PHY801: Survey of Atomic and Condensed Matter Physics
Michigan State University

Homework 3 – Solution

3.1. Consider an open-shell atom with 4 electrons in the p-shell (p^4), such as the oxygen atom.

(i) What is the total number of configurations? Just give the number.

(ii) What are the different multiplets $^{2S+1}L_J$ for this open-shell atom? Give their degeneracies.

(iii) What is the lowest-energy multiplet according to the Hund's 1st rule (ignore the spin-orbit interaction)?

(iv) What is the lowest energy multiplet after the spin-orbit interaction is considered ($H_{so} = \lambda_{so}\vec{L}\cdot\vec{S}$)?

(v) What is the spin-orbit splitting?

Solution:

(i) $\binom{6}{4} = \frac{6!}{4!2!} = \frac{6\times5}{2} = 15.$

(ii) ^3P_J , degeneracy $(2L+1)\times(2S+1) = (2\times1+1)\times(2\times1+1) = 9$
$^1D_2$, degeneracy $= (2\times2+1)\times(2\times0+1) = 5$
$^1S_0$, degeneracy $= (2\times0+1)\times(2\times0+1) = 1$
Total number of states = 9+5+1=15 (agrees with (i)). See Fig. 1 for the individual states.

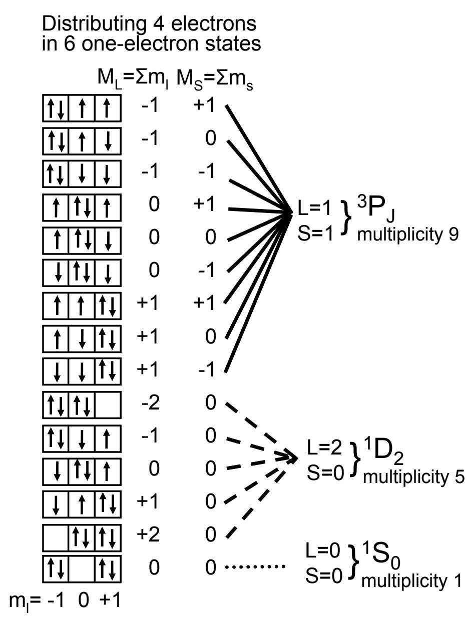

Figure 1: Distributing 4 electrons in 6 one-electron states

(iii) According to Hund's 1st rule, the multiplet with highest spin multiplicity should have the lowest energy. It is ^3P_J.

(iv) Since $L = 1$ and $S = 1$ for the multiplet ^3P_J, thus $J = 2, 1, 0$.
Using $E(L,S,J) = (\lambda_{so}/2)[J(J+1) - L(L+1) - S(S+1)]$, the energies of the states with different

J values are:
$E(1,1,2) = \lambda_{so}$
$E(1,1,1) = -\lambda_{so}$
$E(1,1,0) = -2\lambda_{so}$.
According to Hund's 3rd rule for more than half-filled shell, the multiplet with the highest $J = L+S$ value has the lowest energy. This means that $E(1,1,2)$ should be lowest. This happens because for more than half-filled shell, the spin-orbit coupling constant $\lambda_{so} < 0$.

(v) You can calculate the splitting!

3.2. Using Hund's three rules, work out the lowest energy multiplets of d^1, d^3, d^4, d^7 and f^1, f^3, f^7. Compare your results given in Table 1 and 2 of the Chapter on Diamagnetism and Paramagnetism in Kittel (Ch. 14 in 7th edition, Ch. 11 in 8th edition). Next, calculate the Landé g-factors associated with these lowest-energy multiplets. (Once you know how to do it for a few cases, it should be straight-forward to do the rest.)

Solution: d^n
n=1: $^2D_{3/2}$
n=3: $^4F_{3/2}$
n=4: $^5D_0$
n=7: $^4F_{9/2}$
f^n
n=1: $^2F_{5/2}$
n=3: $^4L = 6_{9/2}$
n=7: $^8S_{7/2}$.

Practice how to calculate the Landé g-factor and effective moment for these multiplets.

3.3. The wave function of the hydrogen atom in its $1s$ ground state is $\psi = (\pi a_B^3)^{-1/2} exp(-r/a_B)$, where a_B is the Bohr radius. Show that for this state $< r^2 >= 3a_B^2$ and calculate the diamagnetic susceptibility for 1 mole of atomic hydrogen enclosed in unit volume. The correct answer is -2.32×10^{-6} cm^3/mole.

Solution:

$$\psi_{1s} = \frac{1}{\sqrt{\pi a_B^3}} e^{-r/a_B}$$

$$< r^2 > = \int \psi_{1s}^* r^2 \psi_{1s} d\vec{r} = \frac{4\pi}{\pi a_B^3} \int_0^\infty e^{-2r/a_B} r^2 r^2 dr = \frac{a_B^2}{8} \int_0^\infty e^{-x} x^4 dx = \frac{a_B^2}{8} 4! = 3a_B^2 \ ,$$

where we have used the substitution $x = 2r/a_B$.

The diamagnetic susceptibility for Avogadros number of atoms is given by

$$\chi_{dia} = -N_A \frac{e^2}{6mc^2} < r^2 >= -N_A \frac{e^2 3a_B^2}{6mc^2} = -N_A \frac{e^2/2a_B}{mc^2} a_B^3 \ .$$

Now use

$$\frac{e^2}{2a_B} = 13.6 \text{ eV} \ ; \ \ mc^2 = 0.522 \text{ MeV} \ ; \ \ a_B = 0.529\times10^{-10} \text{ m} \ ; \ \ N_A = 6.022\times10^{23} \text{ mole}^{-1}$$

to get $\chi_{dia} = -2.32\times10^{-6}$ cm^3/mole.

3.4. Consider the multiplet (L, S, J). Show that the average magnetization $< M >$ for N atoms the presence of an external uniform magnetic field B along the z direction is given by

$$< M >= N\mu_B g_J J B_J(x) \, ,$$

where

$$x = g_J \mu_B J B / k_B T$$

and

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

is the Brillouin function.

Solution:

For a general state Jm_J the energy in the presence of a magnetic field and the magnetic moment are given by

$$E(J, m_J) = \mu_B g_J m_J B \; ; \;\; \mu(J, m_J) = -\mu_B g_J m_J \; .$$

Therefore, at a temperature T, the average magnetic moment of one atom can be obtained by using Boltzmann distribution, as

$$< M >= \frac{-\sum_{m_J=-J}^{m_J=+J} \mu_B g_J m_J e^{-\mu_B g_J m_J B/k_B T}}{\sum_{m_J=-J}^{m_J=+J} e^{-\mu_B g_J m_J B/k_B T}} \; .$$

Put $\mu_B g_J B / k_B T = y$. Then, the average magnetization is given by

$$< M >= \mu_B g_J \frac{-\sum_{m_J=-J}^{m_J=+J} m_J e^{-y m_J}}{\sum_{m_J=-J}^{m_J=+J} e^{-y m_J}} = \mu_B g_J \frac{d}{dy} ln \sum_{m_J=-J}^{m_J=+J} e^{-y m_J} = \mu_B g_J \frac{d}{dy} ln S \; .$$

Here,

$$S = \sum_{m_J=-J}^{m_J=+J} e^{-y m_J} = \frac{e^{Jy}\left(1 - e^{-(2J+1)y}\right)}{(1 - e^{-y})} = \frac{\left[e^{(J+\frac{1}{2})y} - e^{-(J+\frac{1}{2})y}\right]}{\left[e^{y/2} - e^{-y/2}\right]} \; .$$

Then,

$$\frac{d}{dy} ln S = \frac{2J+1}{2} \coth(2J+1)\frac{y}{2} - \frac{1}{2} \coth\frac{y}{2} \; .$$

Substituting for y we get for N atomic magnets

$$< M >= N\mu_B g_J J \left[\frac{(2J+1)}{2J} \coth\frac{(2J+1)\mu_B g_J B}{2k_B T} - \frac{1}{2J} \coth\frac{\mu_B g_J B}{2k_B T}\right] \; .$$

Kittel, in his book, defines the quantity $\mu \equiv \mu_B g_J$. We next define a dimensionless quantity x by

$$x = \frac{\mu_B g_J J B}{k_B T} = \frac{\mu J B}{k_B T} \; .$$

We then get the average magnetic moment

$$< M >= N\mu_B g_J J B_J(x) \, ,$$

where

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

is the Brillouin function.
