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Magnetic moments for lithium quartet S states

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Abstract. The fully correlated calculations of the Zeeman g_J factors for the first three quartet S states of lithium are presented, including relativistic and radiative corrections of orders α^2, $\alpha^2\, m/M$, and α^3. The isotope shifts in g_J are predicted precisely for various isotopes of lithium.

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1 Introduction

The deviation of the Zeeman g_J factor of a bound electron in an atom from its free-electron value provides the most sensitive test on relativistic and radiative effects for the atom in external magnetic fields. Recently we have performed high-precision calculations [1] of the g_J factors for the low-lying doublet states of lithium and the ground state Be$^+$, including relativistic and radiative corrections of orders α^2, $\alpha^2\, m/M$, and α^3 atomic units, based on the extended Breit equation which includes the anomalous magnetic moment interactions [2]. Our theoretical results agree with but are far more accurate than the experimental measurements for the ground states of lithium and Be$^+$. In this paper, we extend our work to the first three quartet S states of lithium $1s2s3s\ ^4$S, $1s2s4s\ ^4$S, and $1s2s5s\ ^4$S, including the isotope shifts in g_J. To the best of our knowledge, no such calculation has been reported in the literature. These core-excited states are truly bound states against autoionization and are accessible to experiment. The measured lifetimes of these states are 6.9(3) ns, 15.4(5) ns, and 34(2) ns [3–5] respectively and are in reasonably good agreement with theoretical predictions [6].

2 Theoretical formulation

The starting point for evaluating the Zeeman g_J factor for lithium in an S state is [7]

$$g_J = -\langle H'_Z\rangle/(\mu_{\rm B} H_M J)\,, \tag{1}$$

where the matrix element is evaluated in the state $M_J = J$, H'_Z is the magnetic-field dependent part of the Hamiltonian, H_M is the external magnetic field, and $\mu_{\rm B}$ is the Bohr magneton. Here a convention has been used [7], in which the g_J factor for the electron is negative. The Hamiltonian H'_Z for S states can be written in the form of (in atomic units throughout) [2]

$$\begin{aligned} H'_Z = &-\mu_{\rm B} g_e H_M \sum_i s_{iz} + \frac{1}{3}(1+g_e)\alpha^2\mu_{\rm B} H_M \\ &\times \sum_{i\neq j} \frac{\mathbf{r}_i\cdot\mathbf{r}_{ij}}{r_{ij}^3} s_{iz} + \frac{1}{3} g_e \alpha^2 \mu_{\rm B} H_M \sum_{i\neq j} \frac{\mathbf{r}_i\cdot\mathbf{r}_{ij}}{r_{ij}^3} s_{jz} \\ &+ \left(\frac{2}{3} - \frac{1}{6} g_e\right)\alpha^2\mu_{\rm B} H_M \sum_i \nabla_i^2 s_{iz} \\ &- \frac{Z}{3}(1+g_e)\alpha^2\mu_{\rm B} H_M \sum_i \frac{1}{r_i} s_{iz} \\ &+ \frac{1}{3} Z \frac{m}{M} g_e \alpha^2 \mu_{\rm B} H_M \sum_i \frac{1}{r_i} s_{iz} \\ &+ \frac{1}{3} Z \frac{m}{M} g_e \alpha^2 \mu_{\rm B} H_M \sum_{i<j} \left(\frac{\mathbf{r}_i\cdot\mathbf{r}_j}{r_i^3} s_{iz} + \frac{\mathbf{r}_i\cdot\mathbf{r}_j}{r_j^3} s_{jz} \right), \end{aligned} \tag{2}$$

where the free electron g_J factor is [8]

$$\begin{aligned} g_e = -2\,[&1 + \alpha/2\pi - 0.328\,478\,965\,(\alpha/\pi)^2 \\ &+ 1.181\,241\,456(\alpha/\pi)^3 + \cdots]\,, \end{aligned} \tag{3}$$

m/M is the electron to nuclear mass ratio, and Z is the nuclear charge. The application of angular momentum algebra yields the following expression

$$\begin{aligned} g_J = \; & g_e + \frac{1}{\sqrt{(2J+1)(J+1)J}} \\ &\times \left[\alpha^2 \left(\frac{g_e}{6} - \frac{2}{3}\right) F_5 + \alpha^2 \frac{Z}{3}(1 + g_e(1-m/M))F_6 \right. \\ &\left. -\alpha^2 \frac{1}{3}(1+g_e) F_7^{(1)} - \alpha^2 \frac{1}{3} g_e F_7^{(2)} - \alpha^2 \frac{Z}{3}\frac{m}{M} g_e F_S \right], \end{aligned} \tag{4}$$

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where the reduced matrix elements F_5, F_6, $F_7^{(1)}$, $F_7^{(2)}$, and F_S are defined with respect to a nonrelativistic wave function Ψ:

$$F_5 = \sum_i \langle\Psi||\nabla_i^2||\Psi\rangle\langle S||s_i||S\rangle\,, \tag{5}$$

$$F_6 = \sum_i \langle\Psi||\frac{1}{r_i}||\Psi\rangle\langle S||s_i||S\rangle\,, \tag{6}$$

$$F_7^{(1)} = \sum_{i\neq j} \langle\Psi||\frac{\mathbf{r}_i\cdot\mathbf{r}_{ij}}{r_{ij}^3}||\Psi\rangle\langle S||s_i||S\rangle\,, \tag{7}$$

$$F_7^{(2)} = \sum_{i\neq j} \langle\Psi||\frac{\mathbf{r}_i\cdot\mathbf{r}_{ij}}{r_{ij}^3}||\Psi\rangle\langle S||s_j||S\rangle\,, \tag{8}$$

$$F_S = \sum_{i\neq j} \langle\Psi||\frac{\mathbf{r}_i\cdot\mathbf{r}_j}{r_i^3}||\Psi\rangle\langle S||s_i||S\rangle\,, \tag{9}$$

with S being the total spin angular momentum.

In order to exhibit all the nuclear mass terms explicitly, we rescale the Hamiltonian for a three-electron atomic system according to $r \to (m/\mu)r$. The resulting Hamiltonian is then

$$H = H_0 + \lambda H'\,, \tag{10}$$

with

$$H_0 = -\frac{1}{2}\sum_{i=1}^{3}\nabla_i^2 - Z\sum_{i=1}^{3}\frac{1}{r_i} + \sum_{i>j}^{3}\frac{1}{r_{ij}}\,, \tag{11}$$

and

$$H' = \sum_{i>j}^{3}\nabla_i\cdot\nabla_j\,, \tag{12}$$

in units of $2R_M$, where $R_M = (1-\mu/M)R_\infty$, $\mu = mM/(m+M)$ is the electron reduced mass, and $\lambda = -\mu/M$, which can be treated as a perturbation parameter. The Schrödinger equation

$$H\Psi = E\Psi \tag{13}$$

can be solved perturbatively by expanding Ψ and E according to

$$\Psi = \Psi_0 + \lambda\Psi_1 + \cdots\,, \tag{14}$$

$$E = \varepsilon_0 + \lambda\varepsilon_1 + \lambda^2\varepsilon_2 + \cdots \tag{15}$$

Thus equation (13) becomes

$$H_0\Psi_0 = \varepsilon_0\Psi_0\,, \tag{16}$$

$$(\varepsilon_0 - H_0)\Psi_1 = (H' - \varepsilon_1)\Psi_0\,. \tag{17}$$

ε_1 and ε_2 are

$$\varepsilon_1 = \langle\Psi_0|H'|\Psi_0\rangle\,, \tag{18}$$

$$\varepsilon_2 = \langle\Psi_0|H'|\Psi_1\rangle - \varepsilon_1\langle\Psi_0|\Psi_1\rangle\cdot \tag{19}$$

Both Ψ_0 and Ψ_1 were solved variationally in multiple basis sets in Hylleraas coordinates containing terms of the form

$$r_1^{j_1}\, r_2^{j_2}\, r_3^{j_3}\, r_{12}^{j_{12}}\, r_{23}^{j_{23}}\, r_{31}^{j_{31}}\, \mathrm{e}^{-\alpha r_1 - \beta r_2 - \gamma r_3}\,\chi_1\,, \tag{20}$$

where χ_1 is a spin function. As described previously [9], all terms from (20) are nominally included such that

$$j_1 + j_2 + j_3 + j_{12} + j_{23} + j_{31} \leq \Omega\,, \tag{21}$$

and the convergence of the eigenvalues is studied as Ω is progressively increased. The perturbing effect of mass polarization $\lambda H'$ on the expectation value of an operator A can be obtained using

$$\Psi = \Psi_0 + \lambda\left(\Psi_1 - \langle\Psi_1|\Psi_0\rangle\Psi_0\right) + \cdots\,, \tag{22}$$

where the extra term $-\langle\Psi_1|\Psi_0\rangle\Psi_0$ is added to Ψ_1 so that the first two terms of the right hand side are orthogonal to each other [10]. Thus,

$$\langle\Psi|A|\Psi\rangle = A_0 + \lambda A_1 + \cdots\,, \tag{23}$$

where

$$A_0 = \langle\Psi_0|A|\Psi_0\rangle, \tag{24}$$

and

$$A_1 = 2\langle\Psi_0|A|\Psi_1\rangle - 2\langle\Psi_0|\Psi_1\rangle\langle\Psi_0|A|\Psi_0\rangle\cdot \tag{25}$$

Furthermore, due to the use of μ-scaled atomic units in equation (10), the units of $\langle\Psi|A|\Psi\rangle$ in equation (23) are $(\mu/m)^n\, 2R_\infty$, where $-n$ is the degree of homogeneity of operator A in three-electron coordinate space such that

$$A(\omega\mathbf{r}_1, \omega\mathbf{r}_2, \omega\mathbf{r}_3) = \omega^{-n}A(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)\,. \tag{26}$$

For example, $n = 2$ for ∇_i^2. We therefore have the explicit mass-dependent formula

$$\langle\Psi|A|\Psi\rangle = \left(\frac{\mu}{m}\right)^n (A_0 + \lambda A_1 + \cdots) \text{ in } 2R_\infty\,. \tag{27}$$

Equation (4) can thus be recast into the following expression which is general for S states and correct to orders α^2, $\alpha^2\, m/M$, and α^3

$$\frac{g_J}{g_e} - 1 = \frac{1}{\sqrt{(2J+1)(J+1)J}} \times \left(\alpha^2 C_{20} + \alpha^3 C_{30} + \alpha^2\frac{m}{M}C_{21}\right), \tag{28}$$

where

$$C_{20} = \frac{1}{2}F_{5\infty} + \frac{1}{6}ZF_{6\infty} - \frac{1}{6}F_{7\infty}^{(1)} - \frac{1}{3}F_{7\infty}^{(2)}\,, \tag{29}$$

$$C_{30} = -\frac{1}{6\pi}F_{5\infty} + \frac{1}{12\pi}ZF_{6\infty} - \frac{1}{12\pi}F_{7\infty}^{(1)}\,, \tag{30}$$

$$C_{21} = -F_{5\infty} - \frac{1}{2}ZF_{6\infty} - \frac{1}{3}ZF_{S\infty} + \frac{1}{6}F_{7\infty}^{(1)} + \frac{1}{3}F_{7\infty}^{(2)} + \frac{1}{2}\tilde{\epsilon}_5 + \frac{1}{6}Z\tilde{\epsilon}_6 - \frac{1}{6}\tilde{\epsilon}_7^{(1)} - \frac{1}{3}\tilde{\epsilon}_7^{(2)}\,, \tag{31}$$

the subscript ∞ means that the reduced matrix elements of F_i are calculated using an infinite nuclear mass wave function, and $\tilde{\epsilon}_5 = -A_1$ in equation (27) for the case

Table 1. Convergence of the reduced matrix elements $F_{5\infty}$, $F_{6\infty}$, $F_{7\infty}$, and $F_{S\infty}$ for the $1s2s3s$ ^{4}S state of lithium. Units are $2R_\infty$.

No. of terms	$F_{5\infty}$	$F_{6\infty}$	$F_{7\infty}$	$F_{S\infty}$
84	–13.459 214 682 6	4.809 046 316 05	0.967 915 717 05	–0.302 722 0
210	–13.459 255 653 0	4.809 055 210 29	0.967 909 935 11	–0.307 352 6
462	–13.459 258 065 9	4.809 055 172 30	0.967 907 474 00	–0.306 128 2
924	–13.459 258 084 5	4.809 055 168 15	0.967 907 415 70	–0.306 185 1
1716	–13.459 258 097 5	4.809 055 171 11	0.967 907 414 98	–0.306 195 9
3003	–13.459 258 099 2	4.809 055 171 33	0.967 907 414 59	–0.306 198 3
4213	–13.459 258 099 5	4.809 055 171 39	0.967 907 414 66	–0.306 198 2
∞	–13.459 258 099 5(3)	4.809 055 171 39(5)	0.967 907 414 66(7)	–0.306 198 2(1)

Table 2. The reduced matrix elements $F_{5\infty}$, $F_{6\infty}$, $F_{7\infty}$, and $F_{S\infty}$, as well as the coefficients $\tilde{\epsilon}_5$, $\tilde{\epsilon}_6$, and $\tilde{\epsilon}_7$ for the $1s2s3s$ ^{4}S, $1s2s4s$ ^{4}S, and $1s2s5s$ ^{4}S states of lithium. Units are $2R_\infty$.

Term	$1s2s3s$ ^{4}S	$1s2s4s$ ^{4}S	$1s2s5s$ ^{4}S
$F_{5\infty}$	–13.459 258 099 5(3)	–13.318 914 674(1)	–13.267 453 193(7)
$F_{6\infty}$	4.809 055 171 39(5)	4.704 841 165 8(4)	4.662 358 548(2)
$F_{7\infty}$	0.967 907 414 66(7)	0.795 608 821 9(2)	0.719 622 445 80(9)
$F_{S\infty}$	–0.306 198 2(1)	–0.249 177(1)	–0.224 455 5(5)
$\tilde{\epsilon}_5$	0.098 626(1)	0.096 150 6(1)	0.092 517 6(3)
$\tilde{\epsilon}_6$	–0.014 170 4(1)	–0.012 174 54(3)	–0.009 881 24(5)
$\tilde{\epsilon}_7$	0.006 801 1(1)	0.011 551 69(1)	0.016 615 06(7)

Table 3. Contributions to $(g_J/g_e - 1) \times 10^6$ for the $1s2s3s$ ^{4}S, $1s2s4s$ ^{4}S, and $1s2s5s$ ^{4}S states of ^{7}Li.

Contribution	$1s2s3s$ ^{4}S	$1s2s4s$ ^{4}S	$1s2s5s$ ^{4}S
α^2	–66.121 817 839 5(8)	–64.688 933 573(6)	–64.104 821 35(2)
α^3	0.107 463 655 644(3)	0.106 343 102 24(1)	0.105 932 214 89(6)
$\alpha^2\, m/M$	0.007 607 505 2(6)	0.007 467 920(1)	0.007 410 225 5(6)
Total	–66.006 746 678(1)	–64.575 122 550(6)	–63.991 478 91(2)

of $A = F_5$, etc. In equation (28), the only nuclear mass dependent term is the one proportional to C_{21}. The isotope shift for two isotopes M_1 and M_2 can thus be expressed in the form

$$\frac{g_J(M_1)}{g_J(M_2)} - 1 = \frac{1}{\sqrt{(2J+1)(J+1)J}} \left(\frac{m}{M_1} - \frac{m}{M_2} \right) \alpha^2\, C_{21}\,. \tag{32}$$

For a quartet S state, it is easy to see that $F_{7\infty}^{(1)} = F_{7\infty}^{(2)}$. Furthermore, the application of the virial theorem $\langle T \rangle = -E$, where T is the kinetic energy operator and E is the total energy, yields

$$-F_{5\infty} = Z F_{6\infty} - F_{7\infty}^{(1)}\,. \tag{33}$$

Thus, for quartet states, we have the following simplified expressions

$$C_{20} = -\frac{Z}{3} F_{6\infty} \tag{34}$$

$$C_{30} = -\frac{1}{4\pi} F_{5\infty} \tag{35}$$

$$C_{21} = -\frac{1}{2} F_{5\infty} - \frac{Z}{3} F_{S\infty} + \frac{1}{2}\tilde{\epsilon}_5 + \frac{Z}{6}\tilde{\epsilon}_6 - \frac{1}{2}\tilde{\epsilon}_7\,, \tag{36}$$

where $\tilde{\epsilon}_7 = \tilde{\epsilon}_7^{(1)} = \tilde{\epsilon}_7^{(2)}$.

3 Results

Equations (16, 17) were solved variationally in Hylleraas basis sets equation (20) for the $1s2s3s$ ^{4}S, $1s2s4s$ ^{4}S, and $1s2s5s$ ^{4}S states of lithium. The details of the solutions can be found in reference [9]. Table 1 lists the convergence study on the reduced matrix elements $F_{5\infty}$, $F_{6\infty}$, $F_{7\infty}$, and $F_{S\infty}$, where $F_{7\infty}$ denotes either $F_{7\infty}^{(1)}$ or $F_{7\infty}^{(2)}$, for the lowest state $1s2s3s$ ^{4}S, as the size of basis set increases progressively. Table 2 presents a complete list of the reduced matrix elements of $F_{5\infty}$, $F_{6\infty}$, $F_{7\infty}$, and $F_{S\infty}$, as well as the coefficients $\tilde{\epsilon}_5$, $\tilde{\epsilon}_6$, and $\tilde{\epsilon}_7$ for the first three quartet S states. From Table 2, one can verify the identity equation (33) numerically. Our final results for the g_J factors and the isotope shifts are contained in Tables 3 and 4. The electron reduced mass to nuclear mass ratios, including the binding energy corrections, are tabulated in Table 5 [11–13]. It should be pointed out that the numbers quoted in brackets in Tables 3 and 4 are computational uncertainties only. The uncertainties from the nuclear masses and the fine structure constant α are not included. Furthermore, the next higher-order relativistic and radiative corrections to g_J not included in the calculation are terms of order α^4. For isotope shifts, the next higher-order terms are of orders $\alpha^2\,(m/M)^2$ and $\alpha^3\, m/M$.

Table 4. Isotope shifts in g_J for lithium in the $1s2s3s\ ^4\mathrm{S}$, $1s2s4s\ ^4\mathrm{S}$, and $1s2s5s\ ^4\mathrm{S}$ states. In the table, $G(^A\mathrm{Li}) = (g_J(^A\mathrm{Li})/g_J(^7\mathrm{Li}) - 1) \times 10^{11}$, where A denotes an isotope of lithium.

Isotope	$1s2s3s\ ^4\mathrm{S}$	$1s2s4s\ ^4\mathrm{S}$	$1s2s5s\ ^4\mathrm{S}$
$G(^6\mathrm{Li})$	126.619 125(9)	124.295 88(2)	123.335 61(2)
$G(^8\mathrm{Li})$	–95.461 575(7)	–93.710 01(2)	–92.986 042(8)
$G(^9\mathrm{Li})$	–169.493 76(1)	–166.383 84(3)	–165.098 41(1)
$G(^{11}\mathrm{Li})$	–277.495 26(2)	–272.403 70(4)	–270.299 18(2)

Table 5. Electron reduced mass to nuclear mass ratios μ/M for lithium isotopes.

Mass number	$\mu/M \times 10^4$
6	0.912 167 591
7	0.782 020 201
8	0.683 896 331
9	0.607 798 153
11	0.496 780 632

All these smaller effects have not yet been studied theoretically. On the other hand, no experimental measurements are available for comparison. I hope, however, that the present work may stimulate future research activities in both theory and experiment.

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