Chapter 8

*1. The first two electrons are in the $1s$ subshell and have $l = 0$, with $m_s = \pm 1/2$. The third electron (on the $2s$ level) has $l = 0$, 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: $1s^2 2s^1$, Be: $1s^2 2s^2$, B: $1s^2 2s^2 2p^1$, C: $1s^2 2s^2 2p^2$, N: $1s^2 2s^2 2p^3$, O: $1s^2 2s^2 2p^4$, F: $1s^2 2s^2 2p^5$, Ne: $1s^2 2s^2 2p^6$

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 $3p^5 4s^1$. By the same reasoning the first excited state of krypton is $4p^5 5s^1$.

5. K: $4s^1$, V: $4s^2 3d^3$, Se: $4s^2 3d^{10} 4p^4$, Zr: $5s^2 4d^2$, Sm: $6s^2 4f^6$, U: $7s^2 6d^1 5f^3$

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

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

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 $l = 1$. 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. 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.

11. 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 $4^2P_{1/2}$.

12. This requires a closed subshell, which we have in He, Be, Ne, Mg, Ar, and Ca.

*13. In the $3d$ state $l=2$ and $s=1/2$, so $j=5/2$ or $3/2$. As usual $m_l=0,\pm1,\pm2$. 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 $3D_{3/2}$.

14. $^1S_0$: $S=0$, $L=0$, $J=0$ $^2D_{5/2}$: $S=1/2$, $L=2$, $J=5/2$
$^5F_1$: $S=2$, $L=3$, $J=1$ $^3F_4$: $S=1$, $L=3$, $J=4$

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

*16. 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 $\theta=28.1°$.

17. 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 $J=1/2$.

18. Al has a ground state configuration $3s^2 3p^1$. 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 $3^2P_{1/2}$.

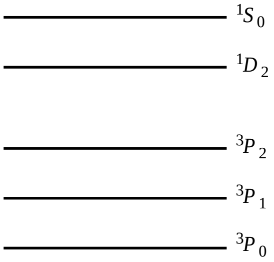
*19.

$$\Delta E = \frac{hc}{\lambda_1} - \frac{hc}{\lambda_2} = (1240\ \mathrm{eV \cdot nm}) \left(\frac{1}{766.41\ \mathrm{nm}} - \frac{1}{769.90\ \mathrm{nm}} \right) = 7.334 \times 10^{-3}\ \mathrm{eV}$$

As in Example 8.6 the internal magnetic field is

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

20. 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.



21. 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.

*22. As in Example 8.6

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

23. 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.

*24. 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

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

25.

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

From the Biot-Savart Law

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

The angular momentum is $L = mvr$, so $v = L/mr$ and

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

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

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

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

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

27. 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 $m_l = 0, \pm 1$. If we choose $m_l = 0$, then 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 36), we have

$$V = \frac{e^2\hbar^2}{4\pi\varepsilon_0 m^2c^2r^3} = \frac{(1.44\ \text{eV}\cdot\text{nm})\,(1240\ \text{eV}\cdot\text{nm})^2}{4\pi^2\,(511\times 10^3\ \text{eV})^2\,(5\times 0.0529\ \text{nm})^3} = 1.2\times 10^{-5}\ \text{eV}$$

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

$$\begin{aligned}\Delta V &= \frac{Z^4\alpha^4}{2n^3}mc^2\left(\frac{2}{2\left(\frac{1}{2}\right)+1} - \frac{2}{2\left(\frac{3}{2}\right)+1}\right)\\ &= \frac{\left(\frac{1}{137}\right)^4}{2\,(2)^3}\left(5.11\times 10^5\ \text{eV}\right)\left(\frac{2}{2\left(\frac{1}{2}\right)+1} - \frac{2}{2\left(\frac{3}{2}\right)+1}\right) = 4.53\times 10^{-5}\ \text{eV}\end{aligned}$$

which is more accurate.

28. In Example 8.8 it was shown that the normal Zeeman effect is expected when the total spin $S = 0$. This is true for all levels. If S is not zero, then the anomalous effect is expected. Therefore, two effects are not expected in the same atom.

29.

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

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

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

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

30.

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

Also $\Delta E = \mu_B B \Delta m_l = e\hbar/2m$ with $\Delta m_l = 1$. 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 3% lower than the experimental value.
Using the experimental data with the known value of $\hbar$,

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

*31. 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 $J = 5/2$

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

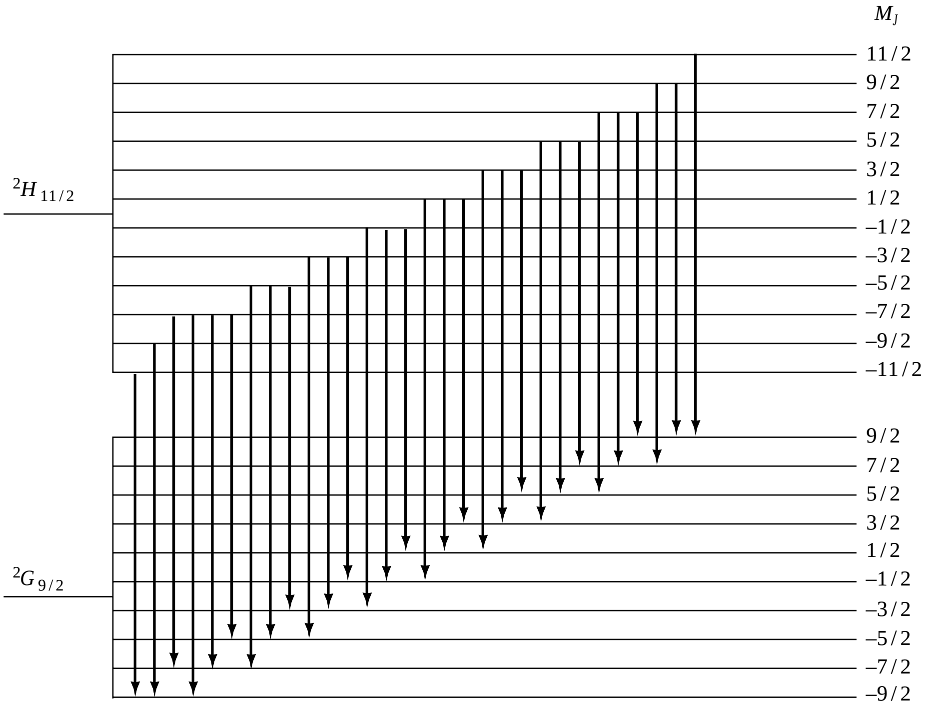
32. Computing the g factors:

$^2G_{9/2}$: $L = 4$, $S = 1/2$, 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 $J = 11/2$

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

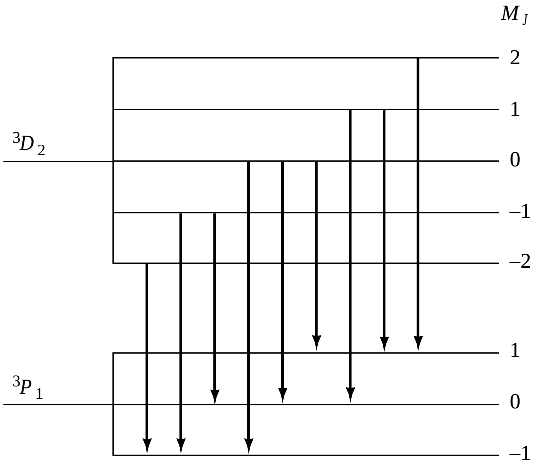


33. $^3P_1$: $L = 1$, $S = 1$, and $J = 1$

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

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

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



34. 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 $V = \pm\frac{1}{3}\mu_B B$.

Thus 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

$$\Delta\lambda = \frac{\lambda^2 \Delta E}{hc} = \frac{\lambda^2}{hc}\frac{8}{3}\mu_B B = \frac{8}{3}\frac{(5.8976 \times 10^{-7}\ \text{m})^2 (9.274 \times 10^{-24}\ \text{J/T})(0.5\ \text{T})}{(6.626 \times 10^{-34}\ \text{J}\cdot\text{s})(2.997 \times 10^{8}\ \text{m/s})} = 2.17{\times}10^{-11}\ \text{m}$$

35. 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

$$\Delta E = \frac{4}{3}\mu_B B = \frac{4}{3}\left(9.274 \times 10^{-24}\ \text{J/T}\right)(0.5\ \text{T}) = 6.18 \times 10^{-14}\ \text{J} \ = 3.86 \times 10^{-5}\ \text{eV}$$