

PHY 491
Home Work Assignment #3
September 19-26, 2011

3.1

What is the total number of configurations for an open shell atom with 4 electrons in the p-shell (p^4), as in the oxygen atom. Just give the number.

$$6 \times 5 \times 4 \times 3 / 4! = 6! / 4!2! = 15$$

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

$${}^3P_J, \text{multiplicity } (2L+1)(2S+1) = (2 \times 1 + 1)(2 \times 1 + 1) = 9$$

$${}^1D_J, \text{multiplicity} = (2 \times 2 + 1)(2 \times 0 + 1) = 5$$

$${}^1S_0, \text{multiplicity} = (2 \times 0 + 1)(2 \times 0 + 1) = 1$$

$$\text{Total number of states} = 9 + 5 + 1 = 15 \text{ (Checks!)}$$

What is the lowest energy multiplet according to the Hund's rule, before allowing for spin orbit interaction?

According to Hund's 1st rule the multiplet with highest spin multiplicity should have the lowest energy. 3P_J

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

Since for the multiplet 3P_J , $L=1, S=1, J=2,1,0$. The energies of the states with different J values are:

$$\text{Use } E(L, S, J) = (\lambda_{so} / 2) [J(J+1) - L(L+1) - S(S+1)]$$

$$E(1,1,2) = \lambda_{so}$$

$$E(1,1,1) = -\lambda_{so}$$

$$E(1,1,0) = -2\lambda_{so}$$

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

What are the spin orbit splittings? 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 the Table 1 and 2 of Chapter 11, Diamagnetism and Paramagnetism, of Kittel.

Calculate the Lande g-factors associated with these lowest energy multiplets.

(Once you know how to do it for a few cases it should be straight forward for the rest)

$$\begin{aligned}
 & d^n \\
 n=1: & \quad {}^2D_{3/2} \\
 n=3: & \quad {}^4F_{3/2} \\
 n=4: & \quad {}^5D_0 \\
 n=7: & \quad {}^4F_{9/2} \\
 & f^n \\
 n=1: & \quad {}^2F_{5/2} \\
 n=3: & \quad {}^4L = 6_{9/2} \\
 n=7: & \quad {}^8S_{7/2} \\
 & f^n
 \end{aligned}$$

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

3.3

The wave function of the hydrogen atom in its ground state (1s) is $\psi = (\pi a^3)^{-1/2} \exp(-r/a)$. Here a is the Bohr radius. Show that for this state $\langle r^2 \rangle = 3a^2$ and calculate the diamagnetic susceptibility for 1 mole of atomic hydrogen. The correct answer is $-2.36 \times 10^{-6} \text{ cm}^3 / \text{mole}$.

$$\begin{aligned}
 \psi_{1s} &= \frac{1}{(\pi a^3)^{1/2}} e^{-r/a} \\
 \langle r^2 \rangle &= \int \psi_{1s}^* r^2 \psi_{1s} d\tau = \frac{4\pi}{\pi a^3} \int_0^\infty e^{-2r/a} r^2 r^2 dr = \frac{a^2}{8} \int_0^\infty e^{-x} x^4 dx = \frac{a^2}{8} 4! = 3a^2
 \end{aligned}$$

In the above derivation we substituted $\frac{2r}{a} = x$.

The diamagnetic susceptibility for Avogadro's number of atoms is given by

$$\chi_{dia} = -N_A \frac{e^2}{6mc^2} \langle r^2 \rangle = -N_A \frac{e^2 3a^2}{6mc^2} = N_A \frac{e^2/2a}{mc^2} a^3$$

Now use: $\frac{e^2}{2a} = 13.6 \text{ eV}$; $mc^2 = 0.522 \text{ MeV}$; $a = 5.29 \times 10^{-9} \text{ cm}$; $N_A = 6.022 \times 10^{23} / \text{mole}$

$$\chi_{dia} = -2.3 \times 10^{-6} \text{ cm}^3 / \text{mole}$$

3.4

For 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

$$M = N g_J \mu_B B_J(x); \quad x = g_J \mu_B B / k_B T$$

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

For a general state $|m_j\rangle$ the energy in the presence of a magnetic field and the magnetic moment are given by

$$E(|m_j\rangle) = \mu_B g_J m_j B; \quad \mu(|m_j\rangle) = -\mu_B g_J m_j$$

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

$$\langle M \rangle = \frac{-\sum_{m_j=-J}^{m_j=+J} \mu_B g_J m_j e^{-\mu_B g_J m_j B / k_B T}}{\sum_{m_j=-J}^{m_j=+J} e^{-\mu_B g_J m_j B / k_B T}}$$

Put $\frac{\mu_B g_J B}{k_B T} = y$. Then the average magnetization is given by

$$\langle M \rangle = -\mu_B g_J \frac{\sum_{m_j=-J}^{m_j=+J} m_j e^{-y m_j}}{\sum_{m_j=-J}^{m_j=+J} e^{-y m_j}} = \mu_B g_J \frac{d}{dy} \ln \sum_{m_j=-J}^{m_j=+J} e^{-y m_j} = \mu_B g_J \frac{d}{dy} \ln S$$

$$S = \sum_{m_j=-J}^{m_j=+J} e^{-y m_j} = \frac{e^{Jy} (1 - e^{-(2J+1)y})}{(1 - e^{-y})} = \frac{[e^{(J+\frac{1}{2})y} - e^{-(J+\frac{1}{2})y}]}{[e^{y/2} - e^{-y/2}]}$$

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

Substituting for y we get for N atomic magnets

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

In Kittel's book he defines a quantity $\mu \equiv \mu_B g_J$. If we define a dimensionless quantity x

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

Then we get the average magnetic moment in the form of Brillouin function, $B_J(x)$.

$$\langle M \rangle = N \mu_B g_J B_J(x)$$

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