Chapter 7 - Many-Electron Atoms

7-1: (a) Using Equations (7.4) and (6.41), the energy difference is

$$\Delta E = 2\,\mu_{sz}\,B = 2\,\mu_B\,B = 2\,\left(5.788\times10^{-5}\ \text{eV/T}\right)\,(1.20\ \text{T}) = 1.39\times10^{-4}\ \text{eV}.$$

(b) The wavelength of the radiation that corrsponds to this energy is

$$\lambda = \frac{hc}{\Delta E} = \frac{1.240\times10^{-6}\ \text{eV}\cdot\text{m}}{1.389\times10^{-4}\ \text{eV}} = 8.93\ \text{mm}.$$

Note that a more precise value of ΔE was needed in the intermediate calculation to avoid roundoff error.

7-3: For an electron, $s = \left(\sqrt{3}/2\right)\,\hbar$, $s_z = \pm(1/2)\,\hbar$, and so the possible angles are given by

$$\arccos\left(\frac{\pm(1/2)\,\hbar}{\left(\sqrt{3}/2\right)\,\hbar}\right) = \arccos\left(\pm\frac{1}{\sqrt{3}}\right) = 54.7^\circ,\ 125.3^\circ.$$

7-5: ${}^4_2$He atoms contain even numbers of spin-$\frac{1}{2}$ particles, which pair off to give zero or integral spins for the atoms. Such atoms do not obey the exclusion principle. ${}^3_2$He atoms contain odd numbers of spin-$\frac{1}{2}$ particles, and so have net spins of $\frac{1}{2}$, $\frac{3}{2}$ or $\frac{5}{2}$, and they obey the exclusion principle.

7-7: An alkali metal atom has one electron outside closed inner shells: A halogen atom lacks one electron of having a closed outer shell: An inert gas atom has a closed outer shell.

7-9: For and f subshell, with $l = 3$, the possbile values of m_l are ±2, ±2, ±1 or 0, for a total of $2\,l + 1 = 7$ values of m_l. Each state can have two electrons of opposite spins, for a total of 14 electrons.

7-11: The number of elements would be the total number of electrons in all of the shells. Repeated use of Equation (7.14) gives

$$2\,n^2 + 2\,(n-1)^2 + \cdots + 2\,(1)^2 = 2\,(36+25+16+9+4+1) = 182.$$

In general, using the expression for the sum of the squares of the first n integers, the number of elements would be

$$2\left(\frac{1}{6}\,n\,(2\,n+1)\,(n+1)\right) = \frac{1}{3}\left(n\,(2\,n+1)\,(n+1)\right),$$

which gives a total of 182 elements when $n = 6$.

7-13: All of the atoms are hydrogenlike, in that there is a completely filled subshell that screens the nuclear charge and causes the atom to "appear" to be a single charge. The outermost electron in each of these atoms is further from the nucleus for higher atomic number, and hence has a successively lower binding energy.

7-15: (a) See Table 7.4. The $3d$ subshell is empty, and so the effective nuclear charge is roughly $+2e$, and the outer electron is relatively easy to detach.

(b) Again, see Table 7.4. The completely filled K and L shells shield $+10e$ of the nuclear charge of $= 16e$; the filled $3s^2$ subshell will partially shield the nuclear charge, but not to the same extent as the filled shells, so $+6e$ is a rough estimate for the effective nuclear charge. This outer electron is then relatively hard to detach.

7-17: Cl^- ions have closed shells, whereas a Cl atom is one electron short of having a closed shell and the relatively poorly shielded nuclear charge tends to attract an electron from another atom to fill the shell.

Na^+ ions have closed shells, whereas an Na atom has a single outer electron that can be detached relatively easily in a chemical reaction with another atom.

7-19: The Li atom ($Z = 3$) is larger because the effective nuclear charge acting on its outer electron is less than that acting on the outer electrons of the F atom ($Z = 9$). The Na atom ($Z = 11$) is larger because it has an additional electron shell (see Table 7.4). The Cl atom ($Z = 17$) atom is larger beacuse has an additional electron shell. The Na atom is larger than the Si atom ($Z = 14$) for the same reason as given for the Li atom.

7-21: The only way to produce a normal Zeeman effect is to have no net electron spin; because the electron spin is $\pm\frac{1}{2}$, the total number of electrons must be even. If the total number of electrons were odd, the net spin would be nonzero, and the anamolous Zeeman effect would be observable.

7-23: See Example 7.6. Expressing the difference in energy levels as

$$\Delta E = 2\,\mu_B\,B = hc\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right); \qquad \text{solving for } B,$$

$$\begin{aligned} B &= \frac{hc}{2\,\mu_B}\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right) \\ &= \frac{\left(1.240 \times 10^{-6}\ \text{eV}\cdot\text{m}\right)}{2\ (5.788 \times 10^{-5}\ \text{eV/T})}\left(\frac{1}{589.0 \times 10^{-9}\ \text{m}} - \frac{1}{589.6 \times 10^{-9}\ \text{m}}\right) = 18.5\ \text{T}. \end{aligned}$$

7-25: The possible values of l are $j + \frac{1}{2} = 3$ and $j - \frac{1}{2} = 2$.

7-27: For the ground state to be a singlet state with no net angular momentum, all of the subshells must be filled.

7-29: For this doublet state, $\mathsf{L} = 0$, $\mathsf{S} = \mathsf{J} = \frac{1}{2}$. There are no other allowed states. This state has the lowest possible values of L and J, and is the only possible ground state.

7-31: The two $3s$ electrons have no orbital angular momentum, and their spins are aligned oppositely to give no net angular momentum. The $3p$ electron has $l = 1$, so $\mathsf{L} = 1$, and in the ground state $\mathsf{J} = \frac{1}{2}$. The term symbol is ${}^2P_{1/2}$.

7-33: A D state has $\mathsf{L} = 2$; for a $2^2D_{3/2}$ state, $n = 2$ but L must always be strictly less than n, and so this state cannot exist.

7-35: (a) From Equation (7.17), $j = l \pm \frac{1}{2} = \frac{5}{2}, \frac{7}{2}$.

(b) Also from Equation (7.17), the corresponding angular momenta are $\dfrac{\sqrt{35}}{2}\,\hbar$ and $\dfrac{\sqrt{63}}{2}\,\hbar$.

(c) The values of L and S are $\sqrt{12}\,\hbar$ and $\dfrac{\sqrt{3}}{2}\,\hbar$. The law of cosines is

$$\cos\theta = \frac{J^2 - L^2 - S^2}{2\,L\,S},$$

where θ is the angle between $\mathbf{L}$ and $\mathbf{S}$; then the angles are,

$$\arccos\left(\frac{(35/4) - 12 - (3/4)}{2\sqrt{12}\,((\sqrt{3})/2)}\right) = \arccos\left(-\frac{2}{3}\right) = 132.0^\circ$$

and

$$\arccos\left(\frac{(63/4) - 12 - (3/4)}{2\sqrt{12}\,((\sqrt{3})/2)}\right) = \arccos\left(\frac{1}{2}\right) = 60.0^\circ.$$

(d) The multiplicity is $2\left(\frac{1}{2}\right) + 1 = 2$, the state is an f state because the total angular momentum is provided by the f electron, and so the terms symbols are ${}^2F_{5/2}$ and ${}^2F_{7/2}$.

7-37: (a) In Figure 7.15, let the angle between **J** and **S** be α and the angle between **J** and **L** be β. Then, the product $\mu_J\,\hbar$ has magnitude

$$2\,\mu_B\ |\mathbf{S}|\ \cos\alpha + \mu_B\ |\mathbf{L}|\ \cos\beta = \mu_B\ |\mathbf{J}| + \mu_B\ |\mathbf{S}|\cos\alpha = \mu_B\,|\mathbf{J}|\left(1 + \frac{|\mathbf{S}|}{|\mathbf{J}|}\cos\alpha\right).$$

In the above, the factor of 2 in $2\,\mu_B$ relating the electron spin magnetic moment to the Bohr magneton is from Equation (7.3). The middle term is obtained by using $|\mathbf{S}|\cos\alpha + |\mathbf{L}|\cos\beta = |\mathbf{J}|$. The above expression is equal to the product $\mu_J\,\hbar$ because in this form, the magnitudes of the angular momenta include factors of $\hbar$.

From the law of cosines,

$$\cos\alpha = \frac{|\mathbf{L}|^2 - |\mathbf{J}|^2 - |\mathbf{S}|^2}{-2\ |\mathbf{J}|\ |\mathbf{S}|},$$

and so

$$\frac{|\mathbf{S}|}{|\mathbf{J}|}\cos\alpha = \frac{|\mathbf{L}|^2 - |\mathbf{J}|^2 - |\mathbf{S}|^2}{2\ |\mathbf{J}|^2} = \frac{\mathsf{J}\,(\mathsf{J}+1) - \mathsf{L}\,(\mathsf{L}+1) + \mathsf{S}\,(\mathsf{S}+1)}{2\,\mathsf{J}\,(\mathsf{J}+1)},$$

and the expression for μ_J in terms of the quantum numbers is

$$\mu_J\hbar = |\mathbf{J}|\ g_J\,\mu_B, \qquad \text{or} \qquad \mu_J = \mathsf{J}\,(\mathsf{J}+1)\ g_J\,\mu_B, \qquad \text{where}$$

$$g_J = 1 + \frac{\mathsf{J}\,(\mathsf{J}+1) - \mathsf{L}\,(\mathsf{L}+1) + \mathsf{S}\,(\mathsf{S}+1)}{2\,\mathsf{J}\,(\mathsf{J}+1)}.$$

(b) There will be one substate for each value of M_J, where $M_J = -\mathsf{J}\ \ldots\ \mathsf{J}$, for a total of $2\mathsf{J}+1$ substates. The difference in energy between the substates is

$$\Delta E = g_J\,\mu_B\,M_J\,B.$$

7-39: The transitions that give rise to x-ray spectra are the same in all elements since the transitions involve only inner, closed-shell electrons. Optical spectra, however, depend upon the possible states of the outermost electrons, which, together with the transitions permitted for them, are different for atoms of different atomic number.

7-41: From either of Equations (7.21) or (7.22),

$$E = (10.2\text{ eV})\,(Z-1)^2 = (10.2\text{ eV})\ (144) = 1.47\text{ keV}.$$

The wavelength is

$$\lambda = \frac{hc}{E} = \frac{1.240\times10^{-6}\text{ eV}\cdot\text{m}}{14.7\times10^3\text{ eV}} = 8.44\times10^{-10}\text{ m} = 0.844\text{ nm}.$$

7-43: In a singlet state, the spins of the outer electrons are antiparallel. In a triplet state, they are parallel.