Atomic & Molecular Physics Solution to Problem Sheet 2224.2
Issued Thursday 7 February 2008, due in Thursday 14 February 2008

1. If α and β are the simultaneous eigenstates of $\hat{s}^2$ (spin) and $\hat{s}_z$, then:

$$\hat{s}^2\alpha = \frac{1}{2}(\frac{1}{2}+1)\hbar^2\alpha = \frac{3}{4}\hbar^2\alpha;\ \hat{s}_z\alpha = +\frac{1}{2}\hbar\alpha$$

and:

$$\hat{s}^2\beta = \frac{1}{2}(\frac{1}{2}+1)\hbar^2\beta = \frac{3}{2}\hbar^2\beta;\ \hat{s}_z\beta = -\frac{1}{2}\hbar\beta$$

[2]

Possible combinations of two one-electron spin wavefunctions are:

$$\alpha(1)\alpha(2),\ \beta(1)\beta(2),\ \frac{1}{\sqrt{2}}(\alpha(1)\beta(2)+\beta(1)\alpha(2)),\ \frac{1}{\sqrt{2}}(\alpha(1)\beta(2)-\beta(1)\alpha(2))$$

[2]

Operating with $\hat{S}_z$:

$$\begin{aligned}
\hat{S}_z\alpha(1)\alpha(2) &= (\frac{1}{2}+\frac{1}{2})\alpha(1)\alpha(2) \\
&= \alpha(1)\alpha(2) \\
\hat{S}_z\beta(1)\beta(2) &= (-\frac{1}{2}-\frac{1}{2})\beta(1)\beta(2) \\
&= -\beta(1)\beta(2) \\
\hat{S}_z\frac{1}{\sqrt{2}}(\alpha(1)\beta(2)+\beta(1)\alpha(2)) &= (\frac{1}{2}-\frac{1}{2}+\frac{1}{2}-\frac{1}{2})\frac{1}{\sqrt{2}}(\alpha(1)\beta(2)+\beta(1)\alpha(2)) \\
&= 0 \\
\hat{S}_z\frac{1}{\sqrt{2}}(\alpha(1)\beta(2)-\beta(1)\alpha(2)) &= (-\frac{1}{2}+\frac{1}{2}+\frac{1}{2}-\frac{1}{2})\frac{1}{\sqrt{2}}(\alpha(1)\beta(2)+\beta(1)\alpha(2)) \\
&= 0
\end{aligned}$$

[4]

And so the first three wavefunctions canbe grouped as a spin triplet with total spin $S = 1$, as $M_S = 1, 0, -1$ and the states are symmetric under exchange, and the remaining state is a spin singlet ($S = 0$ and antisymmetric). **[2]**

The Pauli exclusion principal means that the symmetric (triplet) spin wavefunction is associated with an antisymmetric spatial wavefunction. In helium this space wavefunction is identically zero if the two electrons have the same spatial co-ordinate, so (qualitatively, semi-classically) the electrons are forced to keep apart by the symmetry of the wavefunction. This is not the case for the spin singlet where the electrons can exist very close to one another. In the triplet state, therefore, the electrons are exposed to a greater Coulomb attraction from the nucleus (no mutual shielding), and are more tightly bound (lower in energy.) **[2]**

2. The central field approximation is a way of dealing with the electron-electron interactions in a multi-electron atom. This is done by writing a spherically symmetric (central) potential which represents the interaction of the electron with the nucleus *screened* by the other electrons. This description is most useful for atoms with a single valence electron which sees a tightly bound inner core of electron screening the nucleus. This atom is then 'hydrogen-like' (i.e. a single optically active electron), and the energy levels are similar to those of hydrogen with a deviation characterised by the *quantum defect*, Δ_{nl}. **[4]**

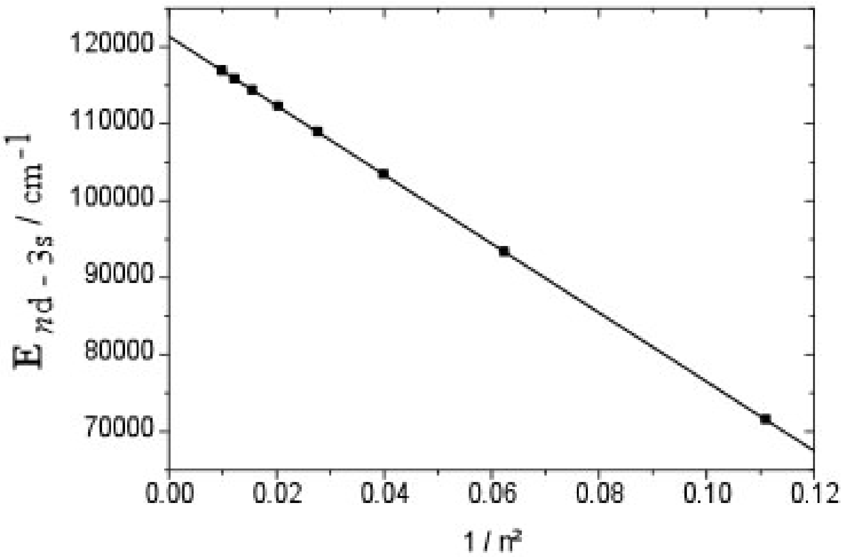
   Since $E_{nl} = -\frac{Z_{\mathrm{eff}}^2 R_\infty}{(n-\Delta_{nl})^2}$ we can derive a Rydberg-like formula for the wavelength of the photon associated with the 2s → nd transition:

$$E_{n\mathrm{d}\rightarrow 3\mathrm{s}} = Z_{eff}^2 R_\infty \left(\frac{1}{(3-\Delta_{3\mathrm{s}})^2} - \frac{1}{(n-\Delta_{n\mathrm{d}})^2} \right)$$

   Quantum defects for d-states are small, so $\Delta_{n\mathrm{d}} \rightarrow 0$, and we can write

$$E_{n\mathrm{p}\rightarrow 3\mathrm{s}} \approx \frac{Z_{eff}^2 R_\infty}{(3-\Delta_{3\mathrm{s}})^2} - \frac{Z_{eff}^2 R_\infty}{n^2}$$

   So a graph of $E_{n\mathrm{d}\rightarrow 3\mathrm{s}}$ vs $\frac{1}{n^2}$ will be approximately a straight line. The graph is plotted below, for plotting the graph: **[5]**



   The intercept on the $E_{n\mathrm{d}\rightarrow 3\mathrm{s}}-$ axis is $\frac{Z_{eff}^2 R_\infty}{(3-\Delta_{3s})^2}$, the energy needed to completely remove the electron, which is

$$\frac{Z_{eff}^2 R_\infty}{(3-\Delta_{3s})^2} = 121344\ \mathrm{cm}^{-1}$$

[1]

3. Hund's Rules for the ordering of terms are:

   1. The term with the largest value of S has the lowest energy. The energy of other terms increases with decreasing S
   2. For a given value of S the term having the maximum value of L has the lowest energy
   3(a) **Normal case** - outershell is less than half-full. The lowest energy in the lowest energy term corresponds to the smallest J value
   3(b) **Inverted case** - outershell is more than half-full. The lowest energy in the lowest energy term corresponds to the largest J value
   3(c) When the subshell is half full there is no multiplet splitting. **[4]**

   The electron configuration for aluminium is $1s^2 2s^2 2p^6 3s^2 3p^1$. **[1]**

   There is just one electron in an unfilled subshell to consider. The spin is $s = \frac{1}{2}$, orbital angular momentum $l = 1$, and so possible values of total angular momentum are $j = 1 \pm \frac{1}{2} = \frac{1}{2}, \text{or} \frac{3}{2}$. The term symbols are therefore

   $$^2p_{\frac{1}{2}}, \text{ and } ^2p_{\frac{3}{2}}$$

   [2]

   As both term have the same s and l we need to use the third Hund's Rule to split them. The ^{2}p subshell is less than half-full, so we have the 'Normal case' (rule 3(a) above), and so the lowest j lies lowest in energy, i.e.

   $$E(^2p_{\frac{1}{2}}) < E(^2p_{\frac{3}{2}})$$

   [1]

   The configuration for Al^+ is therefore $1s^2 2s^2 2p^6 3s^2$. **[1]**

   By comparison with helium, configuration $1s^2$, we can deduce that since we have two electrons in an s-subshell the allowed term must be he same, i.e. $^1S_0$. **[1]**