Paramagnetism.

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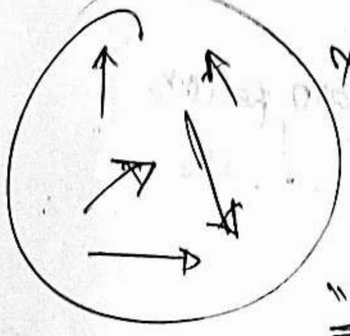


$\chi \sim 10^{-6}$
$\sim 10^{-5}$
$\sim 10^{-4}$
order
"Positive".

$\sum_i l_i = L \neq 0.$
$\sum_i s_i = S \neq 0.$

"unfilled electronic shell."

B is "aligner" force,

$k_B T$ is "disrupter"

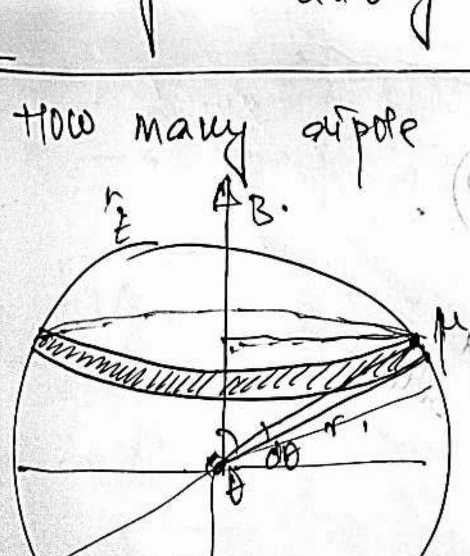
Non interacting spins / dipoles.

Semiclassical theory of PM. & Langevin function.

1. In the classical theory of paramagnetism some atoms are considered to have permanent dipole moment.
2. The interaction of the them are negligibly small.
3. Demagnetization effect is ignored here.
4. In the absence of field these dipoles may have all possible direction.

Now when the magnetic field $\vec{B}$ is applied, it will exert a torque in each dipole & will tend to orient them in the direction of the field, but this being hampered by thermal motion which will try to orient the dipoles randomly. Eventually a steady state will be reached.

How many dipole b/w θ & $\theta + d\theta$?



let θ = angle b/w μ & B.

Dipoles PE $= -\mu \cdot B$

Fraction of dipoles $\propto$ Area.

$= (2\pi r \sin\theta)(r\, d\theta)$ (for $r = 1$).

Total surface Area $= 4\pi r^2$ 1.

Fraction $= \frac{(2\pi r^2 \sin\theta)(r\, d\theta)}{4\pi r^2}$

$= \frac{2\pi \sin\theta\, d\theta}{4\pi} = \frac{1}{2}\sin\theta\, d\theta$

15. At temp T, prob of having dipole moment between θ to $\theta + d\theta$.

1\. Probability $\Rightarrow$ Statistical fraction $\times$ Boltzmann factor.

$$dn = \frac{1}{2}\sin\theta\, d\theta \times \exp\left(\frac{\mu B\cos\theta}{k_B T}\right).$$

$\therefore$ Average magnetic moment. $\langle\mu_z\rangle$ will be $\Rightarrow$

$$\langle\mu_z\rangle = \frac{\int_0^{\pi}\mu\cos\theta\, dn}{\int dn}.$$

$$= \frac{\int_0^{\pi}\mu\cos\theta\,\frac{1}{2}\sin\theta\, d\theta\,\exp\left(\frac{\mu B\cos\theta}{k_B T}\right)}{\int d\theta\,\frac{1}{2}\sin\theta\,\exp\left(\frac{\mu B\cos\theta}{k_B T}\right)} \quad \begin{matrix}\rightarrow \text{I} \\ \rightarrow \text{II}\end{matrix}$$

$u = \cos\theta$

(I) $\frac{\mu}{2}\int_0^{\pi}\cos\theta\,\sin\theta\, d\theta\,\exp(\gamma\cos\theta)$.

$$= \frac{\mu}{2}\int_{1}^{-1} u\, e^{\gamma u}\, du = \frac{\mu}{2}\int_{-1}^{1} u\, e^{\gamma u}\, du.$$

$$= \frac{\mu}{2}\left(\frac{1}{\gamma} - \frac{1}{\gamma^2}\right)\left(e^{\gamma} + e^{-\gamma}\right).$$

$$= \frac{\mu}{2}\left(\frac{k_B T}{\mu B} - \frac{k_B^2 T^2}{\mu B}\right)\left(e^{\frac{\mu B}{k_B T}} + e^{\frac{-\mu B}{k_B T}}\right).$$

$$\text{II} = \frac{1}{2r}\left(e^{r} - e^{-r}\right)$$

$$= \frac{K_B T}{2\mu B}\left(e^{\frac{\mu B}{K_B T}} - e^{-\frac{\mu B}{K_B T}}\right)$$

$$\frac{\text{I}}{\text{II}} = \frac{\cancel{\frac{K_B T}{\mu B}}\left(1 - \frac{K_B T}{\mu B}\right)\left[e^{\frac{\mu B}{KT}} + e^{-\frac{\mu B}{KT}}\right]}{\cancel{\frac{K_B T}{2\mu B}}\left(e^{\frac{\mu B}{K_B T}} - e^{-\frac{\mu B}{KT}}\right)}$$

$$= \mu\left\{\left(1 - \frac{KT}{\mu B}\right)\coth\left(\frac{\mu B}{KT}\right)\right\}$$

Laugevin function. Γ

$$= \mu\,\Gamma\left(\frac{\mu B}{KT}\right)$$

$$\boxed{\Gamma(x) = \left(1 - \frac{1}{x}\right)\coth(x)}$$

$n \longrightarrow$ Number density. { If there are n dipole moment/ unit volume then the magnetisation }.

$$\boxed{M = n.\mu\,\Gamma\left(\frac{\mu B}{KT}\right)}$$

(If you take limit of ~~[illegible]~~ to 0 of the Laugevin function it gives a linear term).

∴ At very large B . $\Gamma\left(\frac{\mu B}{KT}\right) \sim 1$.

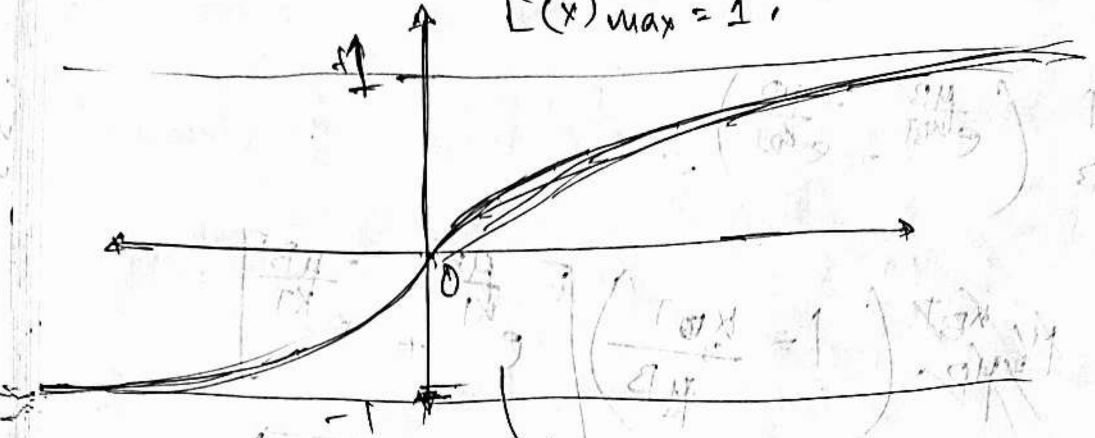
$$\therefore \boxed{M_{@B\gg} = n\mu} \longrightarrow$$ At large B all dipoles will align & reaches steady state

$$\boxed{M_{max} = n\mu}$$

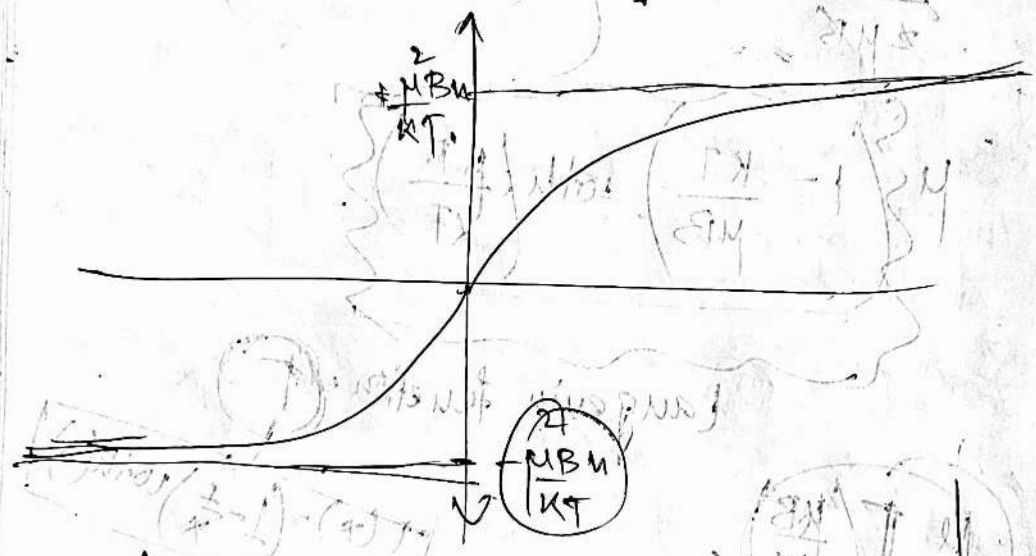
In NBD of 0, $\boxed{\text{Laugevin function}}$ is linear [physical condition: high temperature & low magnetic field $\left(\frac{\mu B}{KT}\right)$ zone] $= (x/3)$ for $\Gamma(x)$

langevin function $\left(\coth(x) - \frac{1}{x}\right)$.

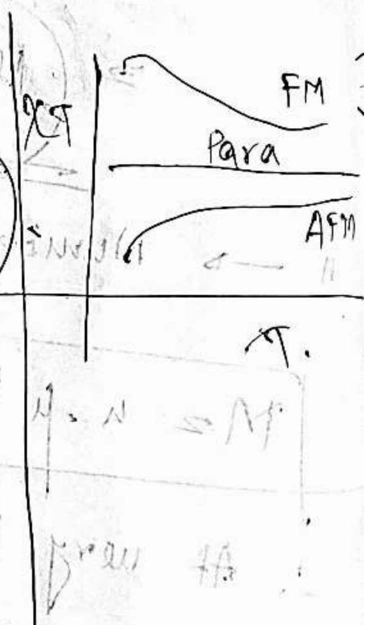
$L(x)_{max} = 1$.



Magnetization plot.



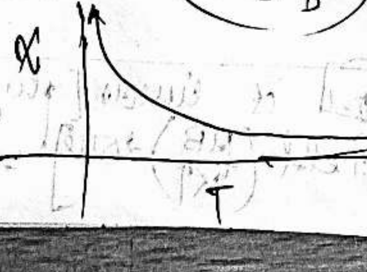
$\chi = \frac{M}{H} = \frac{-n\mu^2 \mu_0 H}{KT \, H} = \frac{n\mu^2 \mu_0}{KT}$.



For Neighbourhood.

$\chi = \frac{-n\mu^2 \mu_0}{3KT}$. (lab instrument restriction).

Curie's law $= \left(\frac{n\mu^2 \mu_0}{3K_B}\right)\frac{1}{T} = C/T$ [curie's const],



QUANTUM theory of PM

Langevin theory provides good description of the T dependence of susceptibility χ of ideal PM. But cannot explain the origin of atomic moment.
But QM treatment gives us the real picture of origin of atomic moment.

The PM moment of an atom or ion in free space:

$$\vec{\mu}_{at} = -g\mu_B \vec{J}.$$

$\vec{J}$ = total L momentum.

$$\boxed{\vec{J} = \vec{L} + \vec{S}}.$$

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}.$$

Now, the energy levels in magnetic field.

$$\vec{U} = -\vec{\mu}\cdot\vec{B} = -g\mu_B(\vec{J}\cdot\vec{B})$$

moment

Bohr magneton $\left(\frac{e\hbar}{2m}\right)$.

J-J coupling

$$= -g\mu_B(\vec{J}_z)B.$$

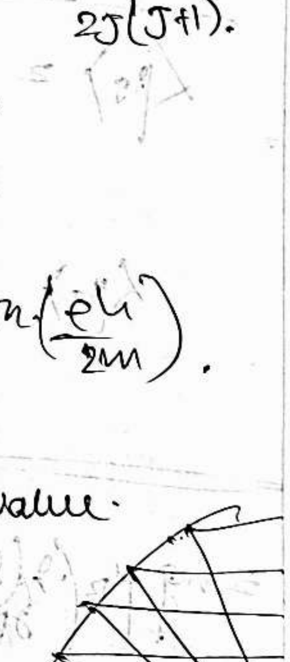
eigenvalue.

$$m_J = [-J, -J+1 \ldots J]$$

$$= (\hbar)\boxed{m_J\, g\,\mu_B\cdot B}.$$

$2J+1$ (m_J)

Russel-Sander coupling



$$|\mu| = g\mu_B\sqrt{J(J+1)}.$$

$$|\mu_z| = m_J\, g\,\mu_B.$$

An increase in magnetic field will tend to align the moment but entropy & thermodynamics will tend to disorder them.

$$e^{-Jx}\; e^{-J+1x} \cdots e^{Jx}$$

1 Partition function

$$Z = \sum_{-J}^{+J} \exp\left(\frac{m_J\, g\, \mu_B B}{kT}\right).$$

$$Z(m_J) = \sum_{-J}^{J} \exp\left(m_J x\right) \qquad x = \frac{g\,\mu_B B}{kT}.$$

$a + a^2 \cdots$ ($r<1$)

$a\left(\frac{1-r^{n}}{1-r}\right)$ → final } geometric series

$\frac{e^{-Jx} - e^{-2J+1x}}{1 - e^{x}}$

$$\langle \mu_J \rangle = \frac{\sum_{-J}^{+J} g\, m_J\, e^{m_J x}}{\sum_{-J}^{+J} e^{m_J x}}$$

$$\langle \mu_J \rangle = \left(\frac{1}{Z}\frac{\partial Z}{\partial x}\right).$$

magnetization

$$P = \frac{\text{Magnetic moment}}{\text{volume}}$$

Average magnetic moment

$$\langle M \rangle = n g \mu_B \langle \mu_J \rangle.$$

$$= n g \mu_B \left(\frac{1}{Z}\frac{\partial Z}{\partial x}\right)$$

$$= n g \mu_B \left(\frac{1}{Z}\frac{\partial Z}{\partial B}\cdot\frac{\partial B}{\partial x}\right)$$

$$x = \frac{g\mu_B B}{k_B T}$$

$$\frac{\partial B}{\partial x} = \frac{kT}{g\mu_B}.$$

$$= n g \mu_B \left(\frac{\partial(\ln Z)}{\partial B}\frac{\partial B}{\partial x}\right)$$

$$= \frac{n g \mu_B\, kT}{g\mu_B}\frac{\partial(\ln Z)}{\partial B}.$$

$$\langle M \rangle = \left((n k_B T)\frac{\partial(\ln Z)}{\partial B}\right).$$

$$\left[\frac{e^{(2J+1)\mu g B/kT} - 1}{e^{\mu g B/kT} - 1}\right]$$

$$Z = e^{-Jx}\left(\frac{e^{Jx} - 1}{e^{x} - 1}\right).$$

$$= e^{-Jx}\left(\frac{e^{(2J+1)x} - 1}{e^{x} - 1}\right)$$

$$= \left(\frac{1}{\;}\right) \frac{e^{x} - 1}{e^{-Jx}}$$

$$\frac{e^{(J+1)\frac{g\mu_B B}{KT}}-1}{e^{g\mu_B B/KT}-1} = \frac{e^{x/2}}{e^{x/2}}\,\frac{\left[e^{(J+\frac{1}{2})x} - e^{-(J+\frac{1}{2})x}\right]/2}{\left[e^{x/2} - e^{-x/2}\right]/2}.$$

$$Z \Rightarrow \frac{\sinh\left[\left(J+\frac{1}{2}\right)x\right]}{\sinh\left(x/2\right)}$$

$\to \lambda B.$ $\left(\lambda = \frac{g\mu_B}{KT}\right)$ const.

$$\ln Z \Rightarrow \ln\left(\sinh\left[\left(J+\tfrac{1}{2}\right)x\right]\right) - \ln\left(\sinh\left(x/2\right)\right)$$

$$\frac{\partial}{\partial B}\ln Z \Rightarrow \lambda\coth\left[\left(J+\tfrac{1}{2}\right)\lambda B\right] - \lambda\coth\left(\frac{\lambda B}{2}\right).$$

$$= \lambda\left(\coth\left[\left(J+\tfrac{1}{2}\right)\lambda B\right] - \coth\left(\lambda B/2\right)\right)$$

$$\frac{\partial}{\partial B}(\ln Z) = \frac{g\mu_B}{KT}\left[\coth\left[\left(J+\tfrac{1}{2}\right)\frac{g\mu_B B}{KT}\right] - \coth\left(\frac{g\mu_B B}{2KT}\right)\right]$$

$$\langle M\rangle = nKT\frac{g\mu_B}{KT}\left[\coth\left[\left(J+\tfrac{1}{2}\right)\frac{g\mu_B B}{KT}\right] - \coth\left[\frac{g\mu_B B}{2KT}\right]\right]$$

$$= ng\mu_B\left[\coth\left[\left(J+\tfrac{1}{2}\right)\frac{g\mu_B B}{KT}\right] - \coth\left[\frac{g\mu_B B}{KT}\right]\right].$$

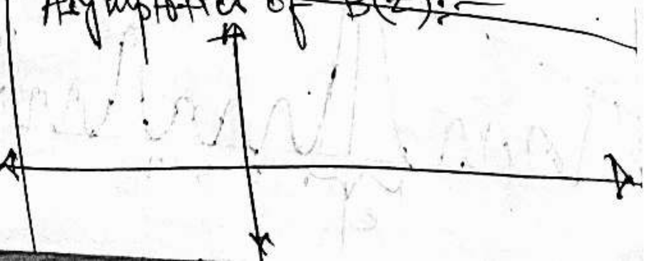
$W = Z$

$$= \boxed{ng\mu_B J\, B_J(z)}.$$

$\to$ Brillouin function.

Brillouin function $\Rightarrow$

~~Asymptotics of B(z):~~



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$$\langle m_J \rangle = \frac{\sum_{m_J=-J}^{J} m_J e^{jx}}{\sum e^{jx}} = \frac{1}{z}\frac{dz}{dx}$$

$$= \frac{d}{dx}(\log z)$$

$$= \frac{d}{dx}\log\left[\log \sinh(J+1/2)x - \sinh(x/2)\right]$$

$$= \frac{\left(\frac{2J+1}{2}\right)\cosh(J+1/2)x}{\sinh(J+1/2)x} - \frac{\cosh(x/2)}{\sinh(x/2)} \times \frac{1}{2}$$

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

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

$xJ = \alpha$

$= J$

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

→ Brillouin fn

$$\langle \mu_z \rangle = g\mu_B \langle m_J \rangle$$

$$= g\mu_B J\left[B_J(\alpha)\right]$$

n = no. of atoms per unit volm

$$\langle M \rangle = n\langle \mu_z \rangle$$

$$\boxed{\langle M \rangle = ng\mu_B J\, B_J(\alpha)}$$

$$\alpha = xJ = \frac{g\mu_B}{K_B}\cdot\frac{BJ}{T}$$

$B_J(\alpha)$ $\alpha \gg 1$

$\alpha \to$ very high

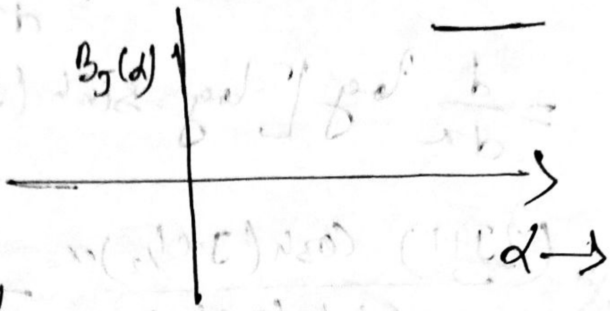
$$B_J(\alpha) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}\right)\alpha - \frac{1}{2J}\coth\left(\frac{\alpha}{2J}\right)$$

$$\coth\left(\frac{2J+1}{2J}\right)\alpha \to 1$$

$$B_J(\alpha) = \frac{2J+1}{2J} - \frac{1}{2J} = \frac{2J+1-1}{2J} = 1$$

$\langle M \rangle = n g \mu_B J B_J(\alpha)$

$\alpha \to$ very high $\boxed{\langle M \rangle = n g \mu_B J}$



$\alpha \to$ small, $y \to$ small

$$\coth y = \frac{e^y + e^{-y}}{e^y - e^{-y}}$$

$$= \frac{1 + y + 1 - y}{1 + y - 1 + y} \approx \frac{1}{y} + \frac{y}{3}$$

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

$$\frac{2J+1}{2J} \cdot \frac{1}{y} - \frac{1}{2J} \cdot \frac{2J}{\alpha}$$

$$= \frac{2J+1}{2J} \cdot \frac{2J}{\alpha(2J+1)} - \frac{1}{\alpha}$$

$$B_J(\alpha) = \frac{2J+1}{2J} \left\{ \frac{2J}{(2J+1)\alpha} + \frac{2J+1}{3 \times 2J} \alpha \right\} - \frac{1}{2J} \left\{ \frac{2J}{\alpha} + \frac{\alpha}{6J} \right\}$$

$$= \frac{1}{\alpha} + \frac{(2J+1)^2}{(2J)^2} \cdot \frac{\alpha}{3} - \frac{1}{\alpha} - \left(\frac{1}{2J}\right)^2 \frac{\alpha}{3}$$

$$= \frac{\alpha}{3} \left[\frac{(2J+1)^2 - 1}{(2J)^2} \right]$$

$$= \frac{\alpha}{3(2J)^2} \left[(2J+1-1)(2J+1+1) \right]$$

$$\frac{\alpha}{3(2J)^2} \times 2J(2J+2)$$

$$= \frac{\alpha}{3 \cdot 2J} 2(J+1)$$

$$= \frac{\alpha}{3J}(J+1)$$

$$\langle M \rangle = ng\mu_B J \cdot \frac{J+1}{3J}\alpha$$

$$= ng\mu_B \cdot \frac{(J+1)}{3} \cdot \frac{g\mu_B BJ}{K_B T}$$

$$\langle M \rangle = n(g\mu_B)^2 \cdot \frac{(J+1)B}{3K_B T}$$

μ_{eff} = effective moment

$$= g\mu_B\sqrt{J(J+1)}$$

$$= p_{eff}\mu_B$$

$$\langle M \rangle = \frac{n\mu_{eff}^2 B}{3K_B T}$$

$$= \frac{n\mu_B^2 p_{eff}^2 B}{3K_B T}$$

$$\chi = \frac{\langle M \rangle}{H} = \frac{n\mu_{eff}^2 \mu_0}{3K_B} \cdot \frac{1}{T} = \frac{C}{T}$$

Problem: ① Prove that $B_J(\alpha) \underset{J\to\infty}{=} L(z)$ classical limit $\to \coth(hz) - \frac{1}{z}$

② Prove that $B_{J=1/2}(\alpha) = \tanh(\alpha)$

for $J=1/2$, $g=2$, $B=1\,T$

$$\alpha = \frac{g\mu_B B}{KT}J = 0.002 \text{ (very small)}$$

$T = 300\,K$

③ $\alpha \to$ very small $B_J(\alpha) = \frac{J+1}{3J}\alpha$

④ Determine the paramagnetic susceptibility of an ideal gas at room temperature assuming $J=1$, $g=2$ (Ideal gas eqn. $pV = nRT$)

The ground of an ion and Hund's rule:

① The atoms containing many electrons in shells

② The filled shells have no net ang|r momentum

③ However there may be unfilled shells and the electrons in these shells can combine to give non-zero spin and orbital ang|r momentum

Thus an atom will have total orbital ang|r momentum $\Sigma l_i = \hbar L$; $\Sigma S_i = \hbar S$

The orbital and spin ang|r momentum can combine in $(2L+1)(2S+1)$ ways

Spin and orbital ang|r momentum effect how well the electron avoid each other and this influences electrostatic repulsion energy

Hence different combination will give different energies and the system prefers lowest energy configuration

Fine structure

Spin ang|r momentum and orbital ang|r momentum do weakly coupled via the spin orbit interaction

If spin orbit interaction acts as a perturbation on the states with well defined L and S. Because of this L and S are not seperately conserved but the ~~the~~ total angr momentum i.e $J = L+S$ is conserved. J can take values from $|L-S|$ to $|L+S|$

$$L^2 = L(L+1) \; ; \; S^2 = S(S+1)$$

Thus spin-orbit interaction takes the form $\lambda \vec{L}\cdot\vec{S}$ $\quad \lambda =$ Const.

$$(\lambda \vec{L}\cdot\vec{S}) = \frac{\lambda}{2}\left[J(J+1) - L(L+1) - S(S+1)\right]$$

The energy of the atom is mainly determined by the values of S and L ~~for~~ weak spin-orbit)

Hence the energy eigenstates can ~~take~~ be labelled with values S and L. Each level in multiplet by $(2S+1)(2L+1)$.

If spin-orbit interaction is added as a perturbation these ~~level~~ multiplet splitted into diffn fine structure levels, each level having degeneracy of $(2J+1)$

The energy seperation between adjacent levels $E(J)$ and $E(J-1)$ of a given multiplet

$$E(J) - E(J-1)$$

$$= \lambda J$$

Lande interval rule

There fore splitting is proportional to J

$$(2L+1)(2S+1) = \sum_{J=|L-S|}^{|L+S|} (2J+1)$$

Lots of possible combination of ang|r momentum qn. no.
which one is the G.S ~~of~~ for a particular ion?

Remedy ⇒ Search for the minimization of energy

⇒ Hund's rule

(1) Arrange ~~to~~ to maximize S
In this way Coulumb repulssion and associated energy will be minimum

(2) After satisfying 1st rule maximize L

(3) Find $J = |L-S|$ if the shell is half filled
$J = |L+S|$ if the shell is more than ~~half~~ half filled

Find out G.S Mn^{+2}, Cr^{+2}, Ni^{+2}