Magnetism in materials

Solutions - Week 02

1. Spin-orbit coupling originates from the interaction between the inherent magnetic moment (spin) of an electron and the magnetic field created by its motion. For a single electron, this interaction is effectively expressed as $A\mathbf{L}\cdot\mathbf{S}$. Show that $[\mathbf{L}\cdot\mathbf{S}, L_x] = i\hbar(\mathbf{L}\times\mathbf{S})_x$. Does $\mathbf{L}\cdot\mathbf{S}$ commute with $\mathbf{L}$ and $\mathbf{S}$? What about $\mathbf{L}^2$ and $\mathbf{S}^2$? Is the total angular momentum operator $\mathbf{J} = \mathbf{L}+\mathbf{S}$ a conserved quantity? Based on the above perspective about conserved quantities, show that the eigenvalues of the spin-orbit Hamiltonian are $\propto j(j+1) - l(l+1) - s(s+1)$.

solution

$$\begin{aligned}
[\mathbf{L}\cdot\mathbf{S}, L_x] &= [L_xS_x + L_yS_y + L_zS_z, L_x] \\
&= [L_xS_x, L_x] + [L_yS_y, L_x] + [L_zS_z, L_x] \\
&= 0 - i\hbar L_zS_y + i\hbar L_yS_z \\
&= i\hbar(\mathbf{L}\times\mathbf{S})_x
\end{aligned}$$

Similarly, $[\mathbf{L}\cdot\mathbf{S}, L_y] = i\hbar(\mathbf{L}\times\mathbf{S})_y$ and $[\mathbf{L}\cdot\mathbf{S}, L_z] = i\hbar(\mathbf{L}\times\mathbf{S})_z$. As, $\mathbf{L}\cdot\mathbf{S}$ does not commute with the individual components of $\mathbf{L}$, $[\mathbf{L}\cdot\mathbf{S}, \mathbf{L}] \neq 0$.

Now,

$$\begin{aligned}
[\mathbf{L}\cdot\mathbf{S}, \mathbf{L}^2] &= [\mathbf{L}\cdot\mathbf{S}, \mathbf{L}\cdot\mathbf{L}] \\
&= [\mathbf{L}\cdot\mathbf{S}, \mathbf{L}]\cdot\mathbf{L} + \mathbf{L}\cdot[\mathbf{L}\cdot\mathbf{S}, \mathbf{L}] \\
&= i\hbar(\mathbf{L}\times\mathbf{S})\cdot\mathbf{L} + i\hbar\mathbf{L}\cdot(\mathbf{L}\times\mathbf{S}) \\
&= 0
\end{aligned}$$

The analysis remain same with $\mathbf{S}$ with $\mathbf{L}\to\mathbf{S}$. For example,

$$\begin{aligned}
[\mathbf{L}\cdot\mathbf{S}, S_x] &= [L_xS_x + L_yS_y + L_zS_z, S_x] \\
&= [L_xS_x, S_x] + [L_yS_y, S_x] + [L_zS_z, S_x] \\
&= 0 - i\hbar L_yS_z + i\hbar L_zS_y.
\end{aligned}$$

Now,

$$\begin{aligned}
[\mathbf{L}\cdot\mathbf{S}, L_x + S_x] &= [\mathbf{L}\cdot\mathbf{S}, L_x] + [\mathbf{L}\cdot\mathbf{S}, S_x] \\
&= -i\hbar L_zS_y + i\hbar L_yS_z - i\hbar L_yS_z + i\hbar L_zS_y. \\
&= 0.
\end{aligned}$$

Therefore, $[\mathbf{L}\cdot\mathbf{S}, \mathbf{J}] = [\mathbf{L}\cdot\mathbf{S}, \mathbf{L}+\mathbf{S}] = 0$.

Use $\mathbf{J}^2 = (\mathbf{L}+\mathbf{S})^2$ to write

$$\mathbf{L}\cdot\mathbf{S} = \frac{1}{2}\left(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2\right).$$

As we have proved that $\mathbf{J}^2$, $\mathbf{L}^2$, and $\mathbf{S}^2$ are all conserved quantities of $\mathbf{L}\cdot\mathbf{S}$, the right-hand side can be replaced by a pure number $j(j+1) - l(l+1) - s(s+1)$.

2. The Brillouin function depends on the angular momentum J and on the variable x which is proportional to B/T.

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

Use the Jupiter notebook Ex1.ipynb to plot the function and observe how it changes when you vary J. What is the limit of the function for $J \to \infty$?
For small x the function is well approximated by a linear trend, find the expression for this line.

solution In the limit $J \to \infty$ the Brillouin function becomes

$$\begin{aligned}
B_\infty(x) &= \coth(x) - \lim_{J\to\infty}\frac{1}{2J}\frac{e^{x/2J}+e^{-x/2J}}{e^{x/2J}-e^{-x/2J}} && (2)\\
&= \coth(x) - \lim_{J\to\infty}\frac{1}{2J}\frac{2+o(x/2J)}{x/J+o(x/2J)} && (3)\\
&= \coth(x) - \frac{1}{x} && (4)
\end{aligned}$$

The Maclaurin expantion of $\coth(x)$ is

$$\coth(x) = \sum_{n=0}^{\infty}\frac{2^{2n}B_{2n}x^{2n-1}}{(2n)!} \tag{5}$$

with B_n the Bernoulli numbers defined as $B_0 = 1$ and $B_n = -\sum_{k=0}^{n-1}\left(\binom{n}{k}\right)\frac{B_k}{n+1-k}$ for $n > 0$. So

$$B_J(x) = \frac{2J+1}{2J}\sum_{n=0}^{\infty}\frac{2^{2n}B_{2n}x^{2n-1}}{(2n)!}\left(\frac{2J+1}{2J}\right)^{2n-1} - \frac{1}{2J}\sum_{n=0}^{\infty}\frac{2^{2n}B_{2n}x^{2n-1}}{(2n)!}\left(\frac{1}{2J}\right)^{2n-1} \tag{6}$$

The therms in sums with $n = 0$ that diverges at $x = 0$ cancels each other and the terms for $n = 1$ gives the linear approximation of the Brillouin function for small x

$$\begin{aligned}
B_{J,\text{lin}}(x) &= \frac{2J+1}{2J}\frac{2^2B_2x}{2!}\frac{2J+1}{2J} - \frac{1}{2J}\frac{2^2B_2x}{2!}\frac{1}{2J} && (7)\\
&= 2B_2x\left[\frac{(2J+1)^2-1}{4J^2}\right] && (8)\\
&= 2B_2x\frac{4J(J+1)}{4J^2} = \frac{(J+1)}{3J}x && (9)
\end{aligned}$$

since $B_2 = \frac{1}{6}$

3. In the regime in which the Brillouin function can be approximated with linear function the magnetic susceptibility χ follows the Curie law

$$\frac{1}{\chi} = \frac{T}{C} \tag{10}$$

Use the Jupiter notebook Ex2.ipynb to plot $1/\chi$ vs T and determine when the Curie law is a good approximation. Use the slider to see the effect of the application of a magnetic field B, what deviations from the Curie law can you observe when the field is applied? Explain why when a finite field B is applied and $T \to 0$ the susceptibility does not diverge as predicted by the Curie law.

Solution The Curie Law is a good approximation at high temperature and in the absence of magnetic fields. At low temperature, when a magnetic field is applied, the susceptibility is smaller than what is predicted by the Curie law, in particular, the curve become almost flat below a certain temperature and the susceptibility does not diverge for T=0. This is because all the spins align to the field and the magnetization saturates to a maximum value.

4. For this exercise, we simulate a measurement of χ at different T and fit the data with the formula

$$\chi(T) = \frac{C}{T} + \chi_0 \tag{11}$$

where χ_0 accounts for Van-Vleck paramagnetism. Use the Jupiter notebook Ex3.ipynb to generate the data and fit them. Based on what you observed in the previous exercises choose for the fit temperatures range $[T_{start}, T_{stop}]$ in which this expression gives a good approximation. Compare the results you get from the fit with the values of C and χ_0 that you can set through the parameters at the beginning of the script for generating the data. With the last part of the script, you can see how the results of the fit vary when the lower limit of the fitting range is changed keeping constant the upper limit at the highest measured Temperature.

solution The Curie constant is given by

$$C = \frac{n\mu_0\mu_{\text{eff}}^2}{3k_B} \tag{12}$$

with

$$\mu_{\text{eff}} = g_J\mu_B\sqrt{J(J+1)} \tag{13}$$

and the Landé factor is

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \tag{14}$$

So the value computed from the parameters set in the simulation is $C \approx 4.71 \times 10^{-6}$ K.

5. Many Uranium compounds are of great current interest as heavy fermion or mixed valent systems. The first thing you want to know is the valence state of uranium and, surprisingly, it is quite difficult to decide whether it is U^{3+} or U^{4+}. You might think that measuring the high-temperature susceptibility which shows a Curie-type behavior, should clinch the point. Let us assume that measurement tells us that the effective moment is $\mu_{\text{eff}} = 3.6\mu_B$, with 1% accuracy. Can you decide whether the valence state is U^{3+} or U^{4+} ?

Hint The orbital configuration for U^{3+} and U^{4+} are respectively $5f^3$ and $5f^2$. The effective moment μ_{eff} is such that we can rewrite the Curie law :

$$\chi = \frac{n\mu_0\mu_{\text{eff}}^2}{3k_BT}$$

Solution The definition of the effective moment and the Landé g factor are :

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$
$$\mu_{\text{eff}} = g_J\mu_0\sqrt{J(J+1)}$$

According to Hund's rules, for U^{3+}, we have :

$$(S, L, J) = \left(\frac{3}{2}, 6, \frac{9}{2}\right)$$
$$g_J = 0.7273$$
$$\frac{\mu_{\text{eff}}}{\mu_B} = 3.6181$$

For U^{4+}, we have :

$$(S, L, J) = (1, 5, 4)$$
$$g_J = 0.8$$
$$\frac{\mu_{\text{eff}}}{\mu_B} = 3.578$$

It is then impossible to choose between those two valence states with the 1% accuracy.

6. SmB_6 is a mixed valent material, containing about 60% trivalent and 40% divalent samarium. Let us assume that only the Sm 4f-electrons contribute to the magnetic susceptibility, ,and that the Sm-ions can be treated as independent (it is a good approximation from $T \approx 100K$ upwards). The Van-Vleck susceptibility is given in this case by :

$$\chi_{VV} = \frac{n\mu_0 2(L+1)S\mu_B^2}{3(J+1)\Delta}$$

With $\Delta = E_{J+1}^0 - E_J^0$ equal to $\Delta/k_B \approx 410K$ for Sm^{2+} ion and $\Delta/k_B \approx 1450K$ for Sm^{3+} ion. $\mathbf{Sm}^{3+}$ and $\mathbf{Sm}^{2+}$ have electronic configuration $[Xe]4f^5$ and $[Xe]4f^6$ respectively. What is the relative importance of the Curie and Van-Vleck terms at room temperature?

Solution Using the Curie's Law and the given Van-Vleck susceptibility :

$$\frac{\chi_{VV}}{\chi_C} = \frac{n\mu_0 2(L+1)S\mu_B^2}{3(J+1)\Delta}\frac{3k_BT}{n\mu_0 g_J^2\mu_B^2 J(J+1)}$$
$$= \frac{2(L+1)Sk_BT}{g_J^2 J(J+1)^2\Delta}$$

According to Hund's rules, for Sm^{3+}, we have :

$$(S, L, J) = \left(\frac{5}{2}, 5, \frac{5}{2}\right)$$
$$g_J = 0.2857$$
$$\frac{\chi_{VV}}{\chi_C} = 2.4828$$

For Sm^{2+}, we have :

$$\begin{aligned}(S, L, J) &= (3, 3, 0)\\ J = 0 &\Rightarrow \chi_C = 0\\ \frac{\chi_{VV}(Sm^{2+})}{\chi_{VV}(Sm^{3+})} &= 9.9024\end{aligned}$$

The total relative importance is then :

$$\frac{0.6\chi_{VV}(Sm^{2+}) + 0.4\chi_{VV}(Sm^{3+})}{0.6\chi_C(Sm^{2+}) + 0.4\chi_C(Sm^{3+})} = \frac{\left(0.6 + 0.4\frac{\chi_{VV}(Sm^{2+})}{\chi_{VV}(Sm^{3+})}\right)}{0.6}\frac{\chi_{VV}(Sm^{3+})}{\chi_C(Sm^{3+})} \approx 18.9$$

7. Oxygen molecules present molecular orbitals as shown in figure 1. Indicates how these orbitals are filled in the ground state. What consequences does this have on the magnetic behaviour of O_2 ?

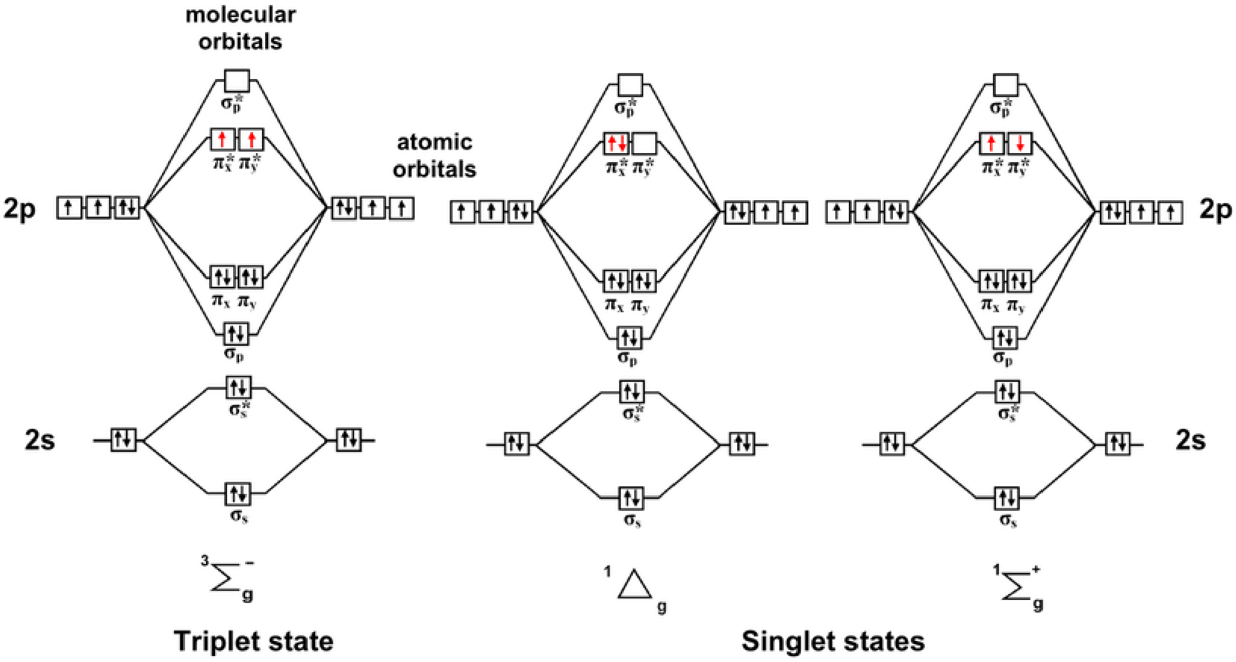

Figure 1:

solution Hund's rules implies that the ground state is the triplet state in which the two electrons in the π^* orbitals have parallel spins. In this state the total spin moment is S=1, so the molecule has non zero magnetic moment and oxygen results paramagnetic.