Assignment 5 Solutions

5.1 For the $2s^2\,3s$ configuration, we can neglect the two $2s$ electrons because they are in a full subshell. We focus on the single $3s$ electron: it has $s = 1/2$ (only one electron) and thus $S = 1/2$ so that $2S + 1 = 2$ (a doublet state), and it has $l = 0$ (it’s in an s orbital) so that $L = 0$ and the $L$ symbol is $S$. There is only one possible $J$ value: $J = j = l + s = 1/2$. The term symbol is thus $^2S_{1/2}$. Likewise, the $2s^2\,3d$ configuration gives the $^2D_{5/2}$ and $^2D_{3/2}$ states: $l = 2$ (a D term), $s = 1/2$ (doublet again), so $j = J = 2 + 1/2 = 5/2$ or $2 - 1/2 = 3/2$. For the $2s\,2p^2$ configuration, we have three electron spins that make up the total spin quantum number, and we have to consider them all, since none of them are in closed shells or subshells. Each has $s = 1/2$, of course, and we start by adding the first two: $s_{12}$ can be $s_1 + s_2 = 1$ or $s_1 - s_2 = 0$. Then we combine $s_3$ with each $s_{12}$ possibility: $s_{123} = S$ can be $s_{12} + s_3 = 3/2$ or $s_{12} - s_3 = 1/2$ if $s_{12} = 1$ or, for the $s_{12} = 0$ case, $s_{123}$ can be $s_{12} + s_3 = 0 + 1/2 = 1/2$ only, but this is not a new value. Thus the two spin multiplicities possible for the $2s\,2p^2$ configuration are doublet (for $S = s_{123} = 1/2$) and quartet (for $S = s_{123} = 3/2$).

5.2 Figure 13.7 tells us that the ground-state term symbol for Cr is $^7S_3$, and our task is to understand how this term symbol comes from the $4s^1\,3d^5$ configuration. To do so, all we need are Hund’s Rules and the consequence of filled or half-filled shells. Hund’s Rules tell us that the highest spin multiplicity is lowest in energy. For this configuration, the highest multiplicity comes from distributing the spins among the atomic orbitals in a way that has them all unpaired. To satisfy the Pauli Exclusion Principle, we must, therefore, put each electron in a unique orbital, as in the diagram below:

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↑  ↑  ↑  ↑  ↑
4s   3d
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This arrangement has a total spin quantum number $S = 6 × (1/2) = 3$, or a multiplicity $(2S + 1) = 7$, as expected. Now we notice that each atomic orbital is either full (those in the core of the configuration, at energies below the valence electrons’) or half full (those we see here), and for each $l$ value, we have all possible $m$ value orbitals half full. Such configurations make the atom spherical, and spherical atoms have zero total orbital angular momentum. Noorbital angular momentum means $L = 0$, which means we have an S term symbol. If $S = 3$ and $L = 0$, then $J = 3$, and we have the $^7S_3$ term symbol for this configuration. Alternatively, we could start with the $4s^2\,3d^5\,6S_{5/2}$ ground state of Mn, for which $S = 5/2$ and $L = 0$. Since the $4s^2$ configuration makes no contribution (it’s a closed subshell), we see that the lowest energy state from any $3d^5$ configuration must be a $^6S_{5/2}$ state. Thus, for Cr, we couple the $4s^1$ electron ($s = 1/2$, $l = 0$) to this $3d^5$ state and find $S = 5/2 + 1/2 = 3$ at most or $5/2 - 1/2 = 2$ at least. Again, Hund’s Rules tell us to pick $S = 3$ for the ground state, since
the highest $S$ is the lowest energy. Since $l = 0$, $L$ is zero as well, and we again conclude that the Cr ground state is an $S$ term.

Mo behaves like Cr, but W has a $^5D_0$ ground state, and we need to figure out why. If W has the ground-state configuration $6s^1 5d^5$ in analogy with Cr, then Hund says it should have a $^7S_3$ ground-state term symbol. If we look at Table 13.2, we see that a $d^5$ configuration can lead to a $^4D$ term, and if we couple a single $s$ electron to this term, we can arrive at a $^5D$ term, which tells us that the $^5D_0$ observed term is at least possible for the $6s^1 5d^5$ configuration. But this table also tells us that $d^5$ can produce $^4F$ and $^4G$ terms, and if we couple our single $s$ electron to these terms, we would generate two possibilities, $^5F$ and $^5G$, that have greater $L$ values (3 and 4) than $^5D$ has ($L = 2$), which means than W would have to violate both of Hund’s first two rules: not only would the greatest multiplicity term not be lowest, but the greatest $L$ of any one multiplicity would not be lowest either. So we consider the $6s^2 5d^4$ possibility. Table 13.2 tells us that the $d^4$ configuration leads to only one term of highest (quintet) multiplicity, $^5D$, and this is what is observed. Thus, we’re safe in concluding that the ground-state configuration of W is $6s^2 5d^4$ and that Hund’s Rules are obeyed.

5.3 The P ground-state configuration, $3s^2 3p^3$, is like that for N above P in the Periodic Table. Thus, we turn to Table 13.2 to see what's possible for a $p^3$ configuration (because the $s^2$ closed subshell won't contribute to $S$ or $L$). We find that $p^3$ can yield $^2P$, $^2D$, and $^4S$ terms. Adding $J$ values shows that $^4S$ can be only $^4S_{3/2}$ ($S = 3/2$, $L = 0$, so $J = 3/2$ only). For the doublet states, we have $S = 1/2$, and $^2P$ has $L = 1$, so that $J = 3/2$ and 1/2, while $^2D$ has $L = 2$, so $J = 5/2$ and 3/2. Thus, there are five term symbols in all, and Hund’s rules tell us the quartet is lowest, and the $^2D$’s are lower than the $^2P$’s. Moreover, P is not a heavy atom (third row), and we do not expect spin-orbit energy splitting to be large. Using the hint in the problem that minimum $J$ is lower, we can finally conclude that the ground state is $^4S_{3/2}$, the state at 11361.7 cm$^{-1}$ is the $^2D_{3/2}$, 11376.5 cm$^{-1}$ is $^2D_{5/2}$, 18722.4 cm$^{-1}$ is $^2P_{1/2}$, and 18748.1 cm$^{-1}$ is $^2P_{3/2}$.

5.4 The ground state of Be has the configuration $1s^2 2s^2$ and the term symbol $^1S_0$, just like He. If we stick two Be atoms together, we will have the MO configuration $1\sigma_g^2 1\sigma_u^* 2\sigma_g^2 2\sigma_u^*$ for a bond order of zero and a prediction of no bond. (The slight bond energy of Be$_2$ is due to noncovalent interactions, the same forces that hold two Ar atoms together, for example, but only very weakly.) Thus, Be$_2$ is never an abundant species in the gas phase (in contrast to, say, Li$_2$, which, due to its real chemical bond, is sufficiently abundant to be seen in the gas phase even at high temperatures.) In contrast, if we excite one or more Be electrons, as in $1s^2 2s^1 2p^1$ where the p electron could be either $p_z$ (contributing to a $\sigma$ MO) or $p_x$ or $p_y$ (contributing to a $\pi$ MO), then we have a shot at an MO configuration with a nonzero bond order: $1\sigma_g^2 1\sigma_u^* 2\sigma_g^2 2\sigma_u^* 3\sigma_g^1$ or $1\sigma_g^2 1\sigma_u^* 2\sigma_g^2 2\sigma_u^* 1\pi_u^1$. These excited states have all been observed and do indeed have greater bond energies than the ground state.