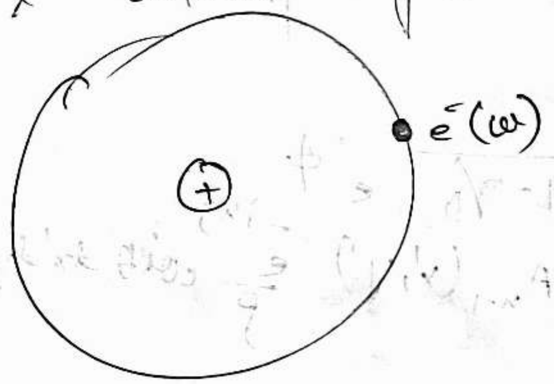
of $\bar{e}$
must be continuous

16/1/25 | Mag & LC |

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.



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

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

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

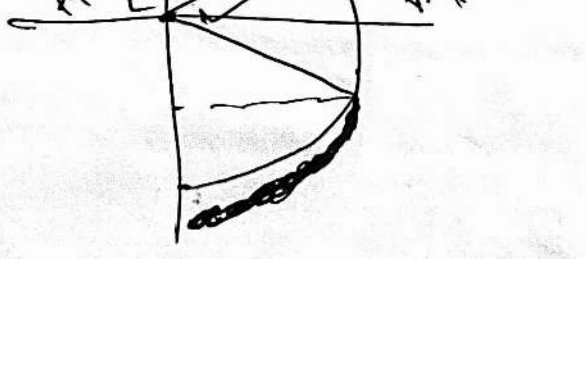
$\hbar L^2 |l, m_l\rangle = \hbar^2 l(l+1) |l, m_l\rangle$
$= \left\{ \hbar \sqrt{l(l+1)} \right\}^2 |l, m_l\rangle$.

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

P1

$L_\pm = L_x \pm i L_y$.

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



$\vec{\mu} = \gamma \vec{L}$ $\quad\quad \vec{\mu}$ & $\vec{L}$ should be $\parallel$.

$(\mu_L)_z = \gamma L_z$ (projection along z (direcⁿ of $\vec{B}$)).

$= \gamma m_\ell \hbar$

$= \left(\frac{-e}{2m}\hbar\right) m_\ell$

$= m_\ell$ (Bohr magneton) $\boxed{m_\ell \mu_B}$

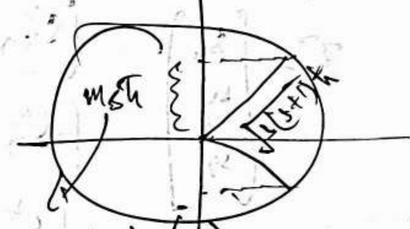
Total μ_z^L (mag dipole moment):

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

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

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

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

landé g factor.

$= \left(\frac{e\hbar g}{2m}\right) m_s = -g\,\mu_B m_s$

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

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

$\boxed{g = 2.0023}$

Zeemann Splitting.

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

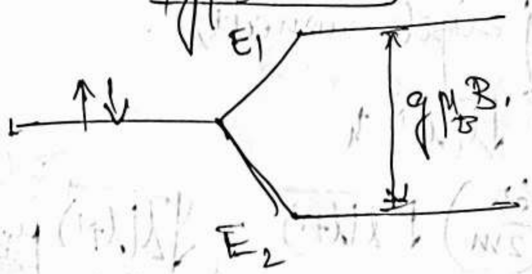
$\vec{B}$ along z | Energy $= -(\mu_s \cdot B)$.

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

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

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

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



This is Zeemann splitting.

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

$[\vec{S}_x, \vec{S}_y] = i S_y$

$[S^2, S_z] = 0$

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

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

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

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

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

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

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

An Atom in a magnetic field.

[magnetization & susceptibility].

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

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

canonical

Let's assume that the interac^n b/w ions or b/w moment of their e^- are completely ignored.

electron momentum $\longleftrightarrow$ Canonical momentum

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

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

In the presence of magnetic field.

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

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

$$-i\hbar \nabla A f = -i\hbar \underbrace{(\nabla\cdot A)}_{0} f - i\hbar A\cdot\nabla f = \boxed{-i\hbar\, A\cdot\nabla f}.$$

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

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

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

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

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

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

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

$A_x = -\frac{By}{2}$, $A_y = +\frac{Bx}{2}$.

$A \leftrightarrow \frac{\vec{B\times r}}{2}$. (gauge invariant choice)

gauge choice, proof

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

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

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

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

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

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

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

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

$$\hat{H} = H_0 + \sum_i \frac{e^2A^2}{2m_e} + \frac{e}{m_e}\frac{\hbar}{2}\vec{L}\cdot\vec{B}$$

$$\hat{H} = H_0 + \left(\frac{e\hbar}{2m_e}\right)\vec{L}\cdot\vec{B} + \frac{e^2}{8m_e}\sum_i (B\times r_i)^2$$

$$= H_0 + \frac{e\hbar}{2m_e}\left(\vec{L}\cdot\vec{B}\right) + \frac{e^2B^2}{8m_e}\sum_i^z (x_i^2+y_i^2)$$

If spin is considered

$$H = H_0 + \frac{e\hbar}{2m_e}^{\mu_B}(L+gs)\vec{B} + \boxed{\frac{e^2B^2}{8m_e}\sum_i^z (x_i^2+y_i^2)}$$

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

$E_n = E_n + \Delta E_n$.

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

PM

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

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

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

1st (Largest contribution) 2nd

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

3rd (higher order term)

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

Van-Vleck Term

Date: 17/01/2025

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

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

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 →

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

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

$\because a_o$ = 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 $\quad \sum s_i = S = 0$
- 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 →

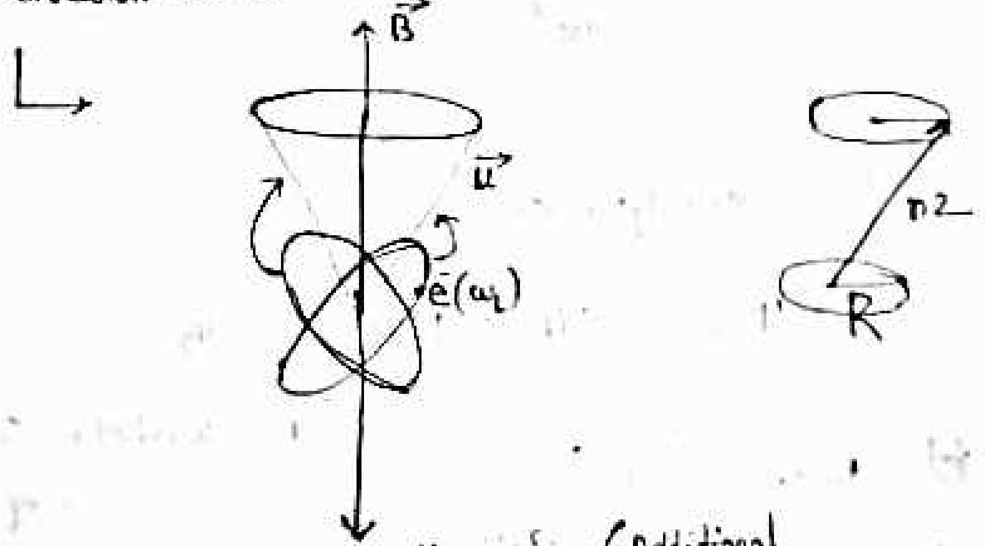
First order shift in the ground state energy due to diamagnetic term —

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

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

☆ electronic orbit

revolution of e^-



μ precision (Additional motion in opposite direction)

↓

origin of diamagnetism ← Lenz's law

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

$$\chi = -ve$$

If we assume spherically symmetric atom —

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

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

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

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

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

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 Z electron of mass m_e) in volume V with all shell filled —

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

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

at ground state

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

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

$\boxed{\text{In S.I.}} \longrightarrow$ unitless

$\boxed{\text{In C.G.S}}$ $\chi_{dia} = -\frac{N e^2}{c^2 6 m_e V} \sum_{i=1}^{Z} \langle r_i^2 \rangle$

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

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

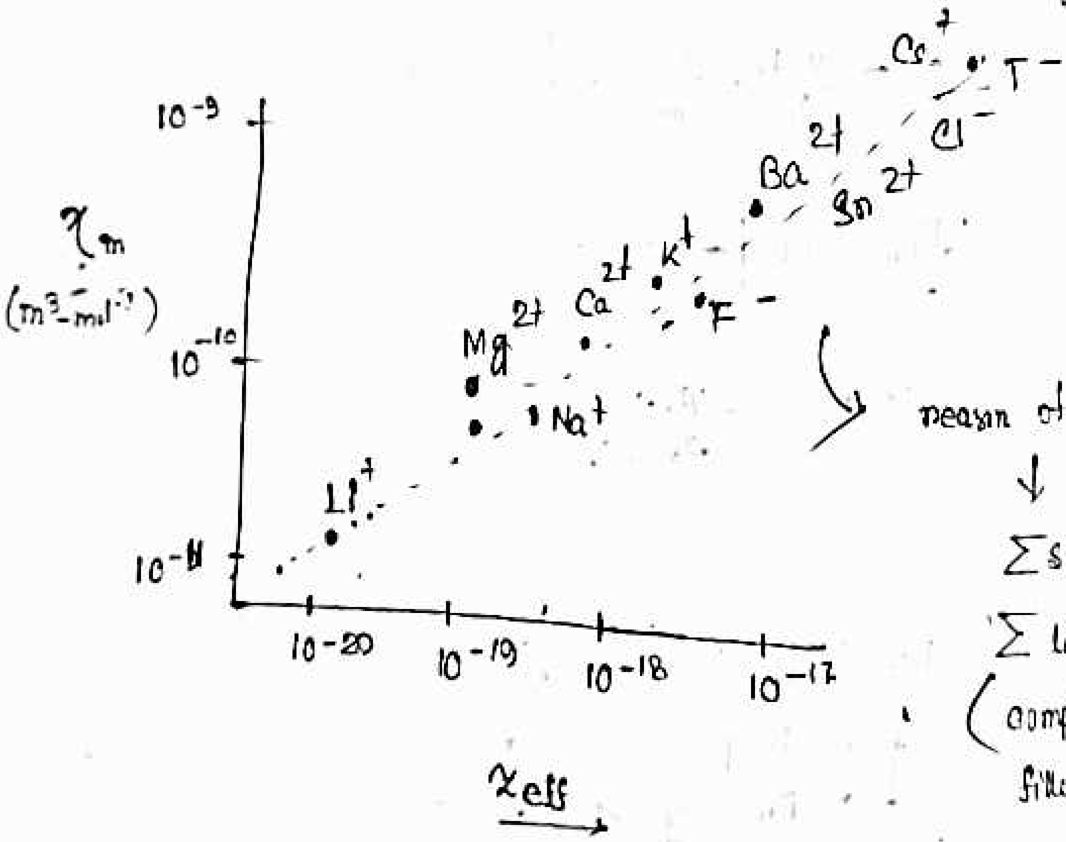
$\langle r_i^2 \rangle \longrightarrow$ mean square of electron distance from nucleus

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)



reason of taking

↓

$\sum s_i = 0$

$\sum l_i = 0$

(completely filled shell)

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,

$$Z = 10 \quad , \quad K = 2 \quad L = 8$$

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

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

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

- Larmour Diamagnets

  Solid composed of atoms with all electron shell filled.

Negative Ions

Elements	Susceptibility (molar susceptibility)
F^-	-9.4×10^{-6} cm³/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}
	Cs^{2+}	-35.1×10^{-6}

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

radius

- density: 2220 kg/m3

$\sqrt{\overline{(r^2)}}\ m$