Condensed Matter Physics 3
Example Workshop 4 – Solution

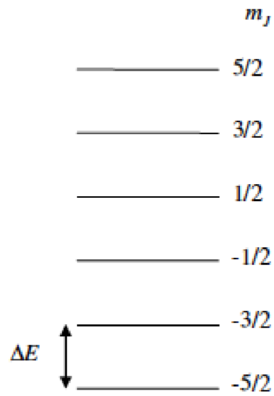
1. Hund's rules and magnetic levels in paramagnetic Cu^{2+} ions

(a) Cu^{2+} (all other shells filled) d^9

m_l	-2	-1	0	1	2
m_s	½	½, -½	½, -½	½, -½	½, -½

Hund's 1st rule: Total spin should be maximised, $S = \sum m_S = 1 \times {}^1/_2 = {}^1/_2$
Hund's 2nd rule: Orbital angular momentum should be maximised consistent with the value of S, $L = \sum m_l = 2 + 2 + 1 + 1 + 0 + 0 - 1 - 1 - 2 = 2$
Hund's 3rd rule: The value of the total angular momentum, *J*, for a more than half filled shell is $J = L + S = 2 + {}^1/_2 = {}^5/_2$

$\Delta E = g\mu_B B \Delta m_J$ where $\Delta m_J = 1$ and $B = 1$



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

$$g = 1 + \frac{\frac{5}{2}\left(\frac{7}{2}\right) + \frac{1}{2}\left(\frac{3}{2}\right) - 2(3)}{5\left(\frac{7}{2}\right)} = 1 + \frac{35/4 + 3/4 - 6}{35/4} = 1.20$$

$\Delta E = 1.20 \times 9.27 \times 10^{-24} \times 1 \times 1 = 1.11 \times 10^{-23}$ J = 6.95 x 10^{-5} eV.

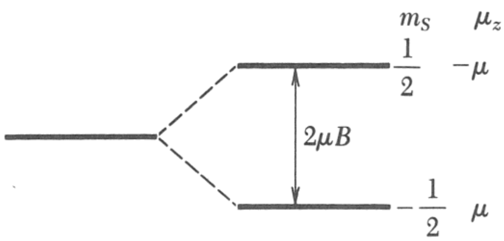
(b) If Cu^{2+} is orbitally quenched then $L = 0$

m_l	0	0	0	0	0
m_s	½	½, -½	½, -½	½, -½	½, -½

Then $J = S = ½$. There are just two levels -1/2 and +1/2 with $g = 1 + \frac{\frac{1}{2}\left(\frac{3}{2}\right)+\frac{1}{2}\left(\frac{3}{2}\right)-0}{1\left(\frac{3}{2}\right)} = 1 + \frac{3/2}{3/2} = 2$

but with an increased (but still very small) splitting

$\Delta E = 2 \times 9.27 \times 10^{-24} \times 1 \times 1 = 1.85 \times 10^{-23}$ J
= 1.16 x 10^{-4} eV.



2. **Paramagnetism, Hund's rules and spin-orbit coupling in Sm^{3+} ions.**

(*a*) Assuming L-S, or Russell-Saunders coupling we need only consider the outermost unfilled shell.
5 electrons in the *f*-shell: $l = 3$, $s = ½$

m_l	-3	-2	-1	0	1	2	3
m_s			+½	+½	+½	+½	+½

Hund's 1st rule: Total spin should be maximised, $S = \sum m_s = 5 \times ½ = 5/2$.
Hund's 2nd rule: Orbital angular momentum should be maximised consistent with the value of S, $L = \sum m_l = 3 + 2 + 1 + 0 - 1 = 5$.
Ground state given by Hund's 3rd rule: The value of the total angular momentum, *J*, for a less than half filled shell is $J = |L - S| = 5 - \frac{5}{2} = 2\frac{1}{2}$.

(*b*) The magnitudes of the angular momenta are:

$$|S| = \{S(S+1)\}^{\frac{1}{2}}\hbar = \left\{2\frac{1}{2}\left(2\frac{1}{2}+1\right)\right\}^{\frac{1}{2}} = 2.96\hbar$$
$$|L| = \{L(L+1)\}^{\frac{1}{2}}\hbar = \{5(5+1)\}^{\frac{1}{2}} = 5.47\hbar$$
$$|J| = \{J(J+1)\}^{\frac{1}{2}}\hbar = \left\{2\frac{1}{2}\left(2\frac{1}{2}+1\right)\right\}^{\frac{1}{2}} = 2.96\hbar$$

The magnitudes of the magnetic moments are:

$$|\mu_S| = \{S(S+1)\}^{\frac{1}{2}} g_S \mu_{\mathrm{B}} = 2.96 \times 2\mu_{\mathrm{B}} = 5.92\mu_{\mathrm{B}}$$
$$|\mu_L| = \{L(L+1)\}^{\frac{1}{2}} \mu_{\mathrm{B}} = 5.47\mu_{\mathrm{B}}$$

Calculating the Landé **g**-factor

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} = 1.5 + \frac{8.75 - 30}{17.5} = 0.29$$

Therefore

$$|\mu_J| = \{J(J+1)\}^{\frac{1}{2}} g_J \mu_{\mathrm{B}} = 2.96 \times 0.29\mu_{\mathrm{B}} = 0.86\mu_{\mathrm{B}}$$

(*c*) There are $2J + 1 = 6$ levels. The energy of each level has the form
$E = -\mu_J \cdot \underline{B} = m_J g \mu_{\mathrm{B}} B$
The magnetic flux density is,
$B = \mu_0 H = 4\pi \times 10^{-7} \times 1.6 \times 10^6 = 2\ \mathrm{T}$,
and the smallest separation between the two levels is
$\Delta E = \Delta m_J g_J \mu_{\mathrm{B}} B = 1 \times 0.29 \times 9.27 \times 10^{-24} \times 2 = 5.38 \times 10^{-24}$ J.

The energy of the photons required to excite a transition between the two levels is $h\nu = \Delta E$. Therefore, the frequency of the electromagnetic radiation is $\nu = 5.38 \times 10^{-24}/6.63 \times 10^{-34} = 0.81 \times 10^{10}$ Hz i.e. 8.1 GHz. This corresponds to microwaves, which are typically used in electron spin resonance.

(*d*) We expect Curie's law to be applicable when $\frac{g_J \mu_{\mathrm{B}} J B}{k_{\mathrm{B}} T} \ll 1$, (or usually, $B/T \ll 1$). For the solid containing Sm^{3+} ions,

$$\frac{g_J \mu_{\mathrm{B}} J B}{k_{\mathrm{B}} T} = \frac{0.29 \times 9.27 \times 10^{-24} \times 2.5 \times 2}{1.38 \times 10^{-23} \times T} = 0.97/T.$$

hence at 300 K, $y = B/T = 0.97/300 = 3.3 \times 10^{-3}$ and we would expect Curie's law to be applicable. Whilst at $T = 1$ K, $y = B/T = 0.97/1 = 0.97$ and it is unlikely that Curie's law would be applicable.

(*e*) The maximum magnetisation value of the solid will occur when the saturation magnetisation, $|M_{\text{sat}}| = ng_J\mu_{\text{B}}J$. Therefore, the maximum magnetic moment of the solid will be $|m_{\text{sat}}| = Ng_J\mu_{\text{B}}J$ where N is the total number of atoms in the solid. Hence for 1 mole of solid containing Avogadro's number of atoms we expect the maximum magnetisation

$$|m_{\text{sat}}| = N_A g_J \mu_{\text{B}} J = 6.022 \times 10^{23} \times 0.29 \times 9.27 \times 10^{-24} \times 2.5 = 4.05 \text{ A m}^2$$

(*f*) The first excited state occurs at $J = |L - S + 1| = 3.5$. The spin-orbit energy of each state is $E_{SO} = \lambda(\underline{L} \cdot \underline{S})$ where $\underline{L} \cdot \underline{S}$ may be determined by starting with $\underline{J} = \underline{L} + \underline{S}$ and taking the dot product of itself:

$$\underline{J} \cdot \underline{J} = (\underline{L} + \underline{S}) \cdot (\underline{L} + \underline{S})$$

$$\underline{J}(\underline{J} + 1) = \underline{L}(\underline{L} + 1) + \underline{S}(\underline{S} + 1) + 2\underline{L} \cdot \underline{S}$$

Re-arranging gives

$$\underline{L} \cdot \underline{S} = \frac{\underline{J}(\underline{J} + 1) - \underline{L}(\underline{L} + 1) - \underline{S}(\underline{S} + 1)}{2}$$

Hence,

$$E_{SO} = \lambda \frac{\underline{J}(\underline{J} + 1) - \underline{L}(\underline{L} + 1) - \underline{S}(\underline{S} + 1)}{2}.$$

For the ground state $S = 2½$, $J = 2½$, and $L = 5$
For the 1st excited state $S = 2½$, $J = 3½$, and $L = 5$
Therefore, as S and L are common to both states,

$$\Delta E_{SO} = E_{SO}(J = 3.5) - E_{SO}(J = 2.5) = \lambda \frac{[3.5(3.5 + 1) - 2.5(2.5 + 1)]}{2} = 28 \times \frac{7}{2} = 99.5 \text{ meV}$$

(*g*) From part (*b*) the effective number of Bohr magnetons, μ_{eff}, is

$$|\mu_J| = \{J(J + 1)\}^{\frac{1}{2}} g_J \mu_{\text{B}} = \mu_{\text{eff}} \mu_{\text{B}} = 0.86\mu_{\text{B}}$$

while the experimental value at room temperature is $1.5\mu_{\text{B}}$. The result of part (*f*) suggests that, given the room temperature thermal energy is about 26 meV, partial occupation of the first excited state is likely. This state has $S = 2½$, $J = 3½$, and $L = 5$

$$g_J = \frac{3}{2} + \frac{S(S + 1) - L(L + 1)}{2J(J + 1)} = 1.5 + \frac{8.75 - 30}{7 \times 4.5} = 0.83$$

and $|\mu_J| = \{J(J + 1)\}^{\frac{1}{2}} g_J \mu_{\text{B}} = \mu_{\text{eff}} \mu_{\text{B}} = 3.4\mu_{\text{B}}$.