Recap: Magnetism of Atom

Many-body atom:

$$L = \sum m_\ell\,, \qquad S = \sum m_s\,, \qquad J$$

How to distribute e^- in atom:

Hund's rules: Within given subshell (n, ℓ)

1. Maximize S.
2. For max. S, maximize L.
3. J follows from L and S:
   - less than half-filled $(< 2\ell+1\ e^-)$: $J = L - S$
   - half-filled $(2\ell+1\ e^-)$: $L = 0$, $J = S$
   - more than half-filled $(> 2\ell+1\ e^-)$: $J = L + S$

Ti: $4s^2\, 3d^2$

d					
				↑	↑
m_ℓ	-2	-1	0	1	2

NB: Hund does not state in which order $(n\,\ell)$ are filled

e.g. ^{56}Ba: $6s^2$ $\qquad$ ^{57}La: $6s^2\, 5d^1$ $\qquad$ ^{58}Ce: $6s^2\, 5d^1\, 4f^1$

Magnetic susceptibilities of atom

Here: Electronic part:

NB: Nuclear part not important for total energy considerations here, but very important in

e.g. nuclear magnetic resonance
precision measurements (MASER)

$$H^{el} = T^{el} + V^{e-ion} + V^{e-e}$$

Electromagnetism: Include $\underline{H}$ fields through "minimal substitution" in T^{e}

$$\underline{p} \to \underline{p} + e\underline{A} \qquad \underline{A} \text{ "vector potential"}$$

homogeneous field: $\underline{A} = -\frac{1}{2}(\underline{r} \times \mu_0 \underline{H})$

so that $\underline{H} = \frac{1}{\mu_0} \underline{\nabla} \times \underline{A}$

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

NB: We here use the magnetic field $\underline{H}$ (internal), not $\underline{B}$.

Classical physics: $\underline{A}$ vanishes in F (free energy)

$$\to \underline{M} = -\frac{1}{V}\frac{\partial F}{\partial \underline{H}} = 0$$

Bohr-van Leeuwen theorem

Quantum mechanics:

$$T^e(H) = \frac{1}{2m} \sum_k \left(p_k + e\underline{A}\right)^2$$

$$= \frac{1}{2m} \sum_k \left(p_k - \frac{e}{2}\left(\underline{r}_k \times \mu_0 \underline{H}\right)\right)^2$$

$$= \sum_k \left[\frac{p_k^2}{2m} + \frac{\mu_0 e}{2m} p_k \cdot \left(\underline{H} \times \underline{r}_k\right) + \frac{e^2 \mu_0^2}{8m} \left(\underline{r}_k \times \underline{H}\right)^2 \right]$$

$$= T_0^e + \frac{\mu_0 e}{2m} \underbrace{\sum_k \left(\underline{r}_k \times p_k\right)}_{\underline{L}} \cdot \underline{H}$$

$$+ \frac{e^2 \mu_0^2}{8m} H^2 \sum_k \left(x_k^2 + y_k^2\right)$$

- $\underline{H} \parallel z$-axis

So:

$$T^e(H) = T_0^e + \mu_B \mu_0 \, \underline{L} \cdot \underline{H} + \frac{e^2 \mu_0^2}{8m} H^2 \sum_k \left(x_k^2 + y_k^2\right)$$

$$\mu_B = \frac{e\hbar}{2m} = 0.579 \cdot 10^{-4} \, \frac{eV}{T}$$

However: We used Schrödinger's equation, no spin!

Rather: Dirac's Eqn.

$$\begin{pmatrix} V & c\underline{\sigma}\cdot\underline{p} \\ c\underline{\sigma}\underline{p} & -2c^2+V \end{pmatrix} \begin{pmatrix} \phi \\ \chi \end{pmatrix} = E \begin{pmatrix} \phi \\ \chi \end{pmatrix} \Big\}\ \text{4 components!}$$

non-rel. limit: $\phi = \begin{pmatrix} \varphi_\uparrow \\ \varphi_\downarrow \end{pmatrix}$ two components for e^-

$\underline{\sigma}$ vector of "Pauli" spin matrices

$\sigma_x, \sigma_y, \sigma_z$
(2x2) matrices

Result of much algebra:

$$\Delta H_{spin} = g_0 \mu_B \cdot \mu_0 \cdot \underline{H} \cdot S_z$$

"g-factor"

Dirac's Eqn: $g_0 = 2$

Reality: $g_0 = 2.0023\ldots$

QED: $g_0 = 2\cdot\left(1+\frac{\alpha}{2\pi} + O(\alpha^2)\right)$

$$\Delta H^e(\underline{H}) = \mu_0\mu_B\left(\underline{L} + g_0\underline{S}\right)\cdot\underline{H} + \frac{e^2\mu_0^2}{8m} H^2 \sum_k (x_k^2+y_k^2)$$

μ_B small: Use perturbation theory.

Second order:

$$\Delta E_n(\underline{H}) = \mu_0\mu_B \underline{H} \langle n | \underline{L} + g_0 \underline{S} | n \rangle \qquad (1)$$

$$+\frac{e^2}{8m} H^2 \mu_0^2 \langle n | \sum_k (x_k^2 + y_k^2) | n \rangle \quad (2)$$

$$+\sum_{n \neq n'} \mu_0^2 \frac{|\langle n | \mu_B \underline{H} \cdot (\underline{L} + g_0 \underline{S}) | n' \rangle|^2}{E_n - E_{n'}} \quad (3)$$

(1) largest term involved
leads to paramagnetism.

However: If $J = 0 \rightarrow \langle n |$ is non-degenerate
$\rightarrow$ can show that (1) vanishes.

(happens for noble gases, or for shells filled "half $-1e^-$"

$\boxed{\;|\uparrow|\uparrow|\uparrow|\uparrow|}$ $\quad L = 2,\ S = 2$
$J = L - S = 0$)

(2) "Larmor" term – Diamagnetism

Ground state:
$$\Delta E_0^{dia} = \frac{e^2 \mu_0^2}{8m} H^2 \sum_k \langle 0 | x_k^2 + y_k^2 | 0 \rangle$$

$$\sim \frac{2}{3} \frac{e^2 \mu_0^2}{8m} H^2 \cdot \underset{\substack{\uparrow \\ \text{number} \\ \text{of electrons}}}{Z} \cdot \overline{r_{atom}^2}$$

$$\overline{x_k^2 + y_k^2} \sim \frac{2}{3} \overline{r_{atom}^2}$$

order of magnitude: $Z = 30$, $\overline{r_{atom}^2} \sim Å^2$

$\Rightarrow E_0^{dia} \sim 10^{-9}$ eV for $H \sim 1T$

why diamagnetic?

$$\chi^{mag,②} = -\frac{1}{\mu_0 V}\frac{\partial^2 E}{\partial H^2} = -\frac{\mu_0}{V}\frac{e^2 \cdot Z \cdot \overline{r_{atom}^2}}{6m}$$

$\sim 10^{-4}$.

note $J=0$, closed shell $\longrightarrow$ this is the only term
(noble gases, closed shell molecules, ...)

③ "van Vleck" paramagnetism.

Again, take ground state and perturb it:

$$\chi^{mag,vleck} = \frac{2\mu_0 \mu_B^2}{V}\sum_{n\neq 0}\frac{|\langle 0|\underline{L}_z + g_0 \underline{S}_z|n\rangle|^2}{E_n - E_0}$$

since $E_n > E_0 \Rightarrow \chi^{mag,vleck} > 0$
paramagnetic term.

If $J=0$, but $L, S \neq 0$ (not closed shell)
$\longrightarrow$ <u>this</u> term gets qualitative agreement!

Magnitude $\sim \chi^{dia}$ often, $\chi^{②}$, $\chi^{③}$
$\sim$ cancel.

back to ①

$J=0$: ① vanishes

$J \neq 0$: Ground state : $J_z = -J, \dots, J$ → label α below

degenerate!

Must fix our perturbation theory :

$$\Delta E_{0,\alpha} = \mu_0 \mu_B H \sum_{\alpha'=1}^{(2J+1)} \langle 0\alpha | \underline{L}_z + g_0 \underline{S}_z | 0\alpha' \rangle$$

$$= \mu_0 \mu_B H \sum_{\alpha'} V_{\alpha\alpha'}$$

Textbook QM : Must diagonalize $V_{\alpha,\alpha'}$ to find out <u>which</u> linear comb. of α's is the g.s. in presence of perturbation

Wigner - Eckart theorem :

Matrix elements of J^2, J_z are proportional to matrix elements of $\underline{J}$

$$\langle J L S \overset{\alpha}{J_z} | \underline{L}_z + g_0 \underline{S}_z | J L S, \overset{\alpha'}{J_z'} \rangle$$

$$\sim \langle J L S, J_z | \underline{J} | J L S, J_z' \rangle$$

$$= g(JLS) \cdot \langle J L S, J_z | \underline{J} | J L S, J_z \rangle$$

but $\langle JLS, J_z | J_z | JLS, J_{z'} \rangle$ is diagonal

→ from basic angular momentum theory:

can conclude that these are the rotated states which we are looking for.

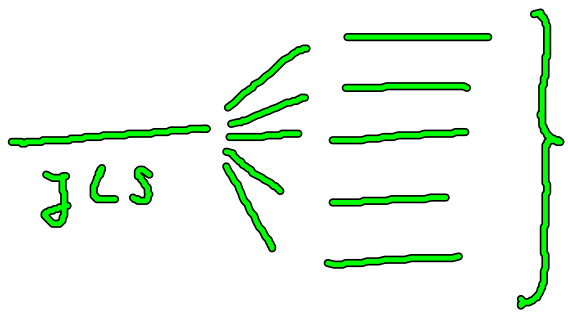
NB: $$g(JLS) = \frac{3}{2} + \frac{1}{2}\left[\frac{S(S+1) - L(L+1)}{J(J+1)}\right]$$

(e.g. Ashcroft) $[g_0 = 2]$

NB: $J = 0$, $J_z = 0$ → no contribution

$J \neq 0$:

if finite $\underline{H}$:



$2J+1$ equidistant levels

$$\Delta E_{JLS, J_z} = g(JLS) \cdot \mu_0 \mu_B J_z H$$

lowest state is $-g(JLS) \cdot \mu_0 \mu_B \cdot J \cdot H$

if $kT \ll g(JLS) \cdot \mu_0 \mu_B H$

→ only lowest state, and

$$\Delta E \sim \underline{m}_{atom} \cdot \underline{H}$$

$$m_{atom} = -g(J(S))\mu_B \cdot J$$

This simple interpretation generally does not hold!

$H \to 0$ (still reasonably large even)

$k T$ matters! (splitting vanishes!)

$$\Delta E_{J(S), J_z} = g(J(S))\mu_0 \mu_B H$$

$$\mu_B = 0.579 \cdot 10^{-4} \frac{eV}{T}$$

$$\mu_0 H \sim 1T$$

$$\Delta E \sim 10^{-4} eV.$$

Paramagnetic susceptibility: Curie's Law.

Need: Free Energy $F(\underline{H})$

$$M(H,T) = -\frac{1}{\mu_0 V} \frac{\partial F(H,T)}{\partial H}\Bigg|_{S,V}$$

$$\chi^{mag}(H,T) = -\frac{1}{\mu_0 V} \frac{\partial^2 F}{\partial H^2}\Bigg|_{S,V}$$

How to get F?

$$F = \bar{E} - TS = U - TS$$

$$F = -k_B T \cdot \ln Z \qquad Z \text{ "partition function"}$$

$$Z = \sum_{\text{states}} e^{-\frac{E_{\text{state}}}{kT}}$$

Here : states $J_z = -J, \dots J$

$$E(J_z) = g(J(S)) \cdot \mu_0 \cdot \mu_B \cdot H \cdot J_z$$

Define $$\eta = \frac{g(J(S))\mu_0 \mu_B H}{k_B T}$$

Now : $$Z = \sum_{J_z=-J}^{J} e^{-\eta J_z} = \frac{e^{-\eta J} - e^{+\eta(J+1)}}{1-e^{\eta}}$$

$$= \frac{e^{-\eta(J+\frac{1}{2})} - e^{\eta(J+\frac{1}{2})}}{e^{-\eta/2} - e^{\eta/2}} = \frac{\sinh[(J+\frac{1}{2})\eta]}{\sinh(\frac{\eta}{2})}$$

$$F = -k_B T \ln Z$$

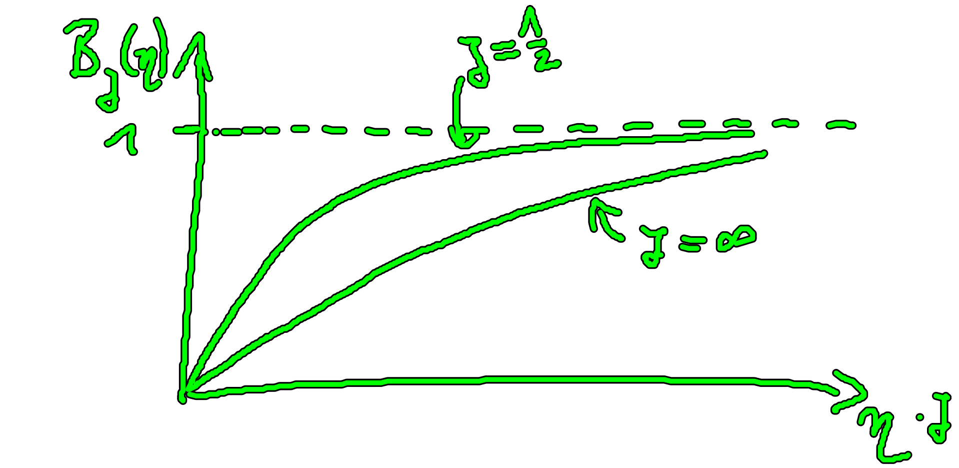
$$M(T) = -\frac{1}{\mu_0 V}\frac{\partial F}{\partial H} = \frac{k_B T}{\mu_0 V}\frac{\partial \ln Z}{\partial H}$$

$$= \frac{k_B T}{\mu_0 V}\frac{\partial \ln Z}{\partial \eta}\frac{\partial \eta}{\partial H}$$

$$= \frac{kT}{\mu_0 V} \cdot \frac{g(J(S)) \cdot \mu_0 \mu_B}{k_B T} \cdot \frac{\partial \ln Z}{\partial \eta}$$

$$=: \frac{g(JLS)}{V}\cdot \mu_B \cdot J \cdot \underbrace{B_J(\eta)}_{\text{"Brillouin function"}}$$

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



$\eta \to \infty \;\hat{=}\; \frac{H}{T}\to\infty$: $\quad B_J(\eta)\to 1$

$$M \approx \frac{m_{atom}}{V} = \text{const.}$$

with $m_{atom} = g(JLS)\, J\, \mu_B$

Finite T $(T\to\infty)$

$\eta \to 0$ can show $B_J(\eta \ll 1) \to \frac{J+1}{3J}\eta$

$$\chi^{mag,para} = \frac{\partial M}{\partial H} = \frac{\mu_0 \mu_B^2\, g(JLS)^2\, J(J+1)}{3Vk_B}\,\frac{1}{T}$$

$$= \frac{C}{T} \quad \text{"Curie's Law"}$$

note $V \sim \mathring{A}^3 \rightarrow \chi^{\text{mag, para}} = 10^{-2}$ at RT.

drowns diamagnetism if it exists.

Susceptibility: Free electron gas (opposite limit wrt electrons)

essentially: two terms

1. existing electrons spins (Pauli)
2. screening currents (orbital L) (Landau)

Consider case 1:

Remember: DOS (no spin)

$$N(\epsilon) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \epsilon^{1/2}$$

and
$$\frac{N}{V} = \int_0^\infty d\epsilon\, N(\epsilon) \cdot \underbrace{f(\epsilon, T)}_{\text{Fermi distribution}}$$

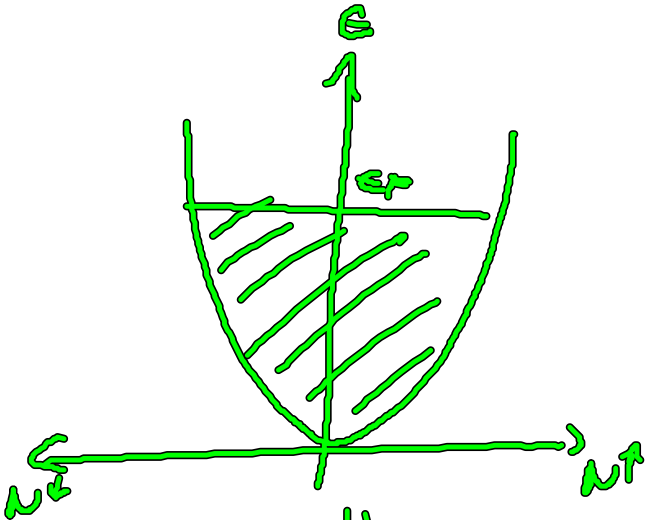
$$\rightarrow \epsilon_F = \frac{50.1\,\text{eV}}{\left(\frac{r_s}{a_B}\right)} \quad \text{at } T \approx 0$$

$$N(\epsilon_F) = \left(\frac{1}{20.7\,\text{eV}}\right)\left(\frac{r_s}{a_B}\right)^{-1}$$

Now include spin:

$$N^{\uparrow}(\epsilon) = N^{\downarrow}(\epsilon) = \frac{1}{2} N(\epsilon)$$ no spin-polarisation

But: $\Delta H_{spin} = \mu_B \cdot g_0 \mu_0 \underline{H} \cdot \underline{S}$ $\begin{cases} \mu_B B & \text{(spin up)} \\ -\mu_B B & \text{(spin down)} \end{cases}$



no $\underline{H}$