Second-Order Hyperfine Effects in Mg and Ca

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Analysis

The second-order contribution to the hyperfine energy of a state F from a nearby fine-structure state with angular momentum J' is

$$W_F^{(2)} = \left\{ \begin{array}{ccc} I & J & F \\ J' & I & 1 \end{array} \right\}^2 \frac{\left|\langle I\|T_1^{(n)}\|I\rangle\right|^2 \left|\langle J\|T_1^{(e)}\|J'\rangle\right|^2}{E_J - E_{J'}}$$
$$+2\left\{ \begin{array}{ccc} I & J & F \\ J' & I & 1 \end{array} \right\}\left\{ \begin{array}{ccc} I & J & F \\ J' & I & 2 \end{array} \right\} \frac{\langle I\|T_1^{(n)}\|I\rangle\langle I\|T_2^{(n)}\|I\rangle\langle J\|T_1^{(e)}\|J'\rangle\langle J\|T_2^{(e)}\|J'\rangle}{E_J - E_{J'}} \quad (1)$$

As shown in Appendix D, the first term on the right-hand side of the above equation cannot contribute to the Z_k (defined in Appendix D) for $k > 2$ and, therefore, cannot influence the C or D coefficients. Now, examine the contribution of the second term in Eq. (1) to Z_k:

$$Z_k^{(2)} = (2k+1)\sum_F (-1)^{I+J+F}(2F+1)\left\{ \begin{array}{ccc} I & J & F \\ J & I & k \end{array} \right\} W_F^{(2)}. \quad (2)$$

The F dependence is contained in the product of sixj symbols. Using identity (6) on page 305 of Varshalovich, we find

$$\sum_F (-1)^{I+J+F}(2F+1)\left\{ \begin{array}{ccc} I & J & F \\ J' & I & 1 \end{array} \right\}\left\{ \begin{array}{ccc} I & J & F \\ J' & I & 2 \end{array} \right\}\left\{ \begin{array}{ccc} I & J & F \\ J & I & k \end{array} \right\} =$$
$$(-1)^{2I+J+J'+k+1}\left\{ \begin{array}{ccc} 1 & 2 & k \\ I & I & I \end{array} \right\}\left\{ \begin{array}{ccc} 1 & 2 & k \\ J & J & J' \end{array} \right\}. \quad (3)$$

Correspondingly, the dipole-quadrupole contribution to $Z_k^{(2)}$ is

$$Z_k^{(2)} = 2(2k+1)(-1)^{2I+J+J'+k+1}\left\{ \begin{array}{ccc} 1 & 2 & k \\ I & I & I \end{array} \right\}\left\{ \begin{array}{ccc} 1 & 2 & k \\ J & J & J' \end{array} \right\}$$
$$\frac{\langle I\|T_1^{(n)}\|I\rangle\langle I\|T_2^{(n)}\|I\rangle\langle J\|T_1^{(e)}\|J'\rangle\langle J\|T_2^{(e)}\|J'\rangle}{E_J - E_{J'}}. \quad (4)$$

Angular momentum selection rules limit $1 \leq k \leq 3$. Therefore, the dipole-quadrupole interference term does contribute to the C coefficient.

Formulas for Hyperfine Constants

Let us write Eq. (1) in the form

$$W_F^{(2)} = \left\{ \begin{array}{ccc} I & J & F \\ J' & I & 1 \end{array} \right\}^2 \eta + \left\{ \begin{array}{ccc} I & J & F \\ J' & I & 1 \end{array} \right\} \left\{ \begin{array}{ccc} I & J & F \\ J' & I & 2 \end{array} \right\} \zeta, \qquad (5)$$

where

$$\eta = \frac{\left|\langle I \| T_1^{(n)} \| I \rangle\right|^2 \left|\langle J \| T_1^{(e)} \| J' \rangle\right|^2}{E_J - E_{J'}} \qquad (6)$$

$$\zeta = 2 \frac{\langle I \| T_1^{(n)} \| I \rangle \langle I \| T_2^{(n)} \| I \rangle \langle J \| T_1^{(e)} \| J' \rangle \langle J \| T_2^{(e)} \| J' \rangle}{E_J - E_{J'}}. \qquad (7)$$

We find the following results for the A, B, C, and D hyperfine constants expressed in terms of energy intervals, assuming $J' = 1$ and $J = 2$.

$I = 3/2$

$$\begin{aligned}
A &= -\frac{3}{50}\delta W_{1/2} - \frac{7}{50}\delta W_{3/2} - \frac{4}{25}\delta W_{5/2} - \frac{\zeta}{250\sqrt{3}} + \frac{\eta}{300} \\
B &= \frac{2}{5}\delta W_{1/2} + \frac{2}{5}\delta W_{3/2} - \frac{16}{35}\delta W_{5/2} + \frac{\zeta}{25\sqrt{3}} + \frac{2\eta}{75} \\
C &= -\frac{1}{50}\delta W_{1/2} + \frac{1}{50}\delta W_{3/2} - \frac{1}{175}\delta W_{5/2} + \frac{\zeta}{500\sqrt{3}} \qquad (8)
\end{aligned}$$

$I = 5/2$

$$\begin{aligned}
A &= -\frac{2}{75}\delta W_{1/2} - \frac{12}{175}\delta W_{3/2} - \frac{18}{175}\delta W_{5/2} - \frac{2}{21}\delta W_{7/2} - \frac{2\sqrt{2}\zeta}{2625} + \frac{\eta}{1050} \\
B &= \frac{8}{21}\delta W_{1/2} + \frac{32}{49}\delta W_{3/2} + \frac{12}{49}\delta W_{5/2} - \frac{100}{147}\delta W_{7/2} + \frac{\sqrt{2}\zeta}{105} + \frac{8\eta}{315} \\
C &= -\frac{1}{30}\delta W_{1/2} - \frac{1}{70}\delta W_{3/2} + \frac{1}{20}\delta W_{5/2} - \frac{5}{252}\delta W_{7/2} + \frac{\zeta}{350\sqrt{2}} \\
D &= \frac{1}{210}\delta W_{1/2} - \frac{3}{490}\delta W_{3/2} + \frac{3}{980}\delta W_{5/2} - \frac{1}{1764}\delta W_{7/2} \qquad (9)
\end{aligned}$$

$I = 7/2$

$$\begin{aligned}
A &= -\frac{1}{35}\delta W_{3/2} - \frac{5}{84}\delta W_{5/2} - \frac{11}{140}\delta W_{7/2} - \frac{1}{15}\delta W_{9/2} - \frac{\zeta}{420\sqrt{15}} + \frac{\eta}{2520} \\
B &= \frac{4}{7}\delta W_{3/2} + \frac{5}{7}\delta W_{5/2} + \frac{11}{105}\delta W_{7/2} - \frac{4}{5}\delta W_{9/2} + \frac{\zeta}{30\sqrt{15}} + \frac{\eta}{45} \\
C &= -\frac{1}{20}\delta W_{3/2} + \frac{1}{15}\delta W_{7/2} - \frac{7}{220}\delta W_{9/2} + \frac{\zeta}{120\sqrt{15}} \\
D &= \frac{1}{140}\delta W_{3/2} - \frac{1}{84}\delta W_{5/2} + \frac{1}{140}\delta W_{7/2} - \frac{1}{660}\delta W_{9/2} \qquad (10)
\end{aligned}$$

$I = 9/2$

$$
\begin{aligned}
A &= -\frac{2}{75}\delta W_{5/2} - \frac{14}{275}\delta W_{7/2} - \frac{52}{825}\delta W_{9/2} - \frac{14}{275}\delta W_{11/2} - \frac{2\sqrt{\frac{2}{3}}\zeta}{4125} + \frac{\eta}{4950} \\
B &= \frac{24}{35}\delta W_{5/2} + \frac{8}{11}\delta W_{7/2} - \frac{48}{55}\delta W_{11/2} + \frac{2}{275}\sqrt{\frac{2}{3}}\zeta + \frac{16\eta}{825} \\
C &= -\frac{3}{50}\delta W_{5/2} + \frac{7}{550}\delta W_{7/2} + \frac{21}{275}\delta W_{9/2} - \frac{147}{3575}\delta W_{11/2} + \frac{7\zeta}{1375\sqrt{6}} \\
D &= \frac{3}{350}\delta W_{5/2} - \frac{9}{550}\delta W_{7/2} + \frac{3}{275}\delta W_{9/2} - \frac{9}{3575}\delta W_{11/2} \qquad (11)
\end{aligned}
$$

Numerical Details

Let us rewrite the expression for ζ for the case $J' = J - 1$ as

$$
\zeta = \frac{(I+1)(2I+1)}{I}\sqrt{\frac{2I+3}{2I-1}}\, Q\, \mu_I \, \frac{\langle J \| T_1^{(e)} \| J-1 \rangle \, \langle J \| T_2^{(e)} \| J-1 \rangle}{E_J - E_{J-1}}. \qquad (12)
$$

The fine-structure intervals $E_J - E_{J'}$ in the denominators of the expressions for ζ are listed in Table 1 and the reduced matrix elements in the numerator are listed in Table 2. Putting these numbers together, we find for the lowest $^3P_2$ state in ^{25}Mg (I=5/2):

$$
\begin{aligned}
\frac{(I+1)(2I+1)}{I}\sqrt{\frac{2I+3}{2I-1}} &= \frac{7\times 6}{5}\sqrt{\frac{8}{4}} = 11.87939 \\
Q\mu_I &= -0.20 \times 0.85545 = -0.17109 \\
\langle J \| T_1^{(e)} \| J' \rangle \, \langle J \| T_2^{(e)} \| J' \rangle &= -0.078172 \times 0.79931 = -0.06248366 \\
E_J - E_{J-1} &= 0.0001855 \\
\text{conv. to MHz} &= \frac{1.307469\times 10^4 \times 2.349650\times 10^2}{6.579684\times 10^9} = 4.669061\times 10^{-4} \\
\zeta(\text{MHz}) &= 0.3196473
\end{aligned}
$$

The contribution to C in ^{25}Mg is

$$
\Delta C[^{25}\text{Mg}] = \frac{\zeta}{350\sqrt{2}} = 646 \text{ Hz}.
$$

For the case of ^{43}Ca, the fine-structure intervals $E_J - E_{J'}$ are listed in Table 1 and the reduced matrix elements are listed in Table 3. We find for the lowest

Table 1: Fine structure intervals ${}^3P_2 - {}^3P_1$ and ${}^3P_2 - {}^1P_1$ for alkaline-earth elements in inverse cm and a.u.. Data from online NIST Handbook

	J=2	J=1 T	Δ T	a.u.	J=1 S	Δ S	a.u.
Be	21981.3	21978.9	2.345	0.0000107	42565.35	-20584.1	-0.09379
Mg	21911.2	21870.5	40.714	0.0001855	35051.26	-13140.1	-0.05987
Ca	15315.9	15210.1	105.880	0.0004824	23652.30	-8336.4	-0.03798
Sr	14898.6	14504.4	394.212	0.0017962	21698.48	-6799.9	-0.03098

Table 2: Dipole and quadrupole hyperfine reduced matrix elements (a.u.) and A & B hyperfine constants (MHz) for ^{25}Mg from a CI calculation assuming μ_I=-0.85545, Q=0.20, $I = 5/2$. Experimental data from Kluge & Sauter, Z. Physik **270** 295 (1974).

Mat. Element	k=1	A (CI)	A (Expt)	k=2	B (CI)	B (Expt)
$\langle {}^3P_2 \Vert T_k \Vert {}^3P_1 \rangle$	-0.078172			0.799310		
$\langle {}^3P_2 \Vert T_k \Vert {}^1P_1 \rangle$	0.118994			0.001631		
$\langle {}^3P_2 \Vert T_k \Vert {}^3P_2 \rangle$	0.156105	-127.51	-128.445(5)	0.703115	15.80	16.009(5)
$\langle {}^3P_1 \Vert T_k \Vert {}^3P_1 \rangle$	0.078403	-143.33	-144.977(5)	-0.462679	-7.94	-8.308(5)
$\langle {}^1P_1 \Vert T_k \Vert {}^1P_1 \rangle$	0.004809	-8.78	-7.7(5)	0.374739	6.43	$0 < B < 16$

${}^3P_2$ state in ^{43}Ca(I=7/2):

$$\begin{aligned}
\frac{(I+1)(2I+1)}{I}\sqrt{\frac{2I+3}{2I-1}} &= \frac{9\times 8}{7}\sqrt{\frac{5}{3}} = 13.27880 \\
Q\mu_I &= 0.049 \times 1.317600 = 0.0645624 \\
\langle J \Vert T_1^{(e)} \Vert J' \rangle \langle J \Vert T_2^{(e)} \Vert J' \rangle &= 0.098196 \times -1.169740 = -0.114864 \\
E_J - E_{J-1} &= 0.0004824 \\
\text{conv. to MHz} &= 4.669061 \times 10^{-4} \\
\zeta(\text{MHz}) &= -0.095311
\end{aligned}$$

The contribution to C in ^{43}Ca is

$$\Delta C[{}^{43}\text{Ca}] = \frac{\zeta}{120\sqrt{15}} = -205 \text{ Hz}.$$

Table 3: Dipole and quadrupole hyperfine reduced matrix elements (a.u.) and A & B hyperfine constants (MHz) for ^{43}Ca from a CI calculation assuming μ_I=-1.3176, Q=0.049, $I = 7/2$. Experimental data from PRL **42**, 1528 (1979) and Spectrochemica Acta B**53**, 709 (1998).

Mat. Element	k=1	A (CI)	A (Expt)	k=2	B (CI)	B (Expt)
$\langle ^3P_2 \| T_k \| ^3P_1 \rangle$	0.098196			-1.169740		
$\langle ^3P_2 \| T_k \| ^1P_1 \rangle$	0.145153			0.003754		
$\langle ^3P_2 \| T_k \| ^3P_2 \rangle$	0.201343	-180.94	-171.962(2)	1.024212	-5.64	-5.436(8)
$\langle ^3P_1 \| T_k \| ^3P_1 \rangle$	0.103140	-207.25		-0.680244	2.86	
$\langle ^1P_1 \| T_k \| ^1P_1 \rangle$	0.007632	-15.34	-15.54(3)	0.842385	-3.54	-3.48(13)