

# Recap: Magnetism of Atom

Many-body atom:

$$L = \sum m_l, \quad S = \sum m_s, \quad J$$

How to distribute  $e^-$  in atom:

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

1. Maximize  $S$ .

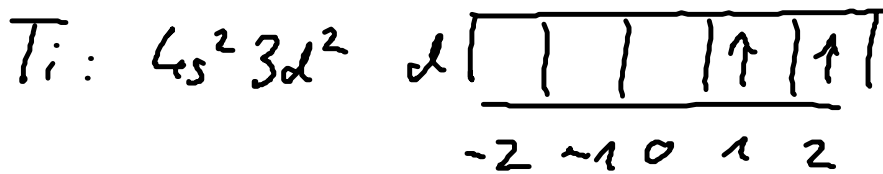
2. For max.  $S$ , maximize  $L$ .

3.  $J$  follows from  $L$  and  $S$ :

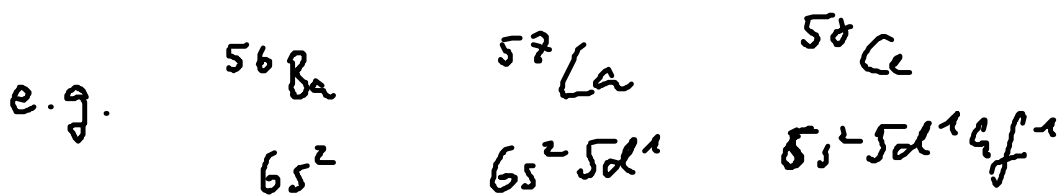
less than half-filled ( $< 2l+1 e^-$ ):  $J = L - S$

half-filled ( $2l+1 e^-$ ):  $L = 0, J = S$

more than half-filled ( $> 2l+1 e^-$ ):  $J = L + S$



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



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  $T^e$

$$\underline{p} \rightarrow \underline{p} + e \underline{A} \quad \underline{A} \text{ "vector potential"}$$

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

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

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

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

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

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

Bohr-van Leeuwen theorem

Quantum mechanics:

$$\begin{aligned} T^e(H) &= \frac{1}{2m} \sum_k (p_k + eA)^2 \\ &= \frac{1}{2m} \sum_k \left( p_k - \frac{e}{2} (\underline{r}_k \times \mu_0 \underline{H}) \right)^2 \\ &= \sum_k \left[ \frac{p_k^2}{2m} + \frac{\mu_0 e}{2m} p_k \cdot (\underline{H} \times \underline{r}_k) + \frac{e^2 \mu_0^2}{8m} (\underline{r}_k \times \underline{H})^2 \right] \\ &= T_0^e + \frac{\mu_0 e}{2m} \underbrace{\sum_k (\underline{r}_k \times p_k)}_{\underline{L}} \cdot \underline{H} \\ &\quad + \frac{e^2 \mu_0^2}{8m} H^2 \sum_k (x_k^2 + y_k^2) \end{aligned}$$

•  $\underline{H} \parallel z$ -axis

So:

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

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

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

Rather: Dirac's Eqn.

$$\begin{pmatrix} V & c\vec{\sigma} \cdot \vec{p} \\ c\vec{\sigma} \cdot \vec{p} & -2c^2 + V \end{pmatrix} \begin{pmatrix} \phi \\ \chi \end{pmatrix} = E \begin{pmatrix} \phi \\ \chi \end{pmatrix} \quad \left. \vphantom{\begin{pmatrix} \phi \\ \chi \end{pmatrix}} \right\} \text{4 components!}$$

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

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

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

Result of much algebra:

$$\Delta H_{\text{spin}} = g_0 \mu_B \mu_0 \underline{H} \cdot \underline{S}_z$$

↑  
"g-factor"

Dirac's Eqn:  $g_0 = 2$

Reality:  $g_0 = 2.0023 \dots$

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

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

$\mu_B$  small: Use perturbation theory.

Second order:

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

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

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

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"  $-1e^{-4}$ )

$$\boxed{|\uparrow| \uparrow | \uparrow | \uparrow} \quad \begin{matrix} L=2, S=2 \\ J=L-S=0 \end{matrix}$$

② "Larmor" term - Diamagnetism

Ground state:

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

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

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

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

why diamagnetic?

$$\chi_{\text{mag}, (2)} = -\frac{1}{\mu_0 V} \frac{\partial^2 E}{\partial H^2} = -\frac{\mu_0}{V} \frac{e^2 \cdot Z \cdot \overline{r^2}}{6m}$$

$$\sim 10^{-4}$$

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

(3) "van Vleck" paramagnetism.

Again, take ground state and perturb it:

$$\chi_{\text{mag, vleck}} = \frac{2\mu_0 \mu_B^2}{V} \sum_{n \neq 0} \frac{|\langle 0 | L_z + g_0 S_z | n \rangle|^2}{E_n - E_0}$$

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

If  $J=0$ , but  $L, S \neq 0$  (not closed shells)

$\rightarrow$  this term gets qualitative agreement!

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

back to (1)

$J=0$  : ① vanishes

$J \neq 0$  : Ground state :  $J_z = -J, \dots, J \rightarrow$  label  $\alpha$   
degenerate!  
below

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 which linear comb.  
of  $\alpha$ '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  $J$

$$\langle JLSJ_z | \underline{L}_z + g_0 \underline{S}_z | JLSJ_z' \rangle$$

$$\sim \langle JLSJ_z | J | JLSJ_z' \rangle$$

$$= g(JLS) \cdot \langle JLSJ_z | J | JLSJ_z \rangle$$

but  $\langle JLS, J_z | J_z | JLS, J_z \rangle$  is diagonal

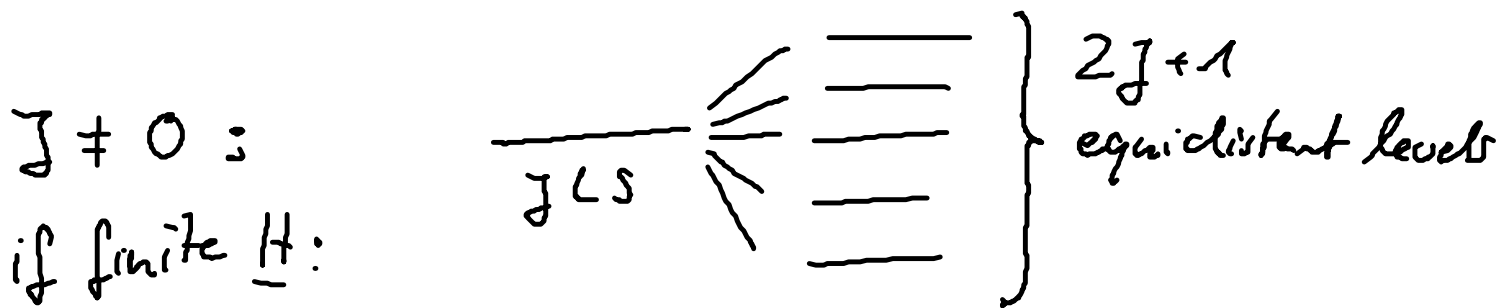
$\Rightarrow$  from basic angular momentum theory:

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

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

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

NB:  $J=0, J_z=0 \rightarrow$  no contribution



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

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

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

$\rightarrow$  only lowest state, and

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



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

This simple interpretation generally does not hold!

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

$kT$  matters! (splitting vanishes!)

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

$$\mu_B = 0.575 \cdot 10^{-4} \frac{\text{eV}}{\text{T}}$$

$$\mu_0 H \sim kT$$

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

Paramagnetic susceptibility: Curie's Law.

Need: Free Energy  $F(H)$

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

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

How to get  $F$ ?

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

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

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

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

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

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

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

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

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

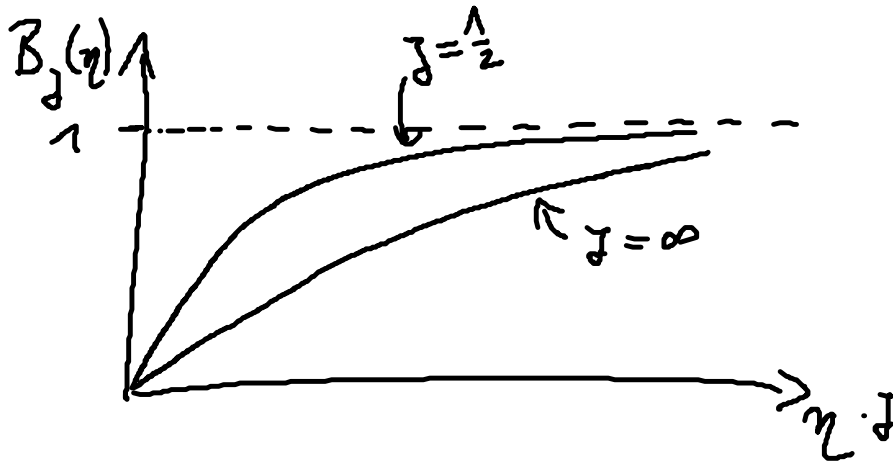
$$M(T) = -\frac{1}{\mu_0 V} \frac{\partial F}{\partial H} = \frac{k_B T}{\mu_0 V} \frac{\partial \ln Z}{\partial H}$$

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

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

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

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



$$\eta \rightarrow \infty \approx \frac{H}{T} \rightarrow \infty : B_J(\eta) \rightarrow 1$$

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

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

Finite  $T$  ( $T \rightarrow \infty$ )

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

$$\chi_{\text{mag, param}} = \frac{\partial M}{\partial H} = \frac{\mu_0 \mu_B^2 g(J\omega)^2 J(J+1)}{3V k_B} \frac{1}{T}$$

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

note  $V \sim \text{\AA}^3 \rightarrow \chi_{\text{mag, param}} = 10^{-2}$   
at RT.

drowns diamagnetism if it exists.

Susceptibility = Free electron gas (opposite limit  
wrt above)

essentially: two laws

(1) existing electron 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 :

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

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

