LECTURE #6

Note Title 9/15/2008

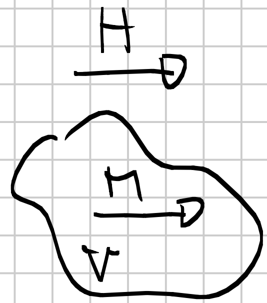
HUND'S RULES : GIVEN # e IN ATOM (ION)

WE CAN FIND $\vec{S}, \vec{L}, \vec{J}$ FOR THE GROUND STATE

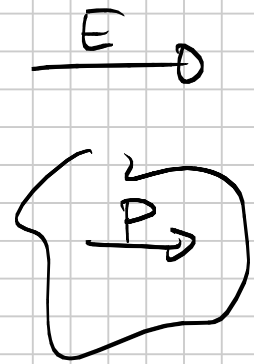
COMPLETE SHELLS HAVE $\vec{S} = \vec{L} = \vec{J} = 0$

$\vec{S}, \vec{L}, \vec{J}$ DETERMINE MAGNETIC PROPERTIES ATOM / ION / SOLIDS

KEY QUANTITY $\vec{M}$



SIMILAR

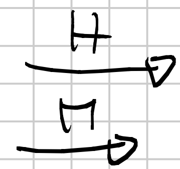


H GENERATES
"CURRENTS" IN THE SYSTEM

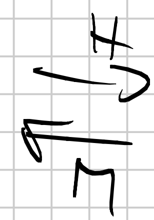
$$\vec{M} = \chi \vec{H}$$

χ ↓ MAGNETIC SUSCEPTIBILITY

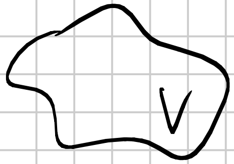
$\chi > 0$ PARAMAGNETIC



$\chi < 0$ DIAMAGNETIC



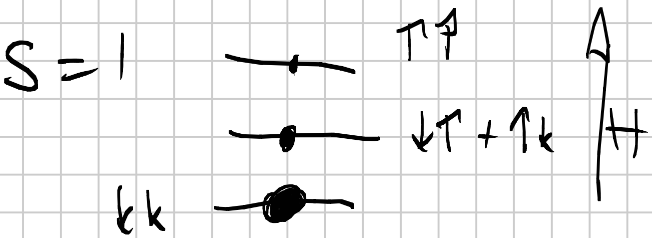
$T=0$



H WILL CHANGE TOTAL ENERY E_0 BY $-\int_V \vec{M}\cdot\vec{H}\,dV$

$$\boxed{M = -\frac{1}{V}\frac{\partial E_0}{\partial H}}$$

$$\chi = -\frac{1}{V}\frac{\partial^2 E_0}{\partial H^2}$$



USE FREE-ENERGY

$$Z = e^{-\beta F} = \sum_m e^{-\beta E_m}$$

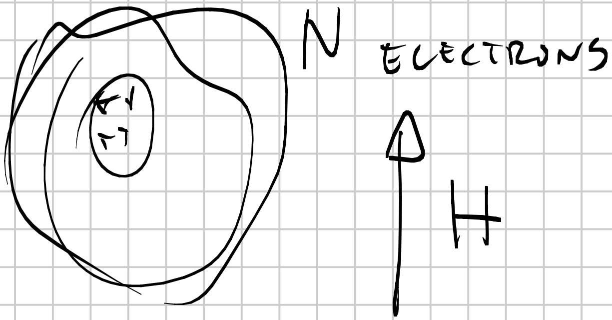
$$\beta = \frac{1}{k_B T}$$

$$M = -\frac{1}{V}\frac{\partial F}{\partial H} = \frac{\sum_m M_m e^{-\beta E_m}}{Z}$$

WHERE

$$M_m(H) = -\frac{1}{V}\frac{\partial E_m}{\partial H}$$

HOW DO WE FIND $E_m(H)$?



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

$$\vec{A} = -\frac{1}{2}\vec{r} \times \vec{H} = -\frac{1}{2}\begin{vmatrix} i & j & k \\ x & y & z \\ 0 & 0 & H \end{vmatrix} = -\frac{1}{2}\left(yH, -xH, 0\right)$$

$$\vec{\nabla} \cdot \vec{A} = 0$$

HAMILTONIAN

① T_0 (KINETIC ENERGY)

$$\downarrow$$

$$\sum_{m=1}^{N} \frac{p_i^2}{2m} \xrightarrow{\text{ADD } H}$$

$$\vec{p} \to \left(\vec{P} - \frac{e}{c}\vec{A}\right)$$

$$\sum_i \frac{\left(p_i - \frac{e}{c}\vec{A}(x_i)\right)^2}{2m}$$

ORBITAL CONTRIBUTION

② SPIN PART

$$\mathcal{H}_{SPIN} = g \mu_B \vec{S} \cdot \vec{H} \qquad \mu_B = \frac{e\hbar}{2mc} \qquad g = 2$$

GIROMAGNETIC FACTOR

(RELATIVISTIC EFFECT)

EXPAND $\left(p - \frac{e}{c} A\right)^2 \qquad \vec{p} = -i\hbar\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$

$$L_z = -i\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \qquad \vec{L} = -i\,\vec{r} \times \vec{p}$$

QUADRATIC IN H

$$\mathcal{H}_{TOT} = \mathcal{H}_0 + \underbrace{\mu_B(\vec{L} + g\vec{S}) \cdot \vec{H}}_{\text{LINEAR IN } H \ ①} + \underbrace{\frac{m}{2} \omega_0^2 \sum_i \left[\left(\frac{x_i}{2}\right)^2 + \left(\frac{y_i}{2}\right)^2\right]}_{②}$$

$$\omega_0 = \left(\frac{eH}{mc}\right)$$

CYCLOTRON FREQUENCY

CASE #1 $L=0$ AND $S=0$ COMPLETE SHELLS

$$\langle G | \mathcal{H} | G \rangle = E_0(H=0) + \Delta E_1 + \Delta E_2$$

$$\Delta E_1 = \langle G, L=0, S=0 | \mu_B (L_z + g S_z) | G, L=0, S=0 \rangle = 0$$

$$\Delta E_2 = \langle G | \alpha \sum_{i=1}^{N} (x_i^2 + y_i^2) | G \rangle \neq 0$$

$\frac{1}{2} m \omega_0^2 x^2 \rightarrow$ HARMONIC POTENTIAL

ΔE_2 POSITIVE ENERGY INCREASE

$$M = -\frac{N}{V} \frac{\partial \Delta E_2}{\partial H} < 0$$

$$\chi = -\frac{N}{V}\frac{\partial^2 E}{\partial H^2} \quad \text{IS} < 0 \quad \Rightarrow \quad \text{DIAMAGNETIC SYSTEM}$$

$\xrightarrow{H}$

$\xleftarrow{M}$

LARMOR DIAMAGNETISM

EXAMPLE : NaCl WEAK MAGNETIC PROPERTIES

Na $[Ne](3s)^1$ Cl $[Ne](3s)^2(3p)^5$

Na^+ Cl^-

$[Ne]$ $[Ar]$

$L=0, S=0$ $L=0, S=0$

CASE #2 PARTIALLY-FILLED SHELLS $L \neq 0 / S \neq 0$

MnO

Mn

$[Ar](3d)^5(4s)^2$

O

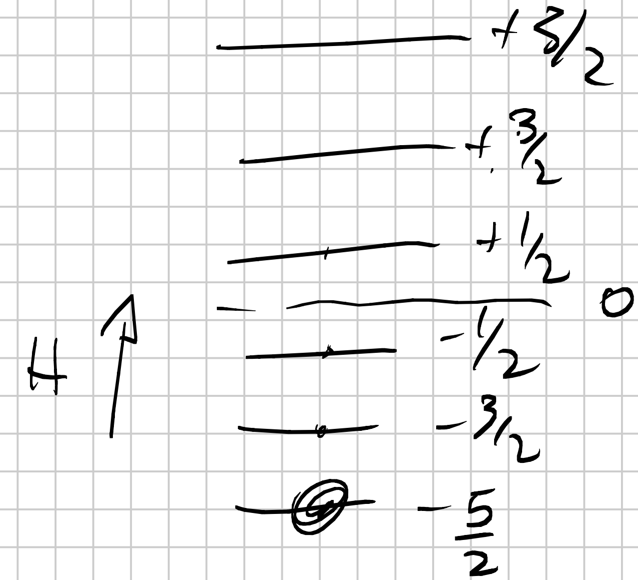
$[He](2s)^2(2p)^4$

Mn^{2+} WITH 5 e IN 3d ORBITALS

O^{2-} [Ar]

-2	-1	0	1	2
↑	↑	↑	↑	↑

$S = \frac{5}{2}$ $L = 0$



$$\Delta E_1 = \mu_B H \langle S=\tfrac{5}{2}, L=0 \,|\, g S_z \,|\, S=\tfrac{5}{2}, L=0 \rangle$$

$$\Delta E_1 = -\frac{5}{2} g \mu_B H \Rightarrow M = -\frac{1}{V}\frac{\partial \Delta E_1}{\partial H} = \frac{1}{V}\frac{5}{2} g \mu_B \cdot \#\,\text{Mn IONS}$$

$\vec{M}$

$\vec{H}$

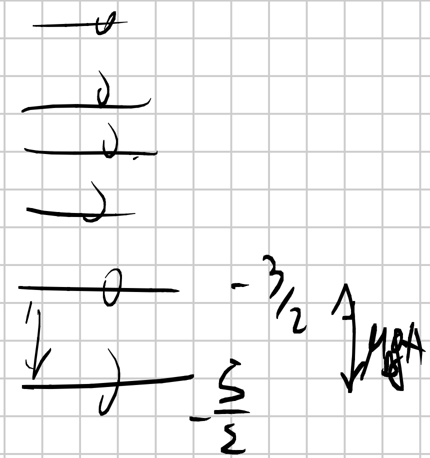
PARAMAGNETISM

$\chi > 0$

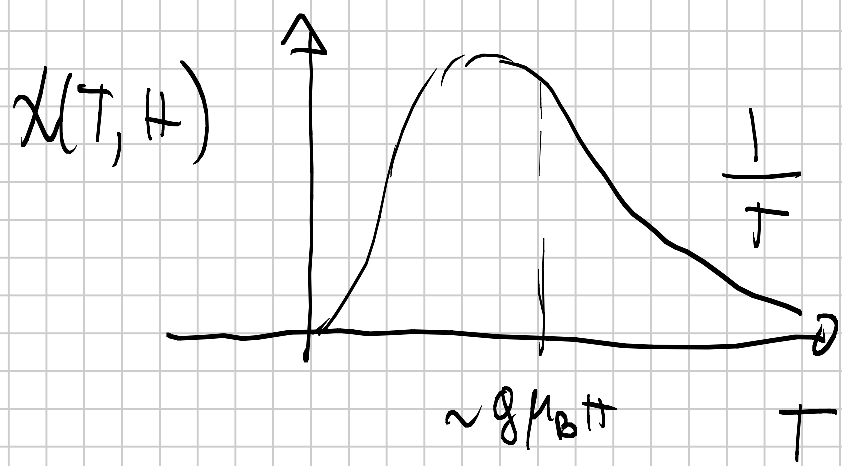
Mn^{2+} HAS MAGNETIC MOMENT OF $5\,\mu_B$

$M(H,T)$

$$Z = \sum_{S_z=-\frac{5}{2}}^{S_z=+\frac{5}{2}} e^{-\beta g \mu_B S_z H} = e^{-\beta F}$$



$$M = -\frac{1}{V}\frac{\partial F}{\partial H} \qquad \chi = -\frac{1}{V}\frac{\partial^2 F}{\partial H^2}$$

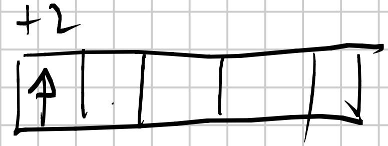


FOR $k_B T \gg g\mu_B H$

CURIE'S LAW

$$\boxed{\chi = \frac{1}{V}\,\frac{1}{3}\,(g\mu_B)^2\,\frac{S(S+1)}{k_B T}}$$

IF BOTH L AND $S \neq 0$



$L = 2$

$S = \frac{1}{2}$

$J = \frac{3}{2}$

$$\langle J_z | L_z + g S_z | J_z \rangle = g^L \langle J_z | J_z | J_z \rangle$$

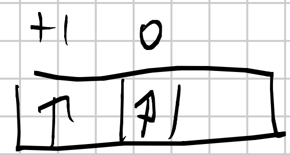
WIGNER-ECKART THEOREM

g^L = LANDÉ FACTOR

USE CLEBSCH-GORDON COEFFICIENT

$$\chi = \frac{1}{V} \frac{(g^L \mu_B)^2}{3} \frac{J(J+1)}{k_B T}$$

(3) HALF-FILLED $- 1\, e$



$L = S \Rightarrow J = 0$

$J = 0 \Rightarrow \Delta E_1 = 0$ NO FIRST ORDER PARAMAGNETISM

$\Rightarrow$ II ORDER PARAMAGNETISM (VAN VLECK PARAMAGNETISM) VERY WEAK

ΔE_1 (IN SECOND ORDER PERTURBATION THEORY)