

Calculations of Magnetic Moments for Three-Electron Atomic Systems

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The first fully correlated calculations of the magnetic moment in lithium are presented. Relative to the free-electron value, the Zeeman g_J factor for the ground state lithium $g_J/g_e - 1$ is calculated to a computational accuracy of 200 parts in 10^9 , 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. The extensions to the first excited S state of lithium and the ground state of Be^+ are made.

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The theoretical calculation of the magnetic moment for an electron is a fundamental problem in atomic physics. The g_J factor of a *bound* electron in an atom is the most sensitive testing ground for relativistic and radiative effects for the atom in external magnetic fields. Furthermore, for a system more complicated than hydrogen, the study of isotope shifts in g_J requires highly accurate atomic wave functions. In this Letter, we report the first significant theoretical progress for lithium since the early work of Hegstrom [1,2]. Definitive values of g_J and its isotope shifts will be established.

Based on the extended Breit equation which includes the anomalous magnetic moment interactions, Hegstrom [1] studied nuclear recoil and anomalous magnetic moment corrections to the Hamiltonian of an n -electron atomic system in external magnetic field and showed that the magnetic-field dependence of the radiative corrections of order α^3 atomic units vanishes for S states. The lowest-order radiative correction of order α^3 atomic units is due entirely to the anomalous magnetic moment of the free electron. Thus, the formalism of Hegstrom in the non-relativistic limit is valid up to the order of α^3 atomic units. Hegstrom [2] then evaluated the g_J factor of the ground state lithium and predicted an isotope shift in the ratio between ${}^6\text{Li}$ and ${}^7\text{Li}$, within the Hartree-Fock framework. Veseth [3] also calculated the g_J factors for lithium and other elements using the spin-extended Hartree-Fock theory. Other theoretical methods include the many-body perturbation theory of Veseth [4], the relativistic coupled-cluster single- and double-excitation approximation of Lindroth and Ynnerman [5], and the four-component nonperturbative relativistic formalism of Marketos [6]. These theoretical results, however, vary

over a considerable range. On the experimental side, the lithium ground state g_J value may be derived from three measurements of the ratios: $g_J(\text{Li})/g_J(\text{K})$, $g_J(\text{K})/g_J(\text{Rb})$, and $g_J(\text{Rb})/g_e$, where g_e is the free-electron value, as reviewed by Arimondo, Inguscio, and Violino [7]. Using a laser fluorescence technique, Wineland, Bollinger, and Itano [8] measured the g_J factor of the ground state Be^+ . For few-electron atomic systems, the only isotope shift in g_J that has been established both theoretically and experimentally is for hydrogen [9,10].

From a computational point of view, for few-electron systems, such as helium and lithium, the central problem for a well-converged evaluation of the g_J factor is the adequate inclusion of electron-electron correlations in the nonrelativistic wave functions. For helium, several calculations have been done in the past thirty years, including two recent ones using fully correlated Hylleraas coordinates [11,12]. For lithium, however, no such calculations have been reported in the literature. The present work is based on our recent advances [13–16] in high-precision variational calculations for the lithium atom, using multiple basis sets in Hylleraas coordinates.

The starting point for evaluating the Zeeman g_J factor for lithium in an S state is [2]

$$g_J = -\langle H'_Z \rangle / (\mu_B H_M J), \quad (1)$$

where the matrix element is evaluated in the state $J = 1/2$ and $M_J = 1/2$, H'_Z is the magnetic-field dependent part of the Hamiltonian, H_M is the external magnetic field, and μ_B is the Bohr magneton. Here a convention has been used [2], 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) [1]

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

where the free electron g_J factor is [17]

$$g_e = -2[1 + \alpha/2\pi - 0.328478965(\alpha/\pi)^2 + 1.17611(\alpha/\pi)^3 + \dots], \quad (3)$$

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:

$$g_J = g_e + \frac{1}{\sqrt{(2J+1)(J+1)J}} \left[\alpha^2 \left(\frac{g_e}{6} - \frac{2}{3} \right) F_5 + \alpha^2 \frac{Z}{3} [1 + g_e(1 - m/M)] F_6 - \alpha^2 \frac{1}{3} (1 + g_e) F_7^{(1)} - \alpha^2 \frac{1}{3} g_e F_7^{(2)} - \alpha^2 \frac{Z}{3} \frac{m}{M} g_e F_S \right], \quad (4)$$

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

$$F_5 = \sum_i \langle \Psi | \nabla_i^2 | \Psi \rangle \langle 1/2 || s_i || 1/2 \rangle, \quad (5)$$

$$F_6 = \sum_i \langle \Psi | \frac{1}{r_i} | \Psi \rangle \langle 1/2 || s_i || 1/2 \rangle, \quad (6)$$

$$F_7^{(1)} = \sum_{i \neq j} \langle \Psi | \frac{\mathbf{r}_i \cdot \mathbf{r}_{ij}}{r_{ij}^3} | \Psi \rangle \langle 1/2 || s_i || 1/2 \rangle, \quad (7)$$

$$F_7^{(2)} = \sum_{i \neq j} \langle \Psi | \frac{\mathbf{r}_i \cdot \mathbf{r}_{ij}}{r_{ij}^3} | \Psi \rangle \langle 1/2 || s_j || 1/2 \rangle, \quad (8)$$

$$F_S = \sum_{i \neq j} \langle \Psi | \frac{\mathbf{r}_i \cdot \mathbf{r}_j}{r_i r_j} | \Psi \rangle \langle 1/2 || s_i || 1/2 \rangle. \quad (9)$$

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

$$H = H_0 + \lambda H', \quad (10)$$

with

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

and

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

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

$$H\Psi = E\Psi \quad (13)$$

can be solved perturbatively by expanding Ψ and E according to

$$\Psi = \Psi_0 + \lambda\Psi_1 + \dots, \quad (14)$$

$$E = \varepsilon_0 + \lambda\varepsilon_1 + \lambda^2\varepsilon_2 + \dots \quad (15)$$

Thus Eq. (13) becomes

$$H_0\Psi_0 = \varepsilon_0\Psi_0, \quad (16)$$

$$(\varepsilon_0 - H_0)\Psi_1 = (H' - \varepsilon_1)\Psi_0. \quad (17)$$

ε_1 and ε_2 are

$$\varepsilon_1 = \langle \Psi_0 | H' | \Psi_0 \rangle, \quad (18)$$

$$\varepsilon_2 = \langle \Psi_0 | H' | \Psi_1 \rangle - \varepsilon_1 \langle \Psi_0 | \Psi_1 \rangle. \quad (19)$$

Both Ψ_0 and Ψ_1 were solved variationally in multiple basis sets in Hylleraas coordinates containing terms of the form [14]

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

where χ_1 is the spin function. The perturbing effect of mass polarization $\lambda H'$ on the expectation value of an operator A can be obtained using

$$\Psi = \Psi_0 + \lambda(\Psi_1 - \langle \Psi_1 | \Psi_0 \rangle \Psi_0) + \dots, \quad (21)$$

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 [18]. Thus,

$$\langle \Psi | A | \Psi \rangle = A_0 + \lambda A_1 + \dots, \quad (22)$$

where

$$A_0 = \langle \Psi_0 | A | \Psi_0 \rangle, \quad (23)$$

and

$$A_1 = 2\langle \Psi_0 | A | \Psi_1 \rangle - 2\langle \Psi_0 | \Psi_1 \rangle \langle \Psi_0 | A | \Psi_0 \rangle. \quad (24)$$

Furthermore, due to the use of μ -scaled atomic units in Eq. (10), the units of $\langle \Psi | A | \Psi \rangle$ in Eq. (22) are $(\mu/m)^n 2R_\infty$, where $-n$ is the degree of homogeneity of operator A in three-electron coordinate space. We therefore have the explicit mass-dependent formula

$$\langle \Psi | A | \Psi \rangle = \left(\frac{\mu}{m} \right)^n (A_0 + \lambda A_1 + \dots) \text{ in } 2R_\infty. \quad (25)$$

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 :

$$\frac{g_J}{g_e} - 1 = \frac{1}{\sqrt{(2J+1)(J+1)J}} \times \left(\alpha^2 C_{20} + \alpha^3 C_{30} + \alpha^2 \frac{m}{M} C_{21} \right), \quad (26)$$

where

$$C_{20} = \frac{1}{2} F_{5\infty} + \frac{1}{6} Z F_{6\infty} - \frac{1}{6} F_{7\infty}^{(1)} - \frac{1}{3} F_{7\infty}^{(2)}, \quad (27)$$

TABLE I. Reduced matrix elements $F_{5\infty}$, $F_{6\infty}$, $F_{7\infty}^{(1)}$, $F_{7\infty}^{(2)}$, and $F_{S\infty}$, as well as the coefficients $\tilde{\epsilon}_5$, $\tilde{\epsilon}_6$, $\tilde{\epsilon}_7^{(1)}$, $\tilde{\epsilon}_7^{(2)}$, and $\tilde{\epsilon}_S$ for the 2^2S state of Li. Units are $2R_\infty$.

Term	Value	Term	Value
$F_{5\infty}$	-0.598 033 56(7) -0.573 37 ^a	$\tilde{\epsilon}_5$	0.018 02(1)
$F_{6\infty}$	0.441 329 87(6) 0.434 24 ^a	$\tilde{\epsilon}_6$	-0.016 642(1)
$F_{7\infty}^{(1)}$	0.725 956 01(5) 0.728 40 ^a	$\tilde{\epsilon}_7^{(1)}$	-0.047 045(2)
$F_{7\infty}^{(2)}$	0.032 708 34(5) 0.026 45 ^a	$\tilde{\epsilon}_7^{(2)}$	0.011 209(3)
$F_{S\infty}$	-0.003 271(2) 0.0 ^a	$\tilde{\epsilon}_S$	0.319 20(5)

^aHegstrom, Ref. [2].

$$C_{30} = -\frac{1}{6\pi} F_{5\infty} + \frac{1}{12\pi} ZF_{6\infty} - \frac{1}{12\pi} F_{7\infty}^{(1)}, \quad (28)$$

$$C_{21} = -F_{5\infty} - \frac{1}{2} ZF_{6\infty} - \frac{1}{3} ZF_{S\infty} + \frac{1}{6} F_{7\infty}^{(1)} + \frac{1}{3} F_{7\infty}^{(2)} + \frac{1}{2} \tilde{\epsilon}_5 + \frac{1}{6} Z\tilde{\epsilon}_6 - \frac{1}{6} \tilde{\epsilon}_7^{(1)} - \frac{1}{3} \tilde{\epsilon}_7^{(2)}, \quad (29)$$

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 Eq. (25) for the case of $A = F_5$, etc. In Eq. (26), 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

$$\frac{g_J(M_1)}{g_J(M_2)} - 1 = \frac{1}{\sqrt{(2J+1)(J+1)J}} \left(\frac{m}{M_1} - \frac{m}{M_2} \right) \alpha^2 C_{21}. \quad (30)$$

Equations (16) and (17) were solved variationally in Hylleraas basis sets Eq. (20). The precision for the ground

state energy of lithium is about 7 parts in 10^{13} . Table I lists the reduced matrix elements of $F_{5\infty}$, $F_{6\infty}$, $F_{7\infty}^{(1)}$, $F_{7\infty}^{(2)}$, and $F_{S\infty}$, as well as their finite nuclear mass corrections $\tilde{\epsilon}_5$, $\tilde{\epsilon}_6$, $\tilde{\epsilon}_7^{(1)}$, $\tilde{\epsilon}_7^{(2)}$, and $\tilde{\epsilon}_S$ for the ground state of lithium, together with a comparison with the work of Hegstrom [2]. Our calculations have dramatically improved the accuracy of Hegstrom's results by several orders of magnitude. Table II lists the contributions to the $g_J/g_e - 1$ for ^7Li in the 2^2S and 3^2S states and for the ground state $^9\text{Be}^+$, together with comparisons with other calculations and experiments. The computational uncertainties that we have achieved for $g_J/g_e - 1$ are 0.2 ppm (parts per million), 3 ppm, and 0.03 ppm for the ^7Li 2^2S , ^7Li 3^2S , and $^9\text{Be}^+$ 2^2S states, respectively. On the other hand, the other theoretical values do not appear to have well converged. For the ground states of ^7Li and $^9\text{Be}^+$, our results are in agreement with the experimental values. However, the errors associated with the experimental values are too large to provide a severe test for orders α^3 and $\alpha^2 m/M$ effects. Finally, the isotope shifts for lithium are contained in Table III. The only available theoretical result is from Hegstrom's work [2] for ^6Li and ^7Li . Note that the finite nuclear mass corrections to the wave functions, which were completely neglected in Hegstrom's calculation, contribute at the 6% level for the ^6Li - ^7Li case. All the atomic masses used in this work were taken from Ref. [19]. To the best of our knowledge, there are no experimental measurements reported for these isotope shifts.

In summary, we have obtained high-precision theoretical values of the g_J factors for lithium and Be^+ , including all relativistic and radiative corrections of orders α^2 , $\alpha^2 m/M$, and α^3 . For the first time, the isotope shifts in g_J have been predicted definitively for the ground and the first excited S states of lithium. For g_J , additional precisions for the experimental values are required in order to test the radiative correction of order α^3 and the relativistic recoil correction of order $\alpha^2 m/M$. On the theoretical side,

TABLE II. Contributions to $(g_J/g_e - 1) \times 10^6$ for the 2^2S and 3^2S states of ^7Li and the 2^2S state of $^9\text{Be}^+$, and comparisons with other calculations and experiments.

Contribution	^7Li 2^2S	^7Li 3^2S	$^9\text{Be}^+$ 2^2S
α^2	-9.141 458(2)	-3.114 536(9)	-28.604 303(1)
Hegstrom [2]	-8.6865		
α^3	0.015 099 624(2)	0.005 235 687(7)	0.047 902 502 4(7)
Hegstrom [2]	0.0145		
$\alpha^2 m/M$	0.000 258 43(2)	0.000 018 96(9)	0.001 587 210(4)
Hegstrom [2]	0.0002		
Total	-9.126 101(2)	-3.109 282(9)	-28.554 814(1)
Hegstrom [2]	-8.6718		
Veseth [3]	-9.209		
Veseth [4]	-8.879		
Lindroth and Ynnerman [5]	-8.85(10)		-28.23(25)
Marketos [6]	-7.022		
Experiment	-9.14(32) ^a		-28.59(21) ^b

^aArimondo *et al.* [7].

^bWineland *et al.* [8].

TABLE III. Isotope shifts in g_J for Li in the 2^2S and 3^2S states. In the table, $G(^A\text{Li}) = [g_J(^A\text{Li})/g_J(^7\text{Li}) - 1] \times 10^{11}$, where A denotes an isotope of Li.

Isotope	2^2S	3^2S
$G(^6\text{Li})$	4.301 3(3) 3.0 ^a	0.315(1)
$G(^8\text{Li})$	-3.242 8(2)	-0.238(1)
$G(^9\text{Li})$	-5.757 8(4)	-0.422(2)
$G(^{11}\text{Li})$	-9.426 6(7)	-0.691(3)

^aHegstrom, [2].

the next higher-order relativistic and QED corrections not included in the calculation are terms of order α^4 which could contribute to $g_J/g_e - 1$ at the 50 ppm level for the lithium ground state and thus could be comparable to the $\alpha^2 m/M$ terms. No analysis on these high-order terms has been reported even for an isolated lithium, although significant progress [20–23] has been made recently for an isolated helium. We hope the present work may stimulate further research activities in both theory and experiment.

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