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Hyperfine Structure of the Stable Lithium Isotopes. II*

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A theoretical treatment of the hfs anomaly between Li^6 and Li^7 is given, and the result compared with that reported in the preceding paper. The distribution of nuclear charge and magnetism, the polarization of the electron wave function by the nuclear electric-quadrupole moment, and the specific mass correction are treated. Agreement with experiment is obtained with a value for the p-nucleon radial parameter not inconsistent with that obtained from electron-scattering experiments.

I. INTRODUCTION

THE hyperfine structure (hfs) anomaly between two isotopes is known to be a consequence of the details of their nuclear structure, thanks to the work of Bohr and Weisskopf[1]; and though it has been studied intensively in the isotopes of hydrogen, it has not come into the same widespread use in nuclear physics as have the nuclear moments, even though its study yields valuable information about the outermost shell of nucleons. This is in part because of the complexity of hfs anomaly calculations. Much basic work has been done[2] which makes possible the interpretation of hfs anomaly measurements for many isotopes; but these treatments cannot be used for the lithium isotopes, and so an interpretation of the measurements reported in the preceding paper[3] is given here.

A number of effects are present in the lithium case: (a) The electron radial wave function is modified inside the nucleus by the distribution of nuclear charge, i.e., the Breit-Rosenthal (BR) effect[4]; (b) the electron distribution interacts with the nuclear magnetism over a finite volume, i.e., the Bohr-Weisskopf (BW) effect[1]; (c) the nuclear motion polarizes the electron distribution in its vicinity, i.e., the Bohr (B) effect[5]; (d) the center of mass of the atom is not at the same place as the center of mass of the nucleus, i.e., the specific mass correction.

Effects arising from nondiagonal matrix elements of the magnetic-dipole and electric-quadrupole operators are neglected. Furthermore, the treatment is nonrelativistic. We obtain an expression for the hfs anomaly Δ_{67}, which contains a number of nuclear parameters, by employing as a nuclear model a spherical α-particle core surrounded by nucleons in p orbital. The radial functions for both the core orbitals and the p orbitals are taken as harmonic-oscillator functions, but with different radii, R_S and R_P, respectively.

The nuclear parameters are then evaluated with an L-S coupled model of the nuclei, a not unreasonable approximation in the light of the calculations done by Kurath.[6] Evaluation of these parameters in intermediate coupling will be the subject of a later article.

II. HAMILTONIAN

The Hamiltonian employed can be split up as follows:

$$\mathcal{H}=\mathcal{H}_N+\mathcal{H}_E+\mathcal{V}_c+\mathcal{V}_{\text{hfs}}, \tag{1}$$

where $\mathcal{H}_N$ is the nuclear Hamiltonian, $\mathcal{H}_E$ is the electron Hamiltonian including an interaction with a nuclear point charge but exclusive of other electric or magnetic effects, $\mathcal{V}_c$ is the correction to the Coulomb potential arising from the finite nuclear size, and $\mathcal{V}_{\text{hfs}}$ is the hyperfine-structure operator.

The Hamiltonian $\mathcal{H}_N$ is not determined; harmonic-oscillator radial functions are employed instead.

Throughout, distances are measured in units of $a_0=\hbar^2/me^2$ and energies in units of mc^2. Thus

$$\mathcal{V}_c=-\alpha^2\sum_{en}\frac{1}{r_{en}}\chi_P(n)+\alpha^2\sum_e\frac{Z}{r_e}, \tag{2}$$

where α is the fine-structure constant, r_e is the distance between the eth electron and the nuclear center of mass, r_{en} is the distance between the eth electron and the nth nucleon, and χ_P is a proton-projection operator,

$$\begin{aligned}\chi_P(n)&\equiv\tfrac{1}{2}-T_z(n),\\ \chi_N(n)&\equiv\tfrac{1}{2}+T_z(n),\end{aligned} \tag{3}$$

where T_z is the z-component of the isospin operator. $\mathcal{V}_c$ can be expanded:

$$\mathcal{V}_c=-\alpha^2\sum_{en}\sum_k w_k\mathbf{C}^{(k)}(e)\cdot\mathbf{C}^{(k)}(n)\chi_P(n)+\alpha^2\sum_e(Z/r_e), \tag{4}$$

where

$$\begin{aligned}w_k&=r_e^k/r_n^{k+1}, & r_e&<r_n\\ &=r_n^k/r_e^{k+1}, & r_e&>r_n.\end{aligned}$$

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[1] A. Bohr and V. F. Weisskopf, Phys. Rev. **77**, 94 (1950).

[2] H. H. Stroke, R. J. Blin-Stoyle, and V. Jaccarino, Phys. Rev. **123**, 1326 (1961); A. S. Reiner, Nucl. Phys. **5**, 544 (1958).

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[5] A. Bohr, Phys. Rev. **81**, 134 and 331 (1951).

[6] D. Kurath, Phys. Rev. **101**, 216 (1956).

Here $\mathbf{C}^{(k)}$ is a spherical harmonic normalized to $4\pi/(2k+1)$.[7]

In Eq. (4) the term in the first sum with $k=0$, $r_e>r_n$ is the usual Coulomb potential, and is cancelled by the second sum. Of the remaining terms in the first sum, the one with $k=0$, $r_e<r_n$ produces the BR effect, and those with $k\neq 0$ produce the B effect. The wave function associated with this total potential $\mathcal{V}_c$ can then be used to evaluate the hfs.

Note that the survival of a nuclear matrix element of $\mathbf{C}^{(k)}(n)$ for $k\geqq 1$ leaves in the potential $\mathcal{V}_c$ terms containing $\mathbf{C}^{(k)}(e)$, which act to destroy J as a good quantum number by admixing states of other electronic angular momenta into the wave function. Thus this effect can be interpreted as a polarization of the electronic state by the nuclear motions. The presence of the radial function w_k assures that this polarization will be large only near the nucleus.

Because of singularities in the nonrelativistic hfs operator, it is convenient for us to calculate relativistically and then perform a nonrelativistic reduction. Therefore, take

$$\mathcal{V}_{\mathrm{hfs}}=\alpha\sum_{en}\boldsymbol{\alpha}(e)\cdot\mathbf{A}(n)\,, \tag{5}$$

where $\boldsymbol{\alpha}(e)$ (the Dirac α matrix) equals $2\rho_1\mathbf{S}(e)$, with

$$\rho_1=\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix},$$

and $\mathbf{A}(n)$ is the vector potential arising from the presence of the nth nucleon,

$$\mathbf{A}(n)=\boldsymbol{\nabla}(e)\times\frac{\boldsymbol{\mu}_S(n)}{r_{en}}+\frac{\mathbf{j}_L(n)}{r_{en}}\,,$$

with

$$\begin{aligned}\boldsymbol{\mu}_S(n)&=(\alpha^2/2m_n)g_S'(n)\mathbf{S}(n)\,,\\ \mathbf{j}_L(n)&=(\alpha^2/m_n)g_L'(n)\mathbf{P}(n)\,,\\ g_S'(n)&=g_N\chi_N(n)+g_P\chi_P(n)\,,\end{aligned} \tag{6}$$

and

$$g_L'(n)=(1-m_n/M)\chi_P(n)\,.$$

Here m_n is the mass of the nth nucleon measured in units of the electron mass, $\boldsymbol{\mu}_S$ is the spin magnetic-moment operator, g_N and g_P are the neutron and proton g factors, respectively, $\mathbf{S}$ and $\mathbf{L}$ are the total spin and orbital angular-momentum operators, and $(1-m_n/M)$ is the reduced-mass correction to the nuclear orbital g factor.[8] Other specific mass corrections are discussed in Appendix II. Now $\mathcal{V}_{\mathrm{hfs}}$ can be re-expressed in tensor-operator form as follows (see Appendix III):

$$\mathcal{V}_{\mathrm{hfs}}=\sum_{K,k,\alpha}\phi_{Kk\alpha}(e,n)\mathbf{U}_{k\alpha}{}^{(K)}(n)\cdot\{\mathbf{C}^{(k)}(e)\mathbf{S}(e)\}^{(K)}\,, \tag{7}$$

where the $\mathbf{U}_{k\alpha}{}^{(K)}$ are given by

$$\begin{aligned}\mathbf{U}_{k1}{}^{(K)}&=\{\mathbf{C}^{(k-1)}(n)\mathbf{S}(n)\}^{(K)}\,,\\ \mathbf{U}_{k2}{}^{(K)}&=\{\mathbf{C}^{(k-1)}(n)\mathbf{L}(n)\}^{(K)}\,,\\ \mathbf{U}_{k3}{}^{(K)}&=\mathbf{C}^{(K)}(n)\,,\\ \mathbf{U}_{k4}{}^{(K)}&=\{\mathbf{C}^{(k+1)}(n)\mathbf{S}(n)\}^{(K)}\,,\\ \mathbf{U}_{k5}{}^{(K)}&=\{\mathbf{C}^{(k+1)}(n)\mathbf{L}(n)\}^{(K)}\,,\end{aligned} \tag{8}$$

and

$$\begin{aligned}\phi_{kK1}&=[(i\alpha^3/m_n)b_{k-1,K}g'_S(n)w_k(e,n)]/r_n\,, && r_e>r_n\\ &=0 &&, \quad r_e<r_n\\ \phi_{kK2}&=[2(i\alpha^3/m_n)(-1)^{K+1}b_{k-1,K}g_L'(n)w_k(e,n)]/(2k+1)r_n\,,\\ \phi_{kK3}&=\left(\frac{i\alpha^3}{m_n}\right)c_{kK}g_L'(n)\left[\frac{w_k(e,n)}{r_n}\right]\frac{\partial}{\partial r_n}\,,\\ \phi_{kK4}&=0 &&, \quad r_e>r_n\\ &=[(i\alpha^3/m_n)b_{kK}g_S'(n)w_k(e,n)]/r_n\,, && r_e<r_n\\ \phi_{kK5}&=[2(i\alpha^3/m_n)b_{kK}g_L'(n)w_k(e,n)]/(2k+1)r_n\,.\end{aligned} \tag{9}$$

Here

$$\begin{aligned}b_{kk}&=(-1)^{k+1}[k(2k+3)]^{1/2}\,, \quad k\geqq 0\\ b_{k,k+1}&=(-1)^{k+1}[(k+2)(2k+1)]^{1/2}\,, \quad k\geqq 0\\ b_{kK}&=0 \text{ otherwise;}\\ c_{k,k+1}&=-[(k+1)/(2k+1)]^{1/2}\,,\\ c_{k,k-1}&=+[k/(2k+1)]^{1/2}\,,\\ c_{kK}&=0 \text{ otherwise.}\end{aligned} \tag{10}$$

This is consistent with the usual result,[1] provided the identity $\{\mathbf{C}^{(2)}\mathbf{L}\}^{(1)}=\mathbf{L}/(10)^{1/2}$ is employed.

The one-electron Dirac wave function used is

$$|jm_j\rangle\equiv\begin{pmatrix}|l_LSjm_j\rangle\\ |l_SSjm_j\rangle\end{pmatrix}, \tag{11}$$

where the radial dependence is made explicit by

$$\begin{aligned}|l_LSjm_j\rangle&=g_j(r)\,|l_LSjm_j)\,,\\ |l_SSjm_j\rangle&=if_j(r)\,|l_SSjm_j)\,.\end{aligned} \tag{12}$$

Now l_L, the orbital quantum number for the large component, must be $j\pm\frac{1}{2}$ for which $l_S=j\mp\frac{1}{2}$.

The total wave function is then

$$|FM_F\rangle=\sum_{j,M_I,M_j}q_j(IM_Ijm_j|FM_F)\,|IM_I\rangle\,|jm_j\rangle\,. \tag{13}$$

Here $(IM_Ijm_j|FM_F)$ is a vector-coupling coefficient, and q_j is an expansion coefficient to include states of different j (arising from the Bohr effect), and $q_{1/2}\equiv 1$.

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[7] The phase of $\mathbf{C}^{(K)}$ is the same as that used by Condon and Shortley, *Theory of Atomic Spectra* (Cambridge University Press, New York, 1935). See for example, A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton 1957), p. 21.

[8] M. Phillips, Phys. Rev. **76**, 1803 (1949).

The single-electron case, calculated first, is based on the assumption that the total hfs arises from the outermost 2*s* electron; and so J is set equal to j. This assumption is known to be false, and so a complete treatment is done also (Appendix I).

In the single-electron case, the first-order perturbation theory yields

$$\langle FM_F|\mathcal{V}_{\mathrm{hfs}}|FM_F\rangle = (-1)^{I+j_0+F}\sum_K\left[\begin{Bmatrix} I & j_0 & F \\ j_0 & I & K \end{Bmatrix} V_{j_0j_0K} + 2\sum_j q_j \begin{Bmatrix} I & j_0 & F \\ j & I & K \end{Bmatrix} V_{jj_0K}\right], \tag{14}$$

where $j_0=\frac{1}{2}$ and where

$$V_{jj'K}=\sum_{k,\alpha,n}(I\|U_{k\alpha}{}^{(K)}\|I)\langle M_{jj'Kk\alpha}\rangle. \tag{15}$$

Here $\langle M_{jj'Kk\alpha}\rangle$ is the average over nuclear radial coordinates of the function

$$M_{jj'Kk\alpha}=\phi_{kK\alpha}(en)[v_1(jj'kK)+v_2(jj'kK)], \tag{16}$$

where

$$\begin{aligned} v_1(jj'kK)=(-1)^{j-j'}&(l_LSj\|\{\mathbf{C}^{(k)}(e)\mathbf{S}(e)\}^{(K)}\|l_S'S'j') \\ &-(l_S'S'j'\|\{\mathbf{C}^{(k)}(e)\mathbf{S}(e)\}^{(K)}\|l_LSj\}, \\ v_2(jj'kK)=(-1)^{j-j'}&(l_SSj\|\{\mathbf{C}^{(k)}(e)\mathbf{S}(e)\}^{(K)}\|l_L'S'j') \\ &-(l_L'S'j'\|\{\mathbf{C}^{(k)}(e)\mathbf{S}(e)\}^{(K)}\|l_SSj). \end{aligned} \tag{17}$$

In the nonrelativistic limit

$$\begin{aligned} M_{jj'Kk\alpha}=\tfrac{1}{4}i\alpha\Big\{&\tfrac{1}{2}[v_1(jj'kK)-v_2(jj'kK)] \\ &\times\int r_e^2\phi_{kK\alpha}\frac{\partial}{\partial r_e}[g_j(r_e)g_{j'}(r_e)]dr_e \\ &+\tfrac{1}{2}[v_1(jj'kK)+v_2(jj'kK)]\int r_e^2\phi_{kK\alpha} \\ &\times\left[g_j(r_e)\frac{\partial}{\partial r_e}g_{j'}(r_e)-g_{j'}(r_e)\frac{\partial}{\partial r_e}g_j(r_e)\right]dr_e \\ &+[\kappa' v_1(jj'kK)-\kappa v_2(jj'kK)] \\ &\times\int r_e\phi_{kK\alpha}g_j(r_e)g_{j'}(r_e)dr_e\Big\}, \end{aligned} \tag{18}$$

and the presence of the first term ensures the survival of surface terms for values of K greater than 1, all of which correspond to delta-function singularities in a strictly nonrelativistic treatment. The quantity κ equals $-j+\frac{1}{2}$ for $l_L=j-\frac{1}{2}$ and equals $j+\frac{3}{2}$ for $l_L=j+\frac{1}{2}$.

III. ONE-ELECTRON ELECTRONIC WAVE FUNCTION; B AND BR EFFECTS

We first treat the case in which the hfs is presumed to arise from a single electron in an *s* orbital, the object being to compute a wave function containing the terms that contribute to the hfs anomaly. In this calculation $\mathcal{V}_{\mathrm{hfs}}$ is omitted, and the perturbations treated arise from $\mathcal{V}_c$.

Ordinary perturbation theory cannot be used because the corrections of interest are appreciable only in the vicinity of the nucleus, and a very large number of excited atomic states would be needed to approximate the correction to the wave function.

What is done is to develop a differential equation in the radial coordinates, which can be easily solved because distances of the order of the nuclear dimension are very small compared to unity in atomic units. To remove all angular dependences from the wave equation, write the nonrelativistic radial function explicitly:

$$|jm_j\rangle=g_j(r)|jm_j), \tag{19}$$

i.e., $|jm_j\rangle$ contains radial dependence, $|jm_j)$ does not. Then introduce an analog of (13)

$$|IjFM_j)=\sum_{M_IM_j}(IM_Ijm_j|FM_F)|IM_I\rangle|jm_j), \tag{20}$$

which depends on the nuclear radial coordinates but not on the electron radial coordinates. Thus $(jm_j|\mathcal{H}_E|jm_j\rangle$ is a radial operator that is called $\mathcal{H}_j$ and operates on $g_j(r)$.

$$\mathcal{H}_j=-\tfrac{1}{2}\alpha^2[\Lambda_l(r)+\mathcal{V}_P+\mathcal{V}_{EE}], \tag{21}$$

where $\Lambda_l(r)=(\partial^2/\partial r^2)+(2/r)(\partial/\partial r)-[l(l+1)/r^2]$ and where l is the orbital quantum number associated with j, $\mathcal{V}_P=Z/r$, and $\mathcal{V}_{EE}$ is the electron-electron interaction potential, which can be neglected in the region close to the nucleus. We then evaluate

$$(I_jFM_F|\mathcal{H}_E+\mathcal{H}_N+\mathcal{V}_c-\mathcal{E}|FM_F\rangle=0$$

and obtain,

$$q_j(\mathcal{H}_j-\mathcal{E}_E)g_j(r) +(-1)^{I+F+j}\sum_k\begin{Bmatrix} I & j_0 & F \\ j & I & k \end{Bmatrix}\mathcal{V}_{jj_0kI}g_{j_0}(r)=0, \tag{22}$$

where

$$\mathcal{V}_{jj_0kI}=-\alpha^2\sum_n(j\|\mathbf{C}^{(k)}(e)\|j_0) \times\langle I\|w_k\mathbf{C}^{(k)}(n)\chi_P(n)\|I\rangle,\quad k\neq 0$$

$$\mathcal{V}_{j_0j_00I}=-\alpha^2\sum_n\sqrt{2}\langle I\|\left(w_0-\frac{1}{r_e}\right)\chi_P(n)\|I\rangle,$$

the $1/r_e$ arising from the subtraction of the point-nucleus Coulomb potential. Terms involving matrix elements not connecting the ground state have been omitted in (22). Since the product of q_j and R_j appears, one of these can be chosen at our convenience. Since

$q_{1/2}=1$, let

$$q_j=\left[\begin{Bmatrix} I & \frac{1}{2} & I+\frac{1}{2} \\ j & I & 2 \end{Bmatrix}(\tfrac{1}{2}\|\mathbf{C}^{(2)}\|j)\right]^{-1}, \quad j\neq\tfrac{1}{2}. \tag{23}$$

Define the BR correction ϵ_{BR} by

$$g_{1/2}=(1+\epsilon_{\mathrm{BR}})g_0, \tag{24}$$

where g_0 is the eigenfunction of $\mathcal{H}_{1/2}$, and define the B correction ϵ_{B} by

$$g_j=\epsilon_{\mathrm{B}}g_0. \tag{25}$$

The energy shift (isotope shift) associated with the perturbation is not important in this problem, since it does not contribute to the hfs. So set $\mathcal{E}_E$ equal to the eigenvalue of $\mathcal{H}_{1/2}$. Neglecting second-order terms $\epsilon_{\mathrm{B}}\epsilon_{\mathrm{BR}}$ and omitting the term

$$\left(\frac{\partial}{\partial r}g_0\right)\left(\frac{\partial}{\partial r}\epsilon\right),$$

which has a negligible effect on the result, we obtain finally

$$\begin{aligned} &\Lambda_0\epsilon_{\mathrm{BR}}+(2/R_P)V_P(x_P)+(4/R_S)V_S(x_S)=0, \quad \mathrm{Li}^6 \text{ and } \mathrm{Li}^7 \\ &\epsilon_{\mathrm{B}}=0, \quad \mathrm{Li}^6 \\ &\Lambda_2\epsilon_{\mathrm{B}}+[2(5)^{1/2}/R_P]Q_7V_2(x_P)=0, \quad \mathrm{Li}^7 \end{aligned} \tag{26}$$

where $x_P=r_e/R_P$, $x_S=r_e/R_S$, and Q_7 is the nuclear-electric-quadrupole moment divided by R_P^2.

$$\begin{aligned} V_P(x)&=-(1/x)+\Phi_2(x)-\tfrac{1}{3}\Phi_3(x), \\ V_S(x)&=-(1/x)+\Phi_2(x), \\ V_2(x)&=\Phi_3(x)-\tfrac{2}{3}\Phi_1(x), \end{aligned} \tag{27}$$

where

$$\begin{aligned} \Phi_1(x)&=(2/\pi^{1/2})\exp(-x^2), \\ \Phi_2(x)&=(1/x)\int_0^x\Phi_1(t)dt, \\ \Phi_3(x)&=(1/x^2)(\Phi_2-\Phi_1). \end{aligned}$$

Equations (27) have the exact solution

$$\begin{aligned} \epsilon_{\mathrm{BR}}=2R_P[&(x_P/2)-\tfrac{1}{2}x_P{}^2\Phi_2(x_P) \\ &-(5/12)\Phi_2(x_P)-\tfrac{1}{4}\Phi_1(x_P)] \\ &+4R_S[\tfrac{1}{2}x_S-\tfrac{1}{2}x_S{}^2\Phi_2(x_S)-\tfrac{1}{4}\Phi_2(x_S)-\tfrac{1}{4}\Phi_1(x_S)] \\ \epsilon_{\mathrm{B}}=0,& \quad \mathrm{Li}^6 \\ \epsilon_{\mathrm{B}}=(5^{1/2}&/3)Q_7R_P[\Phi_2(x_P)-\tfrac{3}{2}\Phi_3(x_P)], \quad \mathrm{Li}^7. \end{aligned} \tag{28}$$

IV. CONCLUSION

The result of the one-electron problem done above is

$$\begin{aligned} \Delta_{67}=[&-(C_{S1}+2C_{S0}-2)(0.778+0.0940\Gamma) \\ &+(0.0177)(C_{S1}+2C_{S0}-12)Q_7-(0.198)C_{S3}Q_7 \\ &+(0.055)C_{L3}Q_7]R_P, \end{aligned} \tag{29}$$

where

$$\Gamma=2r_m(r_m{}^2+2)(r^2-2)-3r_m{}^5(r+1)-3r^3(r-r_m{}^2) \tag{30}$$

for $r=R_S/R_P$, and $r_m=R_SR_P/(R_S{}^2+R_P{}^2)^{1/2}$. The quantities C are parameters of the Li^7 nucleus:

$$\begin{aligned} C_{S0}&=(I\|g_S'\mathbf{S}\|I)/(I\|g_S'\mathbf{S}+g_L'\mathbf{L}\|I), \\ C_{S1}&=10^{1/2}(I\|g_S'\{\mathbf{C}^{(2)}\mathbf{S}\}^{(1)}\|I)/(I\|g_S'\mathbf{S}+g_L'\mathbf{L}\|I), \\ C_{S3}&=[6/5(7^{1/2})](I\|g_S'\{\mathbf{C}^{(2)}\mathbf{S}\}^{(3)}\|I)/ \\ &\qquad\times(I\|g_S'\mathbf{S}+g_L'\mathbf{L}\|I), \\ C_{L3}&=[6/5(7^{1/2})](I\|g_L'\{\mathbf{C}^{(2)}\mathbf{L}\}^{(3)}\|I)/ \\ &\qquad\times(I\|g_S'\mathbf{S}+g_L'\mathbf{L}\|I). \end{aligned} \tag{31}$$

The C parameters were evaluated by means of an L-S coupled model of the Li^7 nucleus having $T=\frac{1}{2}$ and symmetrized with respect to all nucleons, $L=1$, $S=\frac{1}{2}$, $I=\frac{3}{2}$, with the result $C_{S1}=-(8/3)Q_7C_{S0}$, $C_{S3}=1.14\,Q_7C_{S0}$, $C_{L3}=0$, and $C_{S0}=0.907$.

If we employ the values of R_S and R_P obtained by Burleson and Hofstadter[9] on the basis of their electron-scattering experiments, $R_S=0.50\times10^{-4}$, $R_P=0.20\times10^{-4}$ (in units of a_0): i.e., $R_P<R_S$, so that the p nucleons move inside the α-particle core. Their data yield $r=2.48$, $\Gamma=64.6$. The term Q_7, calculated for the L-S coupled model, is $Q_7=-[3/5(5)^{1/2}]=-0.268$, so that $\Delta_{67}=+0.5\times10^{-4}$, i.e., about one-half the experimental result. However, the uncertainty is very large, because if r is raised from 2.48 to 3, while at the same time maintaining a constant average nucleon radius (corresponding to a change in R_P from 0.20×10^{-4} to 0.17×10^{-4}), agreement with experiment is obtained. This occurs because Γ is very sensitive to R_P, and so current measurements of R_P are insufficient for one to compute Δ_{67} accurately. In fact, if intermediate coupling values of the C parameters were employed, the experimental value for Δ_{67} could be used to determine a good value for R_P.

However, if we use the value of Q_7 given above together with the value of R_P from Burleson and Hofstader to calculate the nuclear electric quadrupole moment, we obtain a value an order of magnitude smaller than that obtained by applying the result of the Nesbet and Kahalas[10] calculation to the data of Wharton *et al.*[11] If we use a value of R_P consistent with this quadrupole moment, however, Δ_{67} changes sign. One effect which might resolve this difficulty has been neglected, that is, the polarization of the α-particle nuclear core by the nucleon p orbitals.

Inclusion of the 1s electrons in the hfs problem does not alter the result, as is shown in Appendix I; and so the electron part of the problem can be regarded as properly solved, exclusive of relativistic corrections. The specific mass effect produces a change in the magnetic moment μ only, as is shown in Appendix II, and so does not influence the above.

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[9] George R. Burleson and R. Hofstadter, Phys. Rev. **112**, 1282 (1958).

[10] S. L. Kahalas and R. K. Nesbet, Phys. Rev. Letters **6**, 549 (1961); J. Chem. Phys. **39**, 529 (1963).

[11] L. Wharton, L. P. Gold, and W. Klamperer, J. Chem. Phys. **37**, 2149 (1962); Phys. Rev. **133**, B270 (1964).

In conclusion, it is possible to say that the major effects in the Li^6-Li^7 hfs anomaly are accounted for, and agreement with experiment is obtained with a value of R_P not inconsistent with that given by Burleson and Hofstadter.

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APPENDIX I: EFFECT OF THE 1*s* ORBITALS

We show here that the inclusion of the 1*s* orbitals does not affect the hfs anomaly result, a fact one would anticipate since the anomaly does not depend on the details of the unperturbed electron radial function.

Call the three electron radial functions $R_{1+}(e)$, $R_{1-}(e)$, and $R_{2+}(e)$ (assuming $M=\frac{1}{2}$). Form

$$X_\alpha(ij)=\tfrac{1}{2}\sqrt{2}[R_\beta(i)R_\gamma(j)+R_\beta(j)R_\gamma(i)], \qquad (\mathrm{I.1})$$

where $\alpha\beta\gamma$ are a permutation of $1+$, $1-$, $2+$. Let

$$R(k)=R_{2+}(k)X_{2+}(ij), \quad i\neq j\neq k. \qquad (\mathrm{I.2})$$

The $J=\frac{1}{2}$ function $|00S_0M\rangle$ is then

$$|00S_0M\rangle=N^{-1/2}\begin{vmatrix}1 & \sigma_M(1) & R(1)\\ 1 & \sigma_M(2) & R(2)\\ 1 & \sigma_M(3) & R(3)\end{vmatrix}, \qquad (\mathrm{I.3})$$

or in compressed notation,

$$|J_0M\rangle=N^{-1/2}\det\{1,\sigma_M(j),R(k)\}.$$

Here N is a normalizing factor, and $\sigma_{1/2}(k)$ is defined by

$$\sigma_{1/2}(k)=6^{-1/2}[2\beta(k)\alpha(i)\alpha(j)-\alpha(k)\beta(i)\alpha(j) -\alpha(k)\alpha(i)\beta(j)], \qquad (\mathrm{I.4})$$

where $\alpha(e)$ is a spin function with $M=+\frac{1}{2}$; β is a spin function with $M=-\frac{1}{2}$; and $\sigma_{-1/2}(e)$ is obtained by interchanging α and β.

For the perturbations produced by the Bohr effect, introduce the combination

$$\begin{aligned}R_\alpha'(k)=\tfrac{1}{3}\{&R_{2+}'(k)\mathbf{C}_{M_L}^{(2)}(k)X_{2+}(ij)\\ &+\tfrac{1}{2}\sqrt{2}R_{2+}(k)[R_{1+}'(i)\mathbf{C}_{M_L}^{(2)}(i)R_{1-}(j)\\ &+R_{1+}'(j)\mathbf{C}_{M_L}^{(2)}(j)R_{1-}(i)]\\ &+\tfrac{1}{2}\sqrt{2}R_{2+}(k)[R_{1+}(i)R_{1-}'(j)\mathbf{C}_{M_L}^{(2)}(j)\\ &+R_{1+}(j)R_{1-}'(i)\mathbf{C}_{M_L}^{(2)}(i)]\},\end{aligned} \qquad (\mathrm{I.5})$$

which has the symmetry needed in order to express the perturbed part of the wave function by

$$|L'M_LS_0M_S\rangle=(N^{-1/2})\det\{1,\sigma_{M_S}(j),R'(k)\}, \qquad (\mathrm{I.6})$$

where $L'=2$, $S_0=\frac{1}{2}$.

The total wave function is again

$$|FM_F\rangle=\sum_J q_j|IJFM_F\rangle, \qquad (\mathrm{I.7})$$

where

$$\begin{aligned}|IJFM_F=\sum_{M_IM_LM_S}&(IM_IJM_J|FM_F)\\ &\times(LM_LSM_S|JM_J)|IM_I\rangle|LM_LSM_S\rangle.\end{aligned} \qquad (\mathrm{I.8})$$

Now the projection functions needed to produce a differential equation in the radial coordinates are $(k,S_0M_S|$ and $(L'M_LS_0M_S|$. Define

$$\begin{aligned}(1,S_0M_S|&=\sigma_{M_S}(3)-\sigma_{M_S}(2);\\ (2,S_0M_S|&=\sigma_{M_S}(1)-\sigma_{M_S}(3);\\ (3,S_0M_S|&=\sigma_{M_S}(2)-\sigma_{M_S}(1).\end{aligned}$$

Also, let

$$(L'M_LS_0M_S|=\det\{1,\sigma_{M_S}(j),\mathbf{C}_{M_L}^{(2)}(k)\}.$$

Then the equation

$$(\mathcal{H}_E+\mathcal{H}_N-\mathcal{E}+\mathcal{V}_c)|FM_F\rangle=0, \qquad (\mathrm{I.9})$$

when operated on from the left by

$$\sum_{M_IM_J}(IM_IS_0M_J|FM_F)\langle IM_I|\langle k,S_0M_J|,$$

becomes the first part of Eq. (26) provided we define

$$R_\alpha(k)=[1+\epsilon_{\mathrm{BR}}(k)]R_{\alpha0}(k). \qquad (\mathrm{I.10})$$

Here $R_{\alpha0}(k)$ is the eigenfunction of $\mathcal{H}_E(k)$ and ϵ_{BW} does not depend on α; i.e., it is the same function of r_k for all the orbitals present.

Similarly if we operate on (I.9) with

$$\sum_{M_IM_LM_S}(IM_IJM_J|FM_F)(L'M_LS_0M_S|JM_J) \times\langle IM_I|(L'M_LS_0M_S|,$$

we obtain the second part of Eq. (26), provided $R_\alpha'(k)=\epsilon_{\mathrm{B}}(k)R_{\alpha0}(K)$. Again $\epsilon_{\mathrm{B}}(k)$ does not depend on α.

Since the hfs operator is a one-particle operator, the contribution to the total Li^7 hfs from each electron will contain a factor $1+\Delta_{67}$, and so the result will be the same as that obtained above for a single electron.

APPENDIX II. THE SPECIFIC MASS CORRECTION

The specific mass correction is calculated nonrelativistically. The vector potential arising from the *n*th nucleon at electron *e* is given by

$$A(e,n)=(\alpha^2/m_n)\{[\tfrac{1}{2}g_S'\boldsymbol{\nabla}(e)\times\mathbf{S}(n)]/R_{en} +[\chi_P(n)\mathbf{P}(n)]/R_{en}\}, \qquad (\mathrm{II.1})$$

and the interaction Hamiltonian $\mathcal{H}'$ is then

$$\mathcal{H}'=\alpha^2\sum_{en}\{\mathbf{P}(e)\cdot\mathbf{A}(e,n)+\tfrac{1}{2}g_e\mathbf{S}(e)\cdot\boldsymbol{\nabla}(e)\times\mathbf{A}(e,n)\}, \qquad (\mathrm{II.2})$$

where the coordinates $\mathbf{R}_e$, $\mathbf{R}_n$ are taken in an arbitrary inertial framework; g_S' is defined in Eq. (6) and g_e is the electron-spin g value; all masses are measured in units of the electron mass.

Introducing a coordinate system centered at the center of mass (c.m.) of the nucleus (not the atom), which is taken to be at the position $\mathbf{R}$; and labeling the coordinates in this c.m. frame by $\mathbf{r}_e$ and $\mathbf{r}_n$; we find that $\mathbf{R}_{en}=\mathbf{r}_{en}$, that

$$\nabla(e)=\nabla'(e)+(1/M)\nabla \tag{II.3}$$

and that

$$\mathbf{P}(n)=\left(1-\frac{m_n}{M}\right)\mathbf{p}(n)-\sum_{n'}\frac{1}{M_N}\mathbf{p}(n')$$

$$-\sum_{e}\frac{m_n}{M_N}\mathbf{p}(e)+\frac{m_n}{M_N}\mathbf{P},\ n'\neq n \quad\text{or}\quad n_0. \tag{II.4}$$

Here $\nabla'(e)$, $\mathbf{p}(e)$, and $\mathbf{p}(n)$ refer to the center-of-mass frame, whereas ∇ and $\mathbf{P}$ refer to the c.m. motion in the inertial frame. The mass of the nucleus is M_N, and the total mass of the atom is M; n_0 is the nucleon whose coordinates were eliminated by the introduction of $\mathbf{R}$.

Substitution of $P(e)$ and $P(n)$ into $\mathcal{H}'$ gives

$$\mathcal{H}'=\mathcal{H}_1'+\mathcal{H}_2'+\mathcal{H}_3', \tag{II.5}$$

where

$$\mathcal{H}_1'=\sum_{en}\left(\frac{\alpha^4}{m_n}\right)\Bigg\{\left[\tfrac{1}{2}g_e\chi_P(n)\left(1-\frac{m_n}{M_N}\right)\mathbf{S}(e)\cdot\mathbf{L}(n)\right]\Big/r_{en}^3$$

$$+[\tfrac{1}{2}g_n\mathbf{L}(e)\cdot\mathbf{S}(n)]/r_{en}^3$$

$$+[\tfrac{1}{4}g_eg_n\mathbf{S}(e)\cdot\nabla'(e)\times(\nabla'(e)\times\mathbf{S}(n))]/r_{en}\Bigg\}, \tag{II.6}$$

$$\mathcal{H}_2'=\sum_{en}\left(\frac{\alpha^4}{m_n}\right)\Bigg\{\Bigg[-\tfrac{1}{2}g_e\chi_P(n)$$

$$\times\sum_{n'}\frac{m_n}{M_N}\mathbf{r}_n\times\mathbf{p}(n')\cdot\mathbf{S}(e)\Bigg]\Big/r_{en}^3$$

$$-\left[\chi_P(n)\sum_{e'}\left(\frac{m_n}{M_N}\right)\mathbf{p}(e)\cdot\mathbf{p}(e')\right]\Big/r_{en}$$

$$+\left[\tfrac{1}{2}g_e\chi_P(n)\sum_{e'}\left(\frac{m_n}{M_N}\right)\mathbf{r}_e\times\mathbf{p}(e')\cdot\mathbf{S}(e)\right]\Big/r_{en}^3\Bigg\},$$

$$n'\neq n \quad\text{or}\quad n_0 \tag{II.7}$$

and $\mathcal{H}_3'$ consists of terms containing $\mathbf{R}$ or ∇ or $\mathbf{P}$, and terms such as $p(e)\cdot p(n)$ whose diagonal terms vanish for wave functions having a definite parity for both the electronic and nuclear parts separately.

Here $\mathcal{H}_1'$ is the expected Hamiltonian, and $\mathcal{H}_2'$ is the mass correction. The first term of $\mathcal{H}_2'$ has vanishing diagonal elements for nucleons having a definite l, and the third has vanishing diagonal elements for electrons having definite l. The second term has vanishing diagonal elements for $e\neq e'$, but for $e=e'$ a term proportional to $(1/M)p^2/r$ survives. This term gives no hfs energy shift directly, because both hfs levels will be shifted the same way, but it will affect the wave function, producing a correction similar to the reduced mass correction times $(1/r)$. But the reduced mass correction to the hfs anomaly, $(m_6/m_7)^3$, is about $1-(3\times10^{-5})$, so that corrections of the form $(1/M)p^2/r$ would be negligible. This argument is used also to justify the neglect of nondiagonal elements of $\mathcal{H}_2'$.

Finally, we must consider the Hughes-Eckhart correction.[12] The kinetic-energy operator in the c.m. system, $\mathcal{T}_E$, is

$$\mathcal{T}_E=-\tfrac{1}{2}\alpha^2\sum_e\Bigg\{\left(1+\frac{1}{M_N}\right)\nabla'^2(e)$$

$$+\frac{1}{M_N}\sum_{ef}\nabla_e'\cdot\nabla_f'\Bigg\},\quad e\neq f \tag{II.8}$$

and the $\nabla_e'\cdot\nabla_f'$ term, although its energy shift would not affect the hfs, would alter the wave function. But again, diagonal terms vanish and nondiagonal ones would be negligible.

APPENDIX III. DERIVATION OF EQ. (7)

Since $\boldsymbol{\alpha}(e)=2\rho_1\mathbf{S}(e)$, Eq. (5) shows we must evaluate $\mathbf{S}(e)\cdot\mathbf{A}(n)$, where $\mathbf{A}(n)$ is obtained from Eq. (6):

$$\mathbf{S}(e)\cdot\mathbf{A}(n)=-[\mathbf{S}(e)\cdot\mathbf{r}_{en}\times\boldsymbol{\mu}_S(n)]/r_{en}^3$$

$$+[\mathbf{S}(e)\cdot\mathbf{j}_L(n)]/r_{en}^3. \tag{III.1}$$

Then we employ the relations

$$-\mathbf{S}(e)\cdot\mathbf{r}_{en}\times\boldsymbol{\mu}(n)=[\mathbf{r}_e\times\mathbf{S}(e)]$$

$$\cdot\boldsymbol{\mu}(n)+\mathbf{S}(e)\cdot[\mathbf{r}_n\times\boldsymbol{\mu}(n)], \tag{III.2}$$

$$\mathbf{P}(n)=(i\sqrt{2}/r_n)\{\mathbf{C}^{(1)}(n)\mathbf{L}(n)\}^{(1)}-i\mathbf{C}^{(1)}(n)\partial/\partial r_n, \tag{III.3}$$

$$\frac{1}{r_{en}^3}=\frac{1}{r_e^2-r_n^2}\sum_k(2k+1)\frac{r_n^k}{r_e^{k+1}}\mathbf{C}^{(k)}(e)\cdot\mathbf{C}^{(k)}(n),$$

$$\text{for}\quad r_e>r_n \tag{III.4}$$

and

$$\frac{1}{r_{en}^3}=\frac{1}{r_n^2-r_e^2}\sum_k(2k+1)\frac{r_e^k}{r_n^{k+1}}\mathbf{C}^{(k)}(e)\cdot\mathbf{C}^{(k)}(n),$$

$$\text{for}\quad r_e<r_n. \tag{III.5}$$

These latter three relations are taken from Judd.[13] We then perform a standard recoupling to obtain Eq. (7).

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[12] D. S. Hughes and C. Eckhart, Phys. Rev. **36**, 694 (1930).

[13] B. R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill Book Company, New York, 1963), pp. 88, 92. Note that the relation (III-3) appears in a paper by F. R. Innes and C. W. Ufford, Phys. Rev. **111**, 194 (1958).