Chapter 8

* 1. The first two electrons are in the $1s$ subshell and have $\ell = 0$, with $m_s = \pm 1/2$. The third electron is in the $2s$ subshell and has $\ell = 0$, with either $m_s = 1/2$ or $-1/2$. With four particles there are six possible interactions: the nucleus with electrons 1, 2, 3; electron 1 with electron 2; electron 1 with electron 3; or electron 2 with electron 3. In each case it is possible to have a Coulomb interaction and a magnetic moment interaction.

2. H: $1s^1$, He: $1s^2$. Li: $1s^22s^1$, Be: $1s^22s^2$, B: $1s^22s^22p^1$. C: $1s^22s^22p^2$, N: $1s^22s^22p^3$, O: $1s^22s^22p^4$. F: $1s^22s^22p^5$, Ne: $1s^22s^22p^6$

3. L: $n = 2$. so there are two ($2s$ and $2p$)

   N: $n = 4$. so there are four ($4s$, $4p$, $4d$, and $4f$)

   O: $n = 5$. so there are five ($5s$, $5p$, $5d$, $5f$, and $5g$)

4. In the first excited state. go to the next higher level. In argon one of the $3p$ electrons is promoted to $4s$, so the configuration is $3p^54s^1$. By the same reasoning the first excited state of krypton is $4p^55s^1$.

5. K: [Ar] $4s^1$, V: [Ar] $4s^23d^3$. Se: [Ar] $4s^23d^{10}4p^4$, Zr: [Kr] $5s^24d^2$, Sm: [Xe] $6s^24f^6$, U:[Rn] $7s^26d^15f^3$ where the bracket represents a closed inner shell. For example, [Ar] represents $1s^22s^22p^63s^23p^6$.

6. a) He, Ne, Ar, Kr, Xe, Rn

   b) Li, Na. K, Rb, Cs, Fr

   c) Be, Mg, Ca, Sr, Ba, Ra

* 7. From Figure 8.4 we see that the radius of Na is about 0.19 nm. We know that for single-electron atoms

$$E = -\frac{Ze^2}{8\pi\varepsilon_0 r}$$

Therefore

$$Ze = -\frac{8\pi\varepsilon_0 rE}{e} = -\frac{2\,(0.19\ \text{nm})\,(-5.14\ \text{eV})}{1.44\ \text{V}\cdot\text{nm}} = 1.36e$$

8. The first four electrons (in the $1s$ and $2s$ orbitals) have quantum numbers $(1,0,0,\pm 1/2)$ and $(2,0,0,\pm 1/2)$. The remaining three electrons are in the $2p$ orbital with $n = 2$ and $\ell = 1$. By Hund's rules we expect them all to have $m_s = +1/2$ or $m_s = -1/2$, so the possibilities are $(2,1,1,+1/2)$, $(2,1,0,+1/2)$, and $(2,1,-1,+1/2)$ *or* $(2,1,1,-1/2)$, $(2,1,0,-1/2)$. and $(2,1,-1,-1/2)$.

9. a) 5 electrons, B

   b) 11 electrons, Na

   c) filled $3p$: Ar

* 10. Pd: [Kr] $4d^{10}$, Hf: [Xe] $4f^{14}5d^26s2$, Sb: [Kr] $4d^{10}5s^25p^3$ where the bracket represents a closed inner shell. For example, [Kr] represents $1s^22s^22p^63s^23p^64s^23d^{10}4p^6$.

where we have used the fact that $\mu_0 = \dfrac{1}{c^2\varepsilon_0}$. The directions of the vectors follow from the right-hand rule.

28. Using the fact that $g = 2$ we have

$$\vec{\mu}_s = g\frac{e\vec{S}}{2m} = \frac{e\vec{S}}{m}$$

$$\vec{\mu}_s \cdot \vec{B} = \frac{Ze^2}{4\pi\varepsilon_0 m^2c^2r^3}\,\vec{S}\cdot\vec{L}$$

29. a) In order to use the result of the previous problem, we need to know the directions of $\vec{S}$ and $\vec{L}$. The electron has $S = \pm 1/2$, so $\left\|\vec{S}\right\| = \sqrt{3/4}\,\hbar$ and the angle $\vec{S}$ makes with the $+z$-axis is

$$\theta = \cos^{-1}\left(\frac{\pm 1/2}{\sqrt{3/4}}\right) = 54.7^\circ \text{ or } 125.3^\circ$$

With $L = 1$ we have $\left\|\vec{L}\right\| = \sqrt{2}\hbar$ and the vector $\vec{L}$ can have three possible orientations, corresponding to $m_\ell = 0, \pm 1$. If we choose $m_\ell = 0$, then the orientation of the $\vec{L}$ vector is in the xy plane. Therefore for either spin state the angle between $\vec{L}$ and $\vec{S}$ is 35.3° and

$$\vec{S}\cdot\vec{L} = \sqrt{\frac{3}{4}}\,\hbar\,\sqrt{2}\,\hbar\cos(35.3^\circ) = \hbar^2$$

Then using $r = 5a_0$ for a $2p$ electron (see Chapter 7 Problem 40), we have

$$V = \frac{e^2\hbar^2}{4\pi\varepsilon_0 m^2c^2r^3} = \frac{(1.44\text{ eV}\cdot\text{nm})(1240\text{ eV}\cdot\text{nm})^2}{4\pi^2(5.11\times10^5\text{ eV})^2(5\times0.0529\text{ nm})^3} = 1.2\times10^{-5}\text{ eV}$$

The difference between spin-up and spin-down states is twice this amount, or 2.4×10^{-5} eV, which is just over half the measured value.

b) The two possibilities are $j = 1/2$ and $j = 3/2$. The difference between these two is

$$\begin{aligned}\Delta V &= \frac{Z^4\alpha^4}{2n^3}mc^2\left(\frac{2}{2\left(\frac{1}{2}\right)+1} - \frac{2}{2\left(\frac{3}{2}\right)+1}\right)\\ &= \frac{\left(\frac{1}{137}\right)^4}{2(2)^3}(5.11\times10^5\text{ eV})\left(\frac{2}{2\left(\frac{1}{2}\right)+1} - \frac{2}{2\left(\frac{3}{2}\right)+1}\right) = 4.53\times10^{-5}\text{ eV}\end{aligned}$$

which gives a more accurate result.

30. In Example 8.10, it was shown that the normal Zeeman effect is expected when the total spin $S = 0$. The normal Zeeman effect is due to the interaction of the external magnetic field and the orbital angular momentum. This is true for all levels. If S is not zero, then the anomalous effect is expected. Therefore the two effects are not expected in the same atom.

31.

$$\vec{\mu} = -\frac{\mu_B}{\hbar}\left(\vec{L} + 2\vec{S}\right) \qquad\qquad \vec{J} = \vec{L} + \vec{S}$$

$$\vec{\mu}_{av} = -\frac{\mu_B}{\hbar}\frac{\left(\vec{L} + 2\vec{S}\right)\cdot\left(\vec{L} + \vec{S}\right)}{J^2}\vec{J}$$

Now

$$\left(\vec{L} + 2\vec{S}\right)\cdot\left(\vec{L} + \vec{S}\right) = L^2 + 2S^2 + 3\vec{L}\cdot\vec{S}$$

and using $\vec{J} = \vec{L} + \vec{S}$ we have

$$\vec{J}\cdot\vec{J} = L^2 + S^2 + 2\vec{L}\cdot\vec{S}$$

so

$$\vec{L}\cdot\vec{S} = \frac{J^2 - L^2 - S^2}{2}$$

and

$$\left(\vec{L} + 2\vec{S}\right)\cdot\left(\vec{L} + \vec{S}\right) = \frac{3J^2 + S^2 - L^2}{2}$$

$$\vec{\mu}_{av} = -\frac{\mu_B}{\hbar}\frac{3J^2 + S^2 - L^2}{2J^2}\vec{J}$$

With $\vec{B}$ defined to be in the $+z$-direction,

$$V = -\vec{\mu}_{av}\cdot\vec{B} = \frac{\mu_B B}{\hbar}\frac{3J^2 + S^2 - L^2}{2J^2}J_z$$

As usual $J_z = m_J\hbar$, so

$$V = \mu_B B m_J \frac{3J^2 + S^2 - L^2}{2J^2}$$

Now the vector magnitudes are $J^2 = j(j+1)\hbar^2$, $S^2 = s(s+1)\hbar^2$, and $L^2 = l(l+1)\hbar^2$ so we get $V = \mu_b B m_J g$ where

$$g = \frac{3j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

32.

$$\Delta E = \frac{hc}{\lambda_1} - \frac{hc}{\lambda_2} = \frac{1240\text{ eV}\cdot\text{nm}}{422.7\,\text{nm}} - \frac{1240\,\text{eV}\cdot\text{nm}}{422.713\,\text{nm}} = 9.02\times10^{-5}\text{ eV}$$

Also $\Delta E = \mu_B B \Delta m_\ell = (e\hbar/2m)\,B$ with $\Delta m_\ell = 1$. Thus

$$\frac{e\hbar}{m} = \frac{2\Delta E}{B} = \frac{2\left(9.02\times10^{-5}\text{ eV}\right)}{1.5\text{ T}}\frac{1.602\times10^{-19}\text{ J}}{\text{eV}} = 1.927\times10^{-23}\text{ J/T}$$

The accepted value is

$$\frac{e\hbar}{m} = 2\mu_B = 2\left(9.274\times10^{-24}\text{ J/T}\right) = 1.855\times10^{-23}\text{ J/T}$$

which is about 4% lower than the experimental value.

Using the experimental data with the known value of $\hbar$,

$$\frac{e}{m} = \frac{1.927\times10^{-23}\,\text{J/T}}{1.055\times10^{-34}\,\text{J}\cdot\text{s}} = 1.83\times10^{11}\text{ C/kg}$$

11. a) filled $3d$: As

    b) filled $4p$ and $4d$: Ag

    c) The $4f$ shell fills in the lanthanides: Ho

12. J ranges from $|L-S|$ to $|L+S|$ or 2,3,4. Then in spectroscopic notation ${}^{2S+1}L_J$, we have three possibilities: ${}^3F_2$, ${}^3F_3$, or ${}^3F_4$. The ground state has the lowest J value, or ${}^3F_2$. With $n=4$ the full notation is 4^3F_2.

13. There is a single electron in the $4p$ subshell. Therefore $S=\frac{1}{2}$ and $2S+1=2$. Because it is in the p subshell we have $L=1$. The possible J values are from $|L-S|$ to $|L+S|$, which in this case gives $J=1/2$ or $J=3/2$. Therefore the possible states are ${}^2P_{1/2}$ and ${}^2P_{3/2}$, with ${}^2P_{1/2}$ being the ground state. The full notation is $4^2P_{1/2}$.

14. This requires either a closed subshell ($S=0$), which we have in He, Be, Ne, Mg, Ar, and Ca or $L=0$ which we have in H, Li, Na, and K. (It is the 1st excited state of the alkali metals which accounts for the splitting in the alkali metal spectra with the visible transition begin from the 2nd excited state to the first in Na for example.)

* 15. In the $3d$ state $\ell=2$ and $s=1/2$, so $j=5/2$ or $3/2$. As usual $m_\ell=0,\pm1,\pm2$. The value of m_j ranges from $-j$ to j, so its possible values are $\pm1/2$, $\pm3/2$, and $\pm5/2$. As always $m_s=\pm1/2$. The two possible term notations are $3D_{5/2}$ and $3D_{3/2}$.

16. ${}^1S_0$: $S=0$, $L=0$, $J=0$ ${}^2D_{5/2}$: $S=1/2$, $L=2$, $J=5/2$

    ${}^5F_1$: $S=2$, $L=3$, $J=1$ ${}^3F_4$: $S=1$, $L=3$, $J=4$

17. The quantum number m_J ranges from $-J$ to J, or $-7/2$ to $+7/2$. Then $J_z=m_J\hbar=\pm\hbar/2$, $\pm3\hbar/2$, $\pm5\hbar/2$, $\pm7\hbar/2$.

* 18. a) The quantum number m_J ranges from $-J$ to J, or $-7/2$ to $+7/2$. Then $J_z=m_J\hbar=\pm\hbar/2$, $\pm3\hbar/2$, $\pm5\hbar/2$, $\pm7\hbar/2$.

    b) The minimum angle occurs when m_J is at its maximum value, which is $+7/2$. Then $J_z=7\hbar/2$ and

$$\cos\theta=\frac{J_z}{J}=\frac{m_J\hbar}{\sqrt{J(J+1)}\,\hbar}=\frac{7/2}{\sqrt{(7/2)(9/2)}}=\frac{\sqrt{7}}{3}$$

    so $\theta=28.1°$.

19. The $1s$ subshell is filled, and there is one $2s$ electron. Therefore $L=0$ (which gives the S in the middle of the symbol). The single unpaired electron gives $S=1/2$ or $2S+1=2$. With $L=0$ and $S=1/2$ the only possible value for J is $J=1/2$.

20. Al has a ground state configuration $3s^23p^1$. The single unpaired electron gives $S=1/2$, so $2S+1=2$. The unpaired electron is in a p subshell, so $L=1$, for which the symbol is P. Then $J=L\pm S$ which is 1/2 or 3/2, but the 1/2 state has a slightly lower energy. Therefore the symbol is $3^2P_{1/2}$.

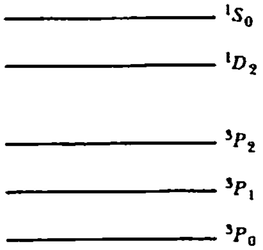
* 21.

$$\Delta E=\frac{hc}{\lambda_1}-\frac{hc}{\lambda_2}=(1240\ \text{eV}\cdot\text{nm})\left(\frac{1}{766.41\ \text{nm}}-\frac{1}{769.90\ \text{nm}}\right)=7.334\times10^{-3}\ \text{eV}$$

As in Example 8.8 the internal magnetic field is

$$B = \frac{m\Delta E}{e\hbar} = \frac{(9.109 \times 10^{-31}\ \text{kg})\,(7.334 \times 10^{-3}\ \text{eV})}{(1.602 \times 10^{-19}\ \text{C})\,(6.582 \times 10^{-16}\ \text{eV}\cdot\text{s})} = 63.4\ \text{T}$$

22. By the selection rules $\Delta L = \pm 1$, $\Delta S = 0$, $\Delta J = 0, \pm 1$, no transitions are allowed between the pictured levels. The selection rule $\Delta S = 0$ prohibits singlet → triplet transitions.



23. The $2s$ to $1s$ transition is forbidden by the $\Delta L = \pm 1$ selection rule. The two lines result from the transitions from the two $2p$ levels to the $1s$ level.

* 24. As in Example 8.8

$$\Delta E = \frac{e\hbar B}{m} = \frac{(1.602 \times 10^{-19}\ \text{C})\,(6.582 \times 10^{-16}\ \text{eV}\cdot\text{s})\,(1.7\ \text{T})}{9.109 \times 10^{-31}\ \text{kg}} = 1.97 \times 10^{-4}\ \text{eV}$$

25. The ground state in He is a singlet, so an excited state may be a singlet or triplet, and the behavior of Ca ($4s^2$) and Sr ($5s^2$) must be the same. Al has a $3s^2 3p^1$ configuration. The single unpaired electron gives $S = 1/2$ and $2S + 1 = 2$, which is a doublet.

* 26. The minimum angle corresponds to the maximum value of J_z and hence the maximum value of m_j, which is $m_j = j$. Then

$$\cos\theta = \frac{J_z}{J} = \frac{m_j \hbar}{\sqrt{j\,(j+1)}\,\hbar} = \frac{j}{\sqrt{j\,(j+1)}}$$

Solving for j we find

$$j = \frac{1}{\frac{1}{\cos^2\theta} - 1} = 2.50 = 5/2$$

27.

$$I = \frac{dq}{dt} = \frac{Ze}{2\pi r/v} = \frac{Zev}{2\pi r}$$

From the Biot-Savart Law

$$B = \frac{\mu_0 I}{2r} = \frac{\mu_0 Zev}{4\pi r^2}$$

With the assumption that the orbit is circular, the angular momentum is $L = mvr$, so $v = \frac{L}{mr}$ and

$$B = \frac{\mu_0 ZeL}{4\pi m r^3} = \frac{ZeL}{4\pi\varepsilon_0 m c^2 r^3}$$

* 33. a) $L = 0,\ S = J = 1/2$

$$g = 1 + \frac{(1/2)(3/2) + (1/2)(3/2)}{2(1/2)(3/2)} = 1 + 1 = 2$$

b) $L = 1,\ S = 1/2$, and $J = 3/2$

$$g = 1 + \frac{(3/2)(5/2) + (1/2)(3/2) - 1(2)}{2(3/2)(5/2)} = 1 + \frac{1}{3} = \frac{4}{3}$$

c) $L = 2,\ S = 1/2$, and $J = 5/2$

$$g = 1 + \frac{(5/2)(7/2) + (1/2)(3/2) - 2(3)}{2(5/2)(7/2)} = 1 + \frac{1}{5} = \frac{6}{5}$$

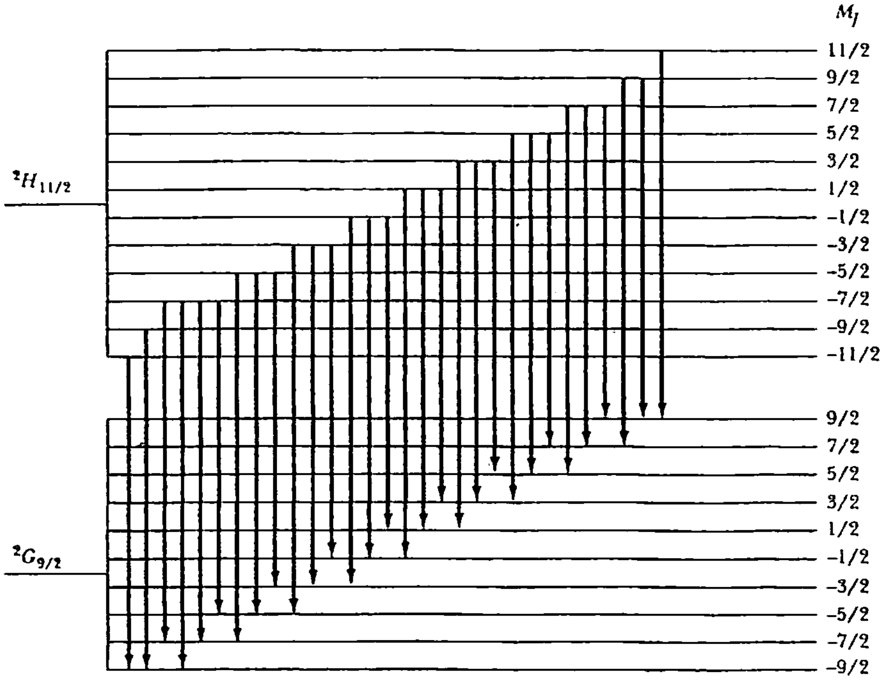
34. Computing the g factors:

${}^2G_{9/2}$: $L = 4,\ S = 1/2$, and $J = 9/2$

$$g = 1 + \frac{(9/2)(11/2) + (1/2)(3/2) - 4(5)}{2(9/2)(11/2)} = 1 + \frac{1}{9} = \frac{10}{9}$$

${}^2H_{11/2}$: $L = 5,\ S = 1/2$, and $J = 11/2$

$$g = 1 + \frac{(11/2)(13/2) + (1/2)(3/2) - 5(6)}{2(11/2)(13/2)} = 1 + \frac{1}{11} = \frac{12}{11}$$

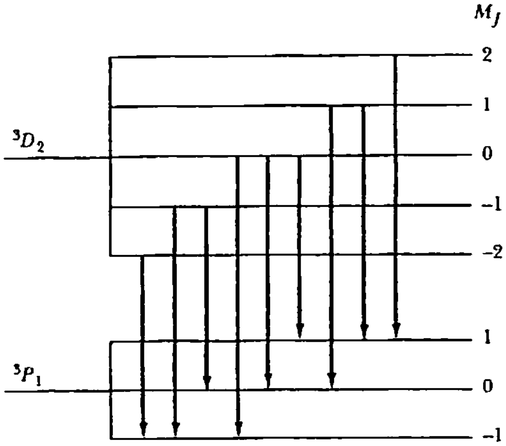


35. ${}^3P_1$: $L = 1$, $S = 1$, and $J = 1$

$$g = 1 + \frac{(1)(2) + (1)(2) - 1(2)}{2(1)(2)} = 1 + \frac{1}{2} = \frac{3}{2}$$

${}^3D_2$: $L = 2$, $S = 1$, and $J = 2$

$$g = 1 + \frac{(2)(3) + (1)(2) - 2(3)}{2(2)(3)} = 1 + \frac{1}{6} = \frac{7}{6}$$



36. From Equation (8.22) we have an energy splitting of $V = \mu_B B g m_J$.

For the ${}^2S_{1/2}$ state $g = 2$, so $V = 2\mu_B B m_J$. Now m_J can vary from $-J$ to $+J$, so $m_J = \pm 1/2$ and we find $V = \pm\mu_B B$.

For the ${}^2P_{1/2}$ state $g = 2/3$, so $V = \frac{2}{3}\mu_B B m_J$. Now m_J can vary from $-J$ to $+J$, so $m_J = \pm 1/2$ and we find $V = \pm\frac{1}{3}\mu_B B$.

The maximum difference is from $+\frac{1}{3}\mu_B B$ to $-\mu_B B$ or from $-\frac{1}{3}\mu_B B$ to $+\mu_B B$. In each case the magnitude of the energy difference is $\frac{4}{3}\mu_B B$ for a total difference of $\frac{8}{3}\mu_B B$. Calling this difference ΔE, it will show up as the usual wavelength difference $\Delta\lambda$ with $\Delta E = \left(hc/\lambda^2\right)\Delta\lambda$. Thus

$$\begin{aligned}\Delta\lambda &= \frac{\lambda^2 \Delta E}{hc} = \frac{\lambda^2}{hc}\frac{8}{3}\mu_B B = \frac{8}{3}\frac{\left(5.8976\times10^{-7}\text{ m}\right)^2\left(9.274\times10^{-24}\text{ J/T}\right)(0.5\text{ T})}{\left(6.626\times10^{-34}\text{ J}\cdot\text{s}\right)\left(2.997\times10^{8}\text{ m/s}\right)}\\ &= 2.17\times10^{-11}\text{ m}\end{aligned}$$

37. As in the previous problem we have $g = 4/3$ for the ${}^2P_{3/2}$ state and $V = \frac{4}{3}\mu_B B m_J$. The states are split by $\Delta m_J = 1$ and so the energy difference between two adjacent states is $\Delta E = \frac{4}{3}\mu_B B$. Then

$$\Delta E = \frac{4}{3}\mu_B B = \frac{4}{3}\left(9.274\times10^{-24}\text{ J/T}\right)(0.5\text{ T}) = 6.18\times10^{-24}\text{ J} = 3.86\times10^{-5}\text{ eV}$$

* 38. a) Magnesium has two $3s$ subshell electrons outside a closed $2p^6$ subshell. So the electronic configuration is $1s^2 2s^2 2p^6 3s^2$. Aluminum has one $3p$ electron outside the closed $3s$ level of magnesium, so its electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^1$.

b) The LS coupling for magnesium can be determined since both outer shell electrons have $\ell = 0$, then $L = 0$ and $S = 0$ since one electron will have spin up and one will have spin down. Then $J = L + S$ will also be 0. Therefore in spectroscopic notation, $n^{2S+1}L_J$, magnesium will be 3^1S_0. The $3p$ electron for aluminum will have $\ell = 1$. Therefore $L = 1$ and $S = 1/2$. Now $J = L \pm S$, so $J = 3/2$ or $J = 1/2$. The state with lower J has lower energy, so in spectroscopic notation, aluminum is $3^2P_{1/2}$.

39. a) Scandium (Sc) has one $3d$ and two $4s$ electrons outside a closed $3p^6$ subshell. So Sc^- would have one additional electron in the $3d$ subshell. So the electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$. Aluminum has one $3p$ electron outside the closed $3s$ subshell. So Al^- would have one additional electron in the $3p$ subshell. So its electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^2$.

b) We will use the LS coupling model and Hund's rules to find the lowest energy state. For Sc^- we must consider the two $3d$ electrons. According to Hund's rules, the triplet state $S = 1$ will be lowest in energy. Additionally, we attempt to maximize L as long as we do not violate the exclusion principle. Both $3d$ electrons have $\ell = 2$, so we can have $L = 0,\ 1,\ 2,\ 3,\ \text{or}\ 4$. As discussed in example 8.9 of the text, the antisymmetrization of the wave function requires that the m_ℓ values for the electrons forming the $S = 1$ state must be unequal. The largest allowed L is thus 3. Finally, J should be minimized, so we have $J = 2$. Therefore in spectroscopic notation, $n^{2S+1}L_J$, we have $3\,^3F_2$.

For Al^- we consider the two $3p$ electrons outside the closed subshell. As above, the triplet state $S = 1$ will have lowest energy. The $3p$ electrons have $\ell = 1$ so we can have $L = 0,\ 1,\ \text{or}\ 2$. Again using the antisymmetrization of the wave function requires the m_ℓ values for the electrons forming the $S = 1$ state to be unequal. The largest allowed L is therefore 1. Finally the smallest J will be 0. So in spectroscopic notation we have 3^3P_0.