

## Magnetic moment of atomic lithium

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Bound-state relativistic contributions to the  $g_J$  factor of ground-state atomic lithium are calculated and compared with the experimental value  $g_J(\text{Li})/g_e = 1 - (8.9 \pm 0.4) \times 10^{-6}$ , where  $g_e$  is the free-electron  $g$  factor. This comparison is taken as the basis for judging the accuracy of several different Li wave functions taken from the literature. Most of these wave functions give agreement with the experimental value within the experimental uncertainty. A more precise experimental measurement would be desirable in order to provide a more stringent test. A wave function of the restricted Hartree-Fock type, however, leads to a value which is in disagreement with the experimental value. This is attributed to the inability of the restricted Hartree-Fock function to account for the exchange polarization of the  $1s^2$  core electrons; the latter are found to contribute about  $-1.2 \times 10^{-6}$  to  $g_J(\text{Li})/g_e$ , or about 13% of the total relativistic correction. In addition to the dominant relativistic corrections of order  $\alpha^2$ , radiative corrections (order  $\alpha^3$ ), and nuclear-mass corrections (order  $\alpha^2 m/M$ ) are also calculated. An isotopic shift  $g_J(^6\text{Li})/g_J(^7\text{Li}) = 1 + 3.0 \times 10^{-11}$  is predicted. The experimental measurements for Li are not yet precise enough to test these higher-order corrections.

In the past several years there has been a continuing interest in the precise experimental measurement and theoretical calculation of atomic magnetic moments.<sup>1,2</sup> Experimental measurements of atomic- $g$ -factor ratios are now becoming precise enough to measure effects due to the motion of the nucleus and, to a lesser extent, the bound-state radiative corrections.<sup>2</sup> For  $S$  states these effects are of order  $\alpha^2 m/M$  and  $\alpha^3$ , respectively, and are correspondingly smaller than the dominant relativistic corrections, which are of order  $\alpha^2$ . All of these contributions have been calculated for the  $^2S$  ground state of hydrogenic atoms and for the first excited  $^3S$  state of atomic helium.<sup>1</sup> The corresponding experimental measurements are all in excellent agreement with these calculations.

If one interprets this agreement as a confirmation of the general theory of relativistic contributions to atomic magnetic moments, one can then consider the precise measurement of magnetic moments of larger atoms as a sensitive test for atomic-structure concepts, that is, for the accuracy of atomic wave functions. This paper presents the results of calculations for the  $^2S$  ground state of the lithium atom.<sup>3</sup> Lithium is of special interest since it is the simplest atom (and thus most amenable to calculation) with both an open and a closed shell of electrons. It is also the prototype alkali atom. Unlike hydrogen and  $^3S$  helium, both of which possess only unpaired electrons, the electronic structure of atomic lithium in the simplest picture consists of a single unpaired  $2s$  electron outside a  $1s^2$  closed-shell elec-

tronic core. Since the electron spins in the core are paired, one expects in first approximation no contribution by the core electrons to the magnetic moment for the same reason that ground-state helium possesses no magnetic moment. Then the entire contribution to the lithium magnetic moment would arise from the spin moment of the lithium  $2s$  electron. The calculations presented below partially support this approximate picture, but also show that the spins of the core electrons make a net contribution of about 13% of the total bound-state correction to the  $g$  factor, a rather significant amount. This is seen to be due to the exchange polarization of the core,<sup>4</sup> an effect already well known in hyperfine-structure calculations.<sup>5,6</sup> Since nearly all other atoms with nonzero magnetic moments have a closed-shell plus open-shell structure, one expects this core polarization correction to atomic  $g$  factors to occur quite generally. To my knowledge, this effect on atomic magnetic moments has not been studied previously.

The magnetic moment of atomic lithium is approximately equal to the magnetic moment of a free electron, one Bohr magneton; that is, the atomic  $g$  factor, defined by

$$\vec{\mu} = g_J \mu_B \vec{J}, \quad (1)$$

is approximately equal to  $g_e$ , the free-electron  $g$  factor. For a magnetic field  $\vec{H}$  in the  $z$  direction we have

$$\langle \mathcal{H}_{\text{mag}} \rangle = \langle -\vec{\mu} \cdot \vec{H} \rangle = -g_J \mu_B H \langle J_z \rangle, \quad (2)$$

and thus, taking the "stretched" state  $M_J = J$ , we have

$$g_J = -\langle \mathcal{H}_{\text{mag}} \rangle_{M_J = J} / \mu_B H J. \quad (5)$$

In lowest-order approximation for an atomic S state,  $\mathcal{H}_{\text{mag}} = -g_e \mu_B H \sum_i S_{zi}$ , from which it follows that  $g_J \cong g_e$ . However, the magnetic Hamiltonian<sup>2</sup> contains additional higher-order relativistic and magnetic-interaction terms which can be interpreted as arising from (i) increase of the relativistic mass of the electron due to its motion relative to the laboratory frame, (ii) spin-orbit coupling of the electron in the electric field of the nucleus and of the other electrons, and (iii) spin-other-orbit coupling of the electron spin to the orbital motion of the other electrons and of the nucleus. These corrections are all primarily of order  $\alpha^2 \mu_B H$ , but also contain nuclear-mass corrections of order  $\alpha^2 \mu_B H m/M$  and radiative corrections of order  $\alpha^3 \mu_B H$  (the latter are in addition to the radiative corrections already contained in  $g_e$ ). The complete magnetic Hamiltonian<sup>2</sup> (to order  $\alpha^3$ ) is written

$$\mathcal{H}_{\text{mag}} = \mathcal{H}_{\text{rm}} + \mathcal{H}_{\text{so}} + \mathcal{H}_{\text{soo}}, \quad (4)$$

where  $\mathcal{H}_{\text{rm}}$  describes the lowest-order Zeeman interaction plus the relativistic-mass correction,  $\mathcal{H}_{\text{so}}$  describes the spin-orbit coupling, and  $\mathcal{H}_{\text{soo}}$  the spin-other-orbit coupling. These terms may be written explicitly (S states only)

$$\begin{aligned} \mathcal{H}_{\text{rm}} &= -g_e \mu_B H \sum_i \left( 1 - \frac{p_i^2}{2m^2} \right) S_{zi} \\ &\quad - \frac{1}{3m^2} (g_e + 2) \mu_B H \sum_i p_i^2 S_{zi}, \\ \mathcal{H}_{\text{so}} &= -\frac{Ze^2}{3m} (g_e + 1) \mu_B H \sum_i \frac{1}{r_i} S_{zi} \\ &\quad + \frac{e^2}{3m} (g_e + 1) \mu_B H \sum_{i < j} (f_{ij} S_{zi} + f_{ji} S_{zj}), \end{aligned} \quad (5)$$

$$\begin{aligned} \mathcal{H}_{\text{soo}} &= \frac{e^2}{3m} g_e \mu_B H \sum_{i < j} (f_{ji} S_{zi} + f_{ij} S_{zj}) \\ &\quad + \frac{Ze^2}{3M} g_e \mu_B H \sum_i \frac{1}{r_i} S_{zi} \\ &\quad + \frac{Ze^2}{3M} g_e \mu_B H \sum_{i < j} \vec{r}_i \cdot \vec{r}_j \left( \frac{S_{zi}}{r_i^3} + \frac{S_{zj}}{r_j^3} \right), \end{aligned}$$

where

$$g_e = -2(1 + \alpha/2\pi - 0.32848\alpha^2/\pi^2 \dots),$$

$\alpha$  is the fine-structure constant,  $\mu_B$  is the Bohr magneton,  $m$  is the electron mass,  $M$  is the nuclear mass,  $Z$  is the nuclear charge,  $\vec{r}_i$  measures electron  $i$ 's position relative to the nucleus,  $\vec{p}_i$  is the corresponding canonical momentum, and

$$f_{ij} \equiv \frac{\vec{r}_{ij} \cdot \vec{r}_i}{r_{ij}^3} = -\frac{3}{H} \left[ \nabla_i \left( \frac{1}{r_{ij}} \right) \times \vec{A}_i \right]_z, \quad (6)$$

with  $\vec{A}_i = \frac{1}{2} \vec{H} \times \vec{r}_i$ . Natural units are used, and the summations are over all the electrons in the atom.

The atomic  $g$  factor may be calculated from Eqs. (3)–(5), using first-order perturbation theory<sup>2</sup> to evaluate  $\langle H_{\text{mag}} \rangle$ . The wave functions to be used are solutions to Schrödinger's equation

$$\left( \frac{1}{2\mu} \sum_i p_i^2 - \sum_i \frac{Ze^2}{r_i} + \sum_{i < j} \frac{e^2}{r_{ij}} \right) \psi = E\psi, \quad (7)$$

where  $\mu$  is the reduced mass  $mM/(m+M)$ . One finds the following expressions which are general for atomic S states and correct to orders  $\alpha^3$  and  $\alpha^2 m/M$ :

$$\begin{aligned} g_J &= g_{\text{rm}} + g_{\text{so}} + g_{\text{soo}}, \\ \frac{g_{\text{rm}}}{g_e} &= 1 - \frac{1}{2J} \left( F_p \alpha^2 + \frac{1}{3\pi} F_p \alpha^3 + 2F_p \alpha^2 \frac{m}{M} \right), \\ \frac{g_{\text{so}}}{g_e} &= \frac{1}{6J} \left( (ZF_r - G_a) \alpha^2 + \frac{1}{2\pi} (ZF_r - G_a) \alpha^3 \right. \\ &\quad \left. - (ZF_r - G_a) \alpha^2 \frac{m}{M} \right), \end{aligned} \quad (8)$$

$$\frac{g_{\text{soo}}}{g_e} = \frac{1}{3J} \left( G_b \alpha^2 - (G_b + ZF_r + ZG_c) \alpha^2 \frac{m}{M} \right),$$

where

$$\begin{aligned} F_p &= \left\langle \sum_i p_i^2 S_{zi} \right\rangle_{\text{a.u., } \infty}, \quad F_r = \left\langle \sum_i S_{zi} / r_i \right\rangle_{\text{a.u., } \infty}, \\ G_a &= \left\langle \sum_{i < j} (f_{ij} S_{zi} + f_{ji} S_{zj}) \right\rangle_{\text{a.u., } \infty}, \\ G_b &= -\left\langle \sum_{i < j} (f_{ji} S_{zi} + f_{ij} S_{zj}) \right\rangle_{\text{a.u., } \infty}, \\ G_c &= \left\langle \sum_{i < j} \vec{r}_i \cdot \vec{r}_j \left( \frac{S_{zi}}{r_i^3} + \frac{S_{zj}}{r_j^3} \right) \right\rangle_{\text{a.u., } \infty}. \end{aligned} \quad (9)$$

The subscript "a.u.,  $\infty$ " means that the expectation values are to be expressed in atomic units ( $\hbar = m = e = 1$ ) and calculated assuming an infinite nuclear mass in  $\psi$ . This allows the order of magnitude of each term in the  $g$  factor to be exhibited explicitly in Eq. (8). Also recall that a "stretched" state  $M_J = M_S = S$  is assumed. (For atomic hydrogen, for example,  $F_p = \frac{1}{2}$  and  $F_r = 1$ .) The problem is thus reduced to the calculation of the expectation values given in Eq. (9).

If the wave function taken for the calculation were the exact solution to the nonrelativistic Schrödinger equation, Eq. (7), the calculated  $g$  factor would be accurate to orders  $\alpha^3$  and  $\alpha^2 m/M$ . However, there is an uncertainty introduced by the approximate nature of wave functions available for atomic lithium. In fact, the calculations presented here, when compared with experiment, can be considered to be a sensitive test of the accuracy of these wave functions. Several different wave

functions, all of which have been published in the literature,<sup>5-9</sup> were employed for the calculation of  $g_J(\text{Li})$ . All calculations were performed on an IBM 360/75 computer in double precision. Explicit expressions for the expectation values in Eq. (9) evaluated for each type of wave function are given in the Appendix. The numerical results are given in Table I. From these values one can calculate the various contributions to the  $g$  factor using Eq. (8). The results for the total  $g$  factor calculated for each wave function are given in Table II, along with the experimental values.<sup>10</sup>

The number in parentheses beside each entry is the relative difference, expressed as percentage, between the entry and the experimental value. It can be seen that all of the calculated values lie within the experimental error, except those corresponding to the MPHF and RHF functions. The restricted Hartree-Fock wave function gives a  $g_J/g_e - 1$  value which has a particularly large (15%) disagreement with the experimental value. A similar trend occurs when the spin density at the nucleus is calculated; results of previously published calculations<sup>9</sup> for this quantity are also given in Table II for comparison. It can be seen that a given wave function has about the same percentage difference between calculated and experimental values for both properties. This is not too surprising, since both the relativistic corrections to the  $g$  factor as well as the spin density at the nucleus have a similar dependence upon the spin properties of the wave function. (This is not true for properties such as the total electronic energy,<sup>9</sup> also included in Table II.)

Since the spin-optimized-self-consistent-field (SO-SCF) wave function contains the most complete variation of parameters, and is therefore expected to be the most accurate, one expects the  $g$ -factor correction calculated using this function to be the most accurate, although the error may be as great as 2% or 3%.<sup>11,12</sup> It would be desirable to have a more precise experimental value for

comparison; the uncertainty in the present experimental value is about 5%. More accurate wave functions<sup>13</sup> for Li of the Hylleraas type also exist and should provide the most accurate calculated value for  $g_J(\text{Li})$ . These calculations have not yet been performed. If the cases of disagreement are attributed to inaccuracies in the maximally paired Hartree-Fock (MPHF) and restricted Hartree-Fock (RHF) wave functions, one can conclude that there is agreement between theory and experiment for the atomic-lithium magnetic moment to within the quoted experimental uncertainty.

A rather interesting analysis of the calculated result can be made in terms of orbital contributions to the lithium  $g$  factor. This is most simply done within the Hartree-Fock framework, although a similar analysis could also be made for the other wave functions. The unrestricted Hartree-Fock (UHF) wave function<sup>5</sup> for Li has the form

$$\psi_{\text{UHF}} = \mathcal{Q} \{ (1s\alpha)(1s'\beta)(2s\alpha) \}, \quad (10)$$

where  $\mathcal{Q}$  is an antisymmetrizer,  $1s$ ,  $1s'$ , and  $2s$  are atomic orbitals, and  $\alpha, \beta$  are  $m_s = +\frac{1}{2}$  and  $-\frac{1}{2}$  spin functions, respectively. For this function, write

$$g_J = \sum_i g_i, \quad F_p = \sum_i F_{pi}, \quad \text{etc.}, \quad (11)$$

where the subscript  $i$  labels the atomic orbitals. We then have, in terms of one- and two-electron integrals over atomic orbitals (see Appendix),

$$\begin{aligned} F_{pi} &= m_{si} \langle i | p^2 | i \rangle, \quad F_{ri} = m_{si} \langle i | r^{-1} | i \rangle, \\ G_{ai} &= m_{si} \sum_{j(\neq i)} (\langle ij | f_{12} | ij \rangle - \delta_{m_{si} m_{sj}} \langle ij | f_{12} | ji \rangle), \\ G_{bi} &= -m_{si} \sum_{j(\neq i)} (\langle ji | f_{12} | ji \rangle - \delta_{m_{si} m_{sj}} \langle ji | f_{12} | ij \rangle), \end{aligned} \quad (12)$$

and the corresponding orbital contributions to the  $g$  factor can be calculated. The results through order  $\alpha^2$  are given in Table III. It can be seen

TABLE I. Numerical results for expectation values in Eq. (9).<sup>a</sup>

| Wave function                 | $F_p$    | $F_r$    | $G_a$    | $G_b$     | $G_c$ |
|-------------------------------|----------|----------|----------|-----------|-------|
| RHF <sup>b</sup>              | 0.208 82 | 0.172 69 | 0.299 18 | -0.009 19 | 0     |
| MPHF(G1) <sup>c</sup>         | 0.226 97 | 0.175 96 | 0.297 93 | -0.010 23 | 0     |
| SEHF(GF) <sup>d</sup>         | 0.245 30 | 0.179 66 | 0.296 46 | -0.012 21 | 0     |
| UHF <sup>e</sup>              | 0.237 40 | 0.178 10 | 0.296 91 | -0.011 53 | 0     |
| SO-SCF <sup>f</sup><br>(SOGI) | 0.234 08 | 0.177 28 | 0.297 37 | -0.010 80 | 0     |

<sup>a</sup>All numbers are in atomic units ( $e = \hbar = m = 1$ ).

<sup>b</sup>Restricted Hartree-Fock, Ref. 7.

<sup>c</sup>Maximally paired Hartree-Fock, Refs. 8 and 9.

<sup>d</sup>Spin-extended Hartree-Fock, Refs. 6 and 9.

<sup>e</sup>Unrestricted Hartree-Fock, Ref. 5.

<sup>f</sup>Spin-optimized SCF (self-consistent field),

Ref. 9.

TABLE II. Comparison of calculated and experimental results for Li.

|                         | $1-g_J/g_e$<br>(ppm) | Spin density<br>at nucleus <sup>b</sup> | $E$<br>(hartrees) <sup>b</sup> |
|-------------------------|----------------------|---|--------------------------------|
| RHF <sup>a</sup>        | 7.55 (-15%)          | 0.1674 (-28%)                           | -7.432 73                      |
| MPHF(G1)                | 8.35 (-6%)           | 0.2095 (-9%)                            | -7.447 56                      |
| SEHF(GF)                | 9.18 (+3%)           | 0.2403 (+4%)                            | -7.432 81                      |
| UHF                     | 8.82 (-1%)           | 0.2248 (-3%)                            | -7.432 75                      |
| SO-SCF<br>(SOGI)        | 8.67 (-3%)           | 0.2265 (-2%)                            | -7.447 57                      |
| Experiment <sup>c</sup> | 8.9±0.4              | 0.2313                                  | -7.4780                        |

<sup>a</sup>See Table I for references to wave functions.

<sup>b</sup>Taken from Table V of Ref. 9.

<sup>c</sup>Reference 10.

that the  $1s^2$  electronic core makes a contribution of  $-1.18$  ppm to the relativistic correction and the  $2s$  outer electron contributes  $-7.66$  ppm to give a total correction of  $-8.84$  ppm. In the restricted Hartree-Fock approximation<sup>7</sup> the  $1s\alpha$  and  $1s\beta$  orbitals are forced to be identical; this precludes any contribution from the core to the magnetic moment and the net result is contributed entirely by the  $2s$  electron. It is therefore not coincidental that the  $2s\alpha$  contribution in the UHF approximation very nearly equals the entire RHF result. (The source of the inaccuracy of the RHF wave function also becomes apparent.) Thus one can conclude that the core contributes about 13% of the total relativistic correction. This is due to the difference between the two core orbitals and the corresponding differences in average speeds and distances from the nucleus, as can be seen from Table III and Eq. (12).<sup>14</sup> This effect also occurs in

TABLE III. Relativistic contributions<sup>a</sup> by orbitals to  $g_J(\text{Li})/g_e - 1$  (UHF wave function<sup>b</sup>).

|   | $1s\alpha$ | $1s'\beta$ | $2s\alpha$ | Total  |
|---|------------|------------|------------|--------|
| Relativistic mass<br>increase   | -193.20    | 191.58     | -11.02     | -12.64 |
| Spin-orbit coupling<br>in electric field of<br>nucleus <sup>c</sup>         | 71.65      | -71.35     | 9.18       | 9.49   |
| Spin-orbit coupling<br>in electric field<br>of other electrons <sup>d</sup> | -7.38      | 7.48       | -5.38      | -5.28  |
| Spin-other-orbit<br>coupling  | -20.00     | 20.04      | -0.44      | -0.41  |
| Total   | -148.93    | 147.75     | -7.66      | -8.84  |

<sup>a</sup>All results are in ppm.

<sup>b</sup>Reference 5.

<sup>c</sup>Corresponds to first term in  $\mathcal{H}_{so}$ , Eq. (5).

<sup>d</sup>Corresponds to second term in  $\mathcal{H}_{so}$ , Eq. (5).

the lithium magnetic hyperfine structure.<sup>5,6</sup> and has been called exchange polarization of the core,<sup>4</sup> since it arises because the  $1s\alpha$  and  $1s\beta$  electrons have different exchange interactions with the  $2s\alpha$  electron.

The theoretical framework<sup>2</sup> used in this paper allows the radiative (order  $\alpha^3$ ) and nuclear-mass (order  $\alpha^2 m/M$ ) corrections to the  $g$  factor to be calculated separately from the dominant relativistic (order  $\alpha^2$ ) corrections. Employing the SO-SCF wave function<sup>9</sup> and substituting the numerical values from Table I into Eq. (8) one finds

$$g_J(\text{Li})/g_e = 1 + (-8.6865 + 0.0145 + 0.0002) \times 10^{-6} \\ = 1 - 8.6718 \times 10^{-6}. \quad (13)$$

The radiative correction is 0.0145 ppm and the nuclear-mass correction is 0.0002 ppm. Although the total correction may be in error by (2-3)%,<sup>11</sup> this is primarily due to the uncertainty in the dominant  $\alpha^2$  term ( $-8.6865$  ppm); each of the higher-order corrections is also expected to be accurate to within a few percent. It is possible to obtain a separate experimental test of the nuclear-mass correction by measuring the  $g$ -factor ratio for  ${}^6\text{Li}/{}^7\text{Li}$ , since this ratio is sensitive to the nuclear-mass terms only. Again using the SO-SCF wave function, one obtains

$$g_J({}^6\text{Li})/g_J({}^7\text{Li}) = 1 + 3.0 \times 10^{-11}. \quad (14)$$

To my knowledge there has been no experimental determination of this isotopic shift. On the other hand, the calculated value is consistent with the conclusion of Böklen *et al.*<sup>10</sup> that, to within the limits ( $\pm 3 \times 10^{-7}$ ) of their measurement, there is no isotopic shift between  ${}^6\text{Li}$  and  ${}^7\text{Li}$ .

## APPENDIX

Explicit expressions for the expectation values occurring in Eq. (9) can be obtained for each type of Li wave function considered in this paper. In what follows, the atomic orbitals are abbreviated  $1 \equiv 1s$ ,  $2 \equiv 1s'$ ,  $3 \equiv 2s$ .

For the UHF wave function<sup>5</sup> one obtains

$$F_p = \frac{1}{2}[(1|p^2|1) - (2|p^2|2) + (3|p^2|3)],$$

where  $(a|p^2|b) \equiv \int a(1)p_1^2 b(1) dV_1$ . There is a similar expression for  $F_r$ , except that  $r^{-1}$  replaces  $p^2$ .

Also,

$$G_a = \frac{1}{2}[(12|12) - (21|21) + (13|13) + (31|31) - (23|23) \\ + (32|32) - 2(13|31)],$$

where

$$(ab|cd) \equiv \int \int a(1)b(2)f_{12}c(1)d(2) dV_1 dV_2.$$

An expression for the expectation value  $G_b$  can be obtained by changing everywhere  $(ab|cd)$  to  $-(ba|dc)$  in the expression for  $G_a$ . This follows from the definitions of  $G_a$  and  $G_b$  in Eq. (9) and from the symmetry properties of integrals over  $f_{12}$ .

Corresponding results for the RHF wave functions<sup>7</sup> can be obtained simply by setting  $1s = 1s'$  in the above expressions.

To obtain corresponding expressions for the other wave functions, first note that they can all be expressed in the form<sup>9</sup>

$$\begin{aligned} A &= \frac{1}{4}t_1^2[S_{23}^2(1|p^2|1) + S_{13}^2(2|p^2|2) + 2S_{13}S_{23}(1|p^2|2) + 2(1 + S_{12}^2)(3|p^2|3) - 2(S_{13} + S_{12}S_{23})(1|p^2|3) - 2(S_{23} + S_{12}S_{13})(2|p^2|3)], \\ B &= \frac{1}{12}t_2^2[(4 + 5S_{23}^2)(1|p^2|1) + (4 + 5S_{13}^2)(2|p^2|2) - 2(1 - S_{12}^2)(3|p^2|3) - 2(4S_{12} + 5S_{13}S_{23})(1|p^2|2) \\ &\quad - 2(S_{13} - S_{12}S_{23})(1|p^2|3) - 2(S_{23} - S_{12}S_{13})(2|p^2|3)], \\ C &= (t_1 t_2 / \sqrt{3})[-(1 + \frac{1}{2}S_{23}^2)(1|p^2|1) + (1 + \frac{1}{2}S_{13}^2)(2|p^2|2) + (S_{13} + 2S_{12}S_{23})(1|p^2|3) - (S_{23} + 2S_{12}S_{13})(2|p^2|3)], \\ D &= 1 + (t_1^2 - t_2^2)S_{12}^2 - S_{12}S_{13}S_{23} - \frac{1}{2}(t_1^2 - t_2^2 - 2\sqrt{3}t_1 t_2)S_{13}^2 - \frac{1}{2}(t_1^2 - t_2^2 + 2\sqrt{3}t_1 t_2)S_{23}^2, \end{aligned}$$

where  $S_{ab} = \int a(1)b(1)dV_1$  are overlap integrals. One also obtains

$$G_a = (R + S + T)/D,$$

where

$$\begin{aligned} R &= \frac{1}{2}t_1^2\{(31|31) + (32|32) - (31|13) - (32|23) + S_{12}[(31|32) - (31|23) + (32|31) - (32|13)] \\ &\quad + S_{13}[(21|23) - (21|32) + (12|23) - (12|32)] + S_{23}[(12|13) - (12|31) + (21|13) - (21|31)]\}, \\ S &= \frac{1}{6}t_2^2\{2(13|13) - (31|31) - (13|31) + 2(23|23) - (32|32) - (23|32) + 2(12|12) + 2(21|21) - 4(12|21) \\ &\quad + S_{12}[-4(13|23) + 2(31|32) + (13|32) + (23|31)] + S_{13}[-(12|32) + 5(21|23) - 5(12|23) + (21|32)] \\ &\quad + S_{23}[-(21|31) + 5(12|13) - 5(21|13) + (12|31)]\}, \\ T &= (t_1 t_2 / \sqrt{3})\{-(12|12) + (21|21) - (13|13) + (13|31) + (23|23) - (23|32) + 2S_{12}[(13|32) - (31|23)] \\ &\quad + S_{13}[(12|32) + (21|23) - 2(32|21)] - S_{23}[(12|13) + (21|31) - 2(31|12)]\}. \end{aligned}$$

The corresponding expressions for  $F_r$  and  $G_b$  can be obtained as indicated above. For the SO-SCF wave function, the values of  $t_1$  and  $t_2$  have been obtained by the variation principle, and are given in Ref. 9. The expressions to be used with the MPHF function<sup>8</sup> are obtained by setting  $t_1 = 1, t_2 = 0$ . Those for the spin-extended Hartree-Fock (SEHF) function<sup>6</sup> are obtained by setting  $\Xi = 1s2s1s'$  and then setting  $t_1 = 0, t_2 = 1$ .

All of the above wave functions employ Slater-type basis orbitals  $\chi_b$  to expand the atomic orbitals  $a, b, c$ :

$$a = \sum_q C_{qa} \chi_q, \text{ etc.}$$

In this case, the integrals over basis orbitals are most conveniently calculated using the techniques of Roothaan *et al.*<sup>15</sup> We have, in the notation of Ref. 15 (the index  $\lambda$  is suppressed here because we only have to deal with  $s$  orbitals, for which  $\lambda = 0$ ),

$$\psi = \alpha \Xi \Theta,$$

with  $\Xi = abc$ , a product of atomic orbitals, and  $\Theta = t_1 \theta_1 + t_2 \theta_2$ , where  $t_1$  and  $t_2$  are numerical coefficients and  $\theta_1$  and  $\theta_2$  are spin functions defined by the equations

$$\begin{aligned} \theta_1 &= (\alpha \beta \alpha - \beta \alpha \alpha) / \sqrt{2}, \\ \theta_2 &= (2 \alpha \alpha \beta - \alpha \beta \alpha - \beta \alpha \alpha) / \sqrt{6}. \end{aligned}$$

One obtains

$$F_p = (A + B + C)/D,$$

where

$$(\chi_p | p^2 | \chi_q) = 2T_{pq}, \quad (\chi_p | r^{-1} | \chi_q) = U_{pq}.$$

To evaluate the two-electron integrals of  $f_{12}$ , we make use of the expansion

$$\begin{aligned} f_{12} &= -\frac{3}{H} \left[ \nabla_1 \left( \frac{1}{r_{12}} \right) \times \vec{A}_1 \right]_z = -\vec{r}_1 \cdot \nabla_1 \left( \frac{1}{r_{12}} \right) \\ &= -r_1 \frac{\partial}{\partial r_1} \frac{1}{r_{12}}, \end{aligned}$$

where the last two equalities hold when integrals are to be evaluated using  $s$  orbitals only. One then differentiates, with respect to  $r_1$ , the usual expansion of  $r_{12}^{-1}$  in spherical harmonics. This gives

$$\begin{aligned} f_{12}(r_2 < r_1) &= 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{1+l}{2l+1} \frac{r_2^l}{r_1^{l+1}} Y_{lm}(\Omega_1) Y_{lm}^*(\Omega_2), \\ f_{12}(r_1 < r_2) &= -4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{l}{2l+1} \frac{r_1^l}{r_2^{l+1}} \\ &\quad \times Y_{lm}(\Omega_1) Y_{lm}^*(\Omega_2). \end{aligned}$$

A simple expression for the integrals can now be found by the usual methods. Note that the only contributing term in this expansion is the  $l = m = 0$  term, since basis orbitals of  $s$  symmetry are being used. One finally obtains

$$\begin{aligned} & (\chi_p \chi_q | f_{12} | \chi_r \chi_s) \\ &= [V_{2n_p}(2\xi_p) V_{2n_q}(2\xi_q) V_{2n_r}(2\xi_r) V_{2n_s}(2\xi_s)]^{-1/2} V_{n_p+n_r-1}(\xi_p+\xi_r) V_{n_q+n_s}(\xi_q+\xi_s) C_{n_p+n_r-1, n_q+n_s}(\xi_p+\xi_r)/(\xi_q+\xi_s). \end{aligned}$$

All the quantities appearing on the right-hand side of the above equation are defined in Ref. 15 to which the reader is referred.

- <sup>1</sup>See H. Grotch and R. A. Hegstrom, Phys. Rev. A **8**, 1166 (1973), and references therein.
- <sup>2</sup>R. A. Hegstrom, Phys. Rev. A **7**, 451 (1973); H. Grotch and R. A. Hegstrom, Phys. Rev. A **8**, 2771 (1973).
- <sup>3</sup>W. Perl [Phys. Rev. **91**, 852 (1953)] performed a very approximate calculation and obtained  $g_J(\text{Li})/g_e = 1 - 11 \times 10^{-6}$ . [Note corrections of errors in Perl's paper by V. W. Hughes, in *Recent Research in Molecular Beams*, edited by I. Estermann (Academic, New York, 1959).]
- <sup>4</sup>G. W. Pratt, Jr., Phys. Rev. **102**, 1303 (1956).
- <sup>5</sup>L. M. Sachs, Phys. Rev. **117**, 1504 (1960).
- <sup>6</sup>W. A. Goddard III, Phys. Rev. **157**, 93 (1967).
- <sup>7</sup>E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. **127**, 1618 (1962).
- <sup>8</sup>W. A. Goddard III, Phys. Rev. **169**, 120 (1968). Wave function labeled "Li  $h7$ " in Table I was used.
- <sup>9</sup>U. Kaldor and F. E. Harris, Phys. Rev. **183**, 1 (1969).
- <sup>10</sup>The experimental value for  $g_J(\text{Li})/g_e$  is obtained from a product of three experimentally determined  $g$ -factor ratios:  $g_J(\text{Li})/g_e = [g_J(\text{Li})/g_J(\text{K})] [g_J(\text{K})/g_J(\text{Rb})] [g_J(\text{Rb})/g_e]$ . The ratio  $g_J(\text{Li})/g_J(\text{K}) = 1 + 3.4(0.3) \times 10^{-6}$  was measured by K. D. Böklen, W. Dankwort, E. Pitz, and S. Penselin [Z. Phys. **200**, 467 (1967)]. The ratio  $g_J(\text{K})/g_J(\text{Rb}) = 1 + 18.2(0.2) \times 10^{-6}$  was measured by P. A. Vandenberg, E. Aygun, V. J. Ehlers, T. Incesu, A. Sap-lakoglu, and H. A. Shugart [Phys. Rev. **165**, 88 (1968)]. The ratio  $g_J(\text{Rb})/g_e = 1 + 5.895(0.100) \times 10^{-6}$  has been measured by J. S. Tiedeman and H. G. Robinson [*Atomic Physics 3*, edited by S. J. Smith and G. K. Walters (Plenum, New York, 1973), p. 85]. Combining these

ratios, we obtain the experimental value  $g_J(\text{Li})/g_e = 1 - 8.9(0.4) \times 10^{-6}$ .

- <sup>11</sup>This error is estimated from the corresponding error in the spin density at the nucleus; the estimate should be quite conservative. The relativistic corrections to the  $g$  factor depend upon average values of  $p^2$  and  $r^{-1}$ ; the spin density at the nucleus depends upon the wave function at a single point in space. One expects the former to be calculated more accurately from a variational wave function than the latter.
- <sup>12</sup>Another type of correction to be considered is that arising from the departure from Russell-Saunders coupling. [See M. Phillips, Phys. Rev. **88**, 202 (1952) and Ref. 3.] This correction should be totally negligible for Li to the precision we are considering here. All the wave functions we consider here are obtained within the Russell-Saunders approximation.
- <sup>13</sup>S. Larsson, Phys. Rev. **169**, 49 (1968); S. Larsson and V. H. Smith, Jr., Phys. Rev. **178**, 137 (1969); H. M. James and A. S. Coolidge, Phys. Rev. **49**, 688 (1936).
- <sup>14</sup>The dominant effect is the difference in the relativistic-mass correction. The  $1s\alpha$  electron is closer to the nucleus than the  $1s'\beta$  electron because of the exchange polarization. Thus the  $1s\alpha$  electron has a greater speed and consequently a greater relativistic mass  $\tilde{m}$ . The "relativistic Bohr magneton"  $e/2\tilde{m} \cong (e/2m)(1 - \frac{1}{2}v^2/c^2)$  is hence less for  $1s\alpha$  and the magnetic moment is reduced in magnitude more than for the  $1s'\beta$  electron.
- <sup>15</sup>C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. **32**, 186 (1960).