4.1. Foot 4.3 Quantum defects of sodium

The binding energies of the 3s, 4s, 5s and 6s configurations in sodium are 5.14 eV, 1.92 eV, 1.01 eV, 0.63 eV, respectively. Calculate the quantum defects for these configurations and comment on what you find.

Estimate the binding energy of the 8s configuration and make a comparison to the $n = 8$ shell in hydrogen.

The formula for the binding energy including quantum defects is

\[ E = \frac{hcR_\infty}{(n - \delta)^2}, \]

\[ \delta = n - \sqrt{\frac{hcR_\infty}{E}}. \]

Taking $hcR_\infty = 13.6$ eV, yields

| $\delta_3$ | 1.38 |
| $\delta_4$ | 1.34 |
| $\delta_5$ | 1.33 |
| $\delta_6$ | 1.35 |

For higher values the quantum defect seems to converge to a consistent value, let’s take it to be 1.34. Then we expect $E_8(\text{Na}) = 0.307$ eV, as opposed to $E_8(\text{H}) = 0.213$ eV.

4.2. Foot 4.7 The Z-scaling of fine structure

Calculate the fine-structure splitting of the 3p configuration of the hydrogen-like ion Na$^{+10}$ (in eV). Explain why it is larger than the fine structure of the same configuration in neutral sodium (0.002 eV) and hydrogen ($1.3 \times 10^{-5}$ eV).

In this case, we have a hydrogen-like atom, and no quantum defect terms apply. We also have a total $Z^4$ dependence, with the fine-structure splitting going as

\[ \frac{Z^4\alpha^2hcR_\infty}{n^3l(l + 1)} = 0.196 \text{ eV}. \]
This is larger than in hydrogen, because the electron is pulled much closer to the nucleus by the large charge, and because the large nuclear charge creates a large magnetic field for the electron. It is larger (but less so) that neutral sodium, because there the nuclear charge effects remain, but the electron is not pulled as close due to the repulsion by the core.

4.3. Foot 4.8 Relative intensities of fine-structure components

(a) An emission line in the spectrum of an alkali has three fine-structure components corresponding to the transitions \( ^2P_{3/2} \rightarrow ^2D_{3/2} \), \( ^2P_{3/2} \rightarrow ^2D_{5/2} \), \( ^2P_{1/2} \rightarrow ^2D_{3/2} \). These components have intensities \( a \), \( b \), and \( c \), respectively, that are in the ratio 1 : 9 : 5. Show that these satisfy the rule that the sum of the intensities of the transitions to, or from, a given level is proportional to its statistical weight (\( 2J + 1 \)).

For \( ^2D_{5/2} \), there is weight 6 and total strength 9, for \( ^2D_{3/2} \) there is weight 4 and total strength 1 + 5 = 6, and of course 6/4 = 9/6.

(b) Sketch an energy-level diagram of the fine-structure levels of the two terms \( nd^2D \) and \( n'f^2F \) (for \( n' > n \)). Mark the three allowed electric dipole transitions and find their relative intensities.

Figure 1: (a) The energy levels for part (a). (b) The energy levels for part (b).

To find the relative intensities, we assume the 5/2 \( \rightarrow \) 5/2 line has intensity 1, and write the equations

\[
\begin{align*}
\frac{c + 1}{b} &= \frac{3}{4}, \\
4c + 4 &= 3b, \\
4c - 3b + 4 &= 0, \\
b &= 20,
\end{align*}
\]

\[
\begin{align*}
\frac{b + 1}{c} &= \frac{3}{2}, \\
2b + 2 &= 3c, \\
3c - 2b - 2 &= 0, \\
c &= 14.
\end{align*}
\]

4.4. Foot 5.3 The LS-coupling scheme and the interval rules in calcium
Write down the ground configuration of calcium \((Z = 20)\). The line at 610 nm in the spectrum of neutral calcium consists of three components at relative positions, 0, 106, and 158 (in units of cm\(^{-1}\)). Identify the terms and levels involved in these transitions.

The ground configuration is \(1s^22s^22p^63s^23p^64s^2\). Therefore we can rule out doublets, quadruplets, etc, since there are an even number of fermions. Since there are three components, we know that the smaller of \(L\) or \(S\) is equal to one, as singlet lines only have one component (although there could be multiple terms, e.g. \(^1D\) and \(^1S\), but these would be separated by more in energy). With only two valence electrons, \(S = 1\) is the most we expect, so we’ve identified a triplet line, and by selection rules both states must be triplet. The interval can help us figure out the values of \(J\). Since 158 – 106 = 52 \(\approx\) 106/2, we see a ratio of 2 : 1, suggesting \(J = 2, 1, 0\). Therefore we can identify one level as \(^3P\), and the other as \(^3S\).

The spectrum also contains a multiplet of six lines with wavenumbers 5019, 5033, 5055, 5125, 5139, and 5177 (in units of cm\(^{-1}\)). Identify the terms and levels involved. Draw a diagram of the relevant energy levels and the transitions between them. What further experiment could be carried out to check the assignment of quantum numbers?

This time we have six components, so singlet is out and we have triplet for sure. The first thing to look for is the previous splitting, since we know there is a \(^3P\) level with \(J = 2, 1, 0\) spaced by 0, 106, 158. Sure enough, we find that 5019 + 106 = 5125, 5019 + 158 = 5177, and 5033 + 106 = 5139. Therefore, the same levels are very likely to be involved. The \(J = 2\) level has three transitions associated with it, suggesting the levels \(J' = 3, 2, 1\), since these are the only three unique levels capable of transitions.
with the $J = 2$ level, The $J = 1$ level as two transitions ($J' = 2, 1$), and the $J = 0$ level has only one transition from $J' = 1$. Then we have the splittings $|E_{J'=3} - E_{J'=2}| = 5055 - 5033 = 22$, and $|E_{J'=2} - E_{J'=1}| = 5033 - 5019 = 14$. Since 22/14 $\approx$ 3/2, we have the interval rule obeyed. $J' = 3, 2, 1$ is possible (for triplets) only from $^3D$, so we have a $^3P - ^3D$ transition. Another confirmation could come from intensity ratios, which could be computed and compared to the experimental results.

4.5. **Foot 5.7 Transition from the LS- to jj-coupling**

<table>
<thead>
<tr>
<th>$J$</th>
<th>Energy ($10^6$ m$^{-1}$)</th>
<th>$J$</th>
<th>Energy ($10^6$ m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.968</td>
<td>0</td>
<td>6.154</td>
</tr>
<tr>
<td>1</td>
<td>3.976</td>
<td>1</td>
<td>6.160</td>
</tr>
<tr>
<td>2</td>
<td>3.996</td>
<td>2</td>
<td>6.182</td>
</tr>
<tr>
<td>1</td>
<td>4.099</td>
<td>1</td>
<td>6.188</td>
</tr>
</tbody>
</table>

The table give $J$-values and energies (in units of $10^6$ m$^{-1}$) measured form the ground state) of the levels in the $3p4s$ and $3p7s$ configurations of silicon. Suggest further quantum number to identify the levels.

Why do the two configurations have nearly the same value of $E_{J'=2} - E_{J'=0}$ but quite different energy separations between the two $J = 1$ states?

In the $3p4s$ case, the interval rule is nearly obeyed, the energy differences are 0.008 and 0.020, which is close to 2:1, therefore LS-coupling applies and the first three levels can be the $^3P$, the last one $^1P$. In the $3p7s$ case, the interval rule is not obeyed as well, but the intervals between the first and last pair are nearly equal, suggesting $jj$-coupling, in which case the terms would be ($\frac{1}{2}, \frac{1}{2}$), and ($\frac{1}{2}, \frac{3}{2}$).

The energy difference $E_{J'=2} - E_{J'=0}$ depends only on the spin-orbit coupling, as $J = 0$ and $J = 2$ are both $^3P$ states and therefore have the same electrostatic term in both cases. The spin-orbit in the $3p$ level is the same in both because the $s$ levels have no spin-orbit coupling. The $J = 1$ levels are affected by electrostatic terms, and therefore there is a big difference between $4s$ and $7s$ in terms of the exchange with $3p$. 
