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Perturbative Studies of the ^2S Lithium Atom: Total Energy and Hyperfine Interaction[*]

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Double perturbation theory has been applied to the calculation of the total and hyperfine interaction energies of ground-state lithium. The effective one-electron potential used contains only the Coulomb terms which arise from the $1s$- and $2s$-electrons, multiplied by a factor of $\frac{2}{3}$ for correct asymptotic screening. The first-order perturbed wave functions in correlation and the hyperfine interaction are obtained by a numerical finite-difference solution of their respective two- and one-particle inhomogeneous differential equations. Convergence of both expansions is rapid, giving a total energy of -7.4793 ± 0.0038 a.u. and a spin density at the nucleus of $(2.850 \pm 0.076)a_0^{-3}$, in good agreement with their accurate counterparts: -7.47807 a.u. and $2.9096 a_0^{-3}$.

I. INTRODUCTION

In recent years perturbation theory has made important contributions to the solution of problems in atomic physics. Yet there have been relatively few perturbative treatments of lithium, one of the simplest atoms and prototype system for studying atomic S-state hyperfine interactions. Furthermore, the question of how to choose H_0 for rapid convergence remains unresolved,[1] both in the Rayleigh-Schrodinger (RS) and many-body formulations.[2] In this paper we apply RS perturbation theory to obtain the ^2S Li nonrelativistic total energy and hyperfine interaction (or equivalently in the point-nucleus approximation, the nuclear spin density) using a local "exchangeless" one-electron effective potential.[1a] This potential leads to zeroth-order energies and spin densities at considerable variance with Hartree-Fock values. However, as will be seen, the convergence of the expansions is rapid. Moreover, the local nature of the potential greatly simplifies the calculation and is thus in the spirit of perturbation theory.

In addition to assessing the effect on convergence of a new kind of potential it was also of interest to see whether the perturbation treatment could be implemented by direct numerical finite-difference solution of the relevant ordinary and partial inhomogeneous differential equations which arise in the hyperfine and total energy treatments, respectively. This would obviate the completeness and convergence problems associated with expanding in analytic basis functions or numerical single-particle states. Moreover, it is especially desirable to compute nuclear spin densities by *accurate* numerical methods since even for the relatively simple problem of the the restricted-Hartree-Fock (RHF) ^2S Li spin density a wide range of values [$(2.065$–$2.097)a_0^{-3}$], where a_0 is the Bohr radius, has been obtained (both analytically and numerically). For the correlation problem there are now accurate finite-difference methods for obtaining numerical solutions to the first-order pair correlation equations.[1a, 3, 4] We report here their use for the first time in obtaining third-order energies for a system with more than two electrons and in obtaining nuclear spin densities as well.

Some historical remarks can be made about previous lithium atom perturbation treatments of both hyperfine interaction and total energies. For the former, it was hoped that the simple but important physical effect of exchange or core polarization, when treated perturbatively[5] at the orbital level of approximation would be sufficient; in fact, however, correlation contributions are not negligible. Recent attacks on this problem have been expansions in Hylleraas variables,[6] the Bethe-Goldstone method,[7] "best spatial orbital methods" (referred to as BRNO,[8] SOGI,[9] or SO-SCF[10]), the variation-perturbation method[11] and linked-cluster many-body diagrammatic theory.[12] All of these have now been quantitatively successful for ^2S lithium; however, the most powerful and general seem to us to be the perturbative methods since they express the spin density as a sequence of decreasing terms, allowing convergence to be "watched." (The Bethe-

Goldstone expansion is formally also a hierarchy of corrections.)

For the total energy, the bare nucleus or Z expansion through third order in correlation has recently been realized.[13] The result obtained, -7.47262 a.u., is in moderately good agreement with the accurate value, -7.47807.[14] A better value has been obtained by Chang, Pu, and Das[12] in the many-body perturbation treatment based on a V^{N-1} potential. This paper presents new perturbative treatments of both the hyperfine and total energies which are good through second and third orders in correlation, respectively. Comparison with the previous calculations is made in the final section.

II. GENERAL

A. Formulation of Perturbation Problem

Consider the nonrelativistic Hamiltonian for the lithium atom excluding all magnetic terms but the Fermi contact interaction between the nuclear and electron spins[15]:

$$H=-\tfrac{1}{2}\sum_i \nabla_i^2-\sum_i \frac{3}{r_i}+\sum_{i>j}\frac{1}{r_{ij}} +\tfrac{8}{3}\pi\gamma_e\gamma_{\mathrm{Li}}\vec{\mathrm{I}}\cdot\sum_i \vec{\mathrm{s}}_i\delta(\vec{\mathrm{r}}_i)\,, \qquad (1)$$

where $\vec{\mathrm{I}}$ is the spin of the Li nucleus of gyromagnetic ratio γ_{Li}. Choosing the nuclear spin to lie along the z axis and using the identity

$$\delta(r)=4\pi r^2\delta(\vec{\mathrm{r}})\,, \qquad (2)$$

we may rewrite the Fermi contact perturbation in terms of the radial spin density operator H_{01} (the subscript anticipating a double perturbation expansion) as

$$\mu H_{01}\equiv\tfrac{1}{3}\gamma_e\gamma_{\mathrm{Li}}I_zH_{01}\,, \qquad (3)$$

with

$$H_{01}=2\sum_i s_{zi}[\delta(r_i)/r_i^2]\,. \qquad (4)$$

To render the perturbation procedure tractable it is necessary to divide the noncontact terms of H into an H_0, the sum of identical one-electron Hamiltonians

$$H_0=\sum_i h_0(i)=\sum_i[-\tfrac{1}{2}\nabla_i^2-(3/r_i)+V(\vec{\mathrm{r}}_i)]\,,$$

and a residual correlation term, λH_{10}. Thus, we have

$$H(\lambda,\mu)=H_0+\lambda H_{10}+\mu H_{01}\,, \qquad (5)$$

and we seek to expand the total wave function Ψ and total energy E in the double power series

$$\Psi=\Psi_0+\lambda\Psi_{10}+\mu\Psi_{01}+\lambda\mu\Psi_{11}+\cdots\,, \qquad (6a)$$

$$E=E_0+\lambda E_{10}+\mu E_{01}+\lambda\mu E_{11}+\cdots\,. \qquad (6b)$$

These are only formal expansions, however, since representation of the hyperfine operator by a δ function results in divergencies past the first-order correction. The latter linear hyperfine interaction energy (E_{hfs}) is merely the expectation value of μH_{01} over the exact nonrelativistic wave function and can be rewritten (with $\lambda=1$) as

$$E_{\mathrm{hfs}}=\mu(E_{01}+E_{11}+E_{21}+\cdots)\,, \qquad (7)$$

that is, the sum of all terms first order in nuclear spin. Analogously, the total nonrelativistic energy E_{tot} is given by

$$E_{\mathrm{tot}}=E_0+E_{10}+E_{20}+E_{30}+\cdots\,. \qquad (8)$$

The terms written explicitly in both of these expansions are the ones computed here.

The choice of one-electron potential $V(\vec{\mathrm{r}}_i)$ in $h_0(i)$ is dictated by a compromise between convenience of calculation and rapidity of convergence. Taking V to be spherically symmetric, spin independent, and identical for each electron, and thus eliminating, for example, unrestricted Hartree-Fock (UHF) and Hartree Ψ_0's, we obtain

$$[H_0,\mathcal{A}]=[H_0,S^2]=0\,; \qquad (9)$$

therefore an initial choice of a "restricted" pure doublet Ψ_0,

$$\Psi_0=\mathcal{A}\,1s(1)1s(2)2s(3)\alpha(1)\beta(2)\alpha(3)\,, \qquad (10)$$

will lead to an exact nonrelativistic Ψ which satisfies the Pauli principle and is an eigenfunction of S^2 to all orders in λ (zeroth order in μ).

It should be pointed out in passing that although there is considerable prejudice against the UHF function as Ψ_0 because it is not an eigenfunction of S^2, at least for ^2S Li the convergence in spin space to $\langle S^2\rangle=\frac{3}{4}$ must be exceedingly rapid since through first order in λ it is already 0.75002.[16]

In the present treatment, however, we will proceed within the restricted zeroth-order formalism. Two examples of hyperfine treatments based on spin-independent identical one-electron potentials have been carried out for ^2S Li through first order in λ. Cohen and Dalgarno[17] have obtained the spin density in the bare nucleus or Z expansion and in the screened Z expansion, in which the effective nuclear charge is chosen to make the first-order correction vanish. The bare nucleus treatment is highly oscillatory leading to $1.5a_0^{-3}$, while the latter has only part of the apparently dominant term linear in Z, giving 4.7. The experimental value is 2.9096.[18]

The second example, the RHF treatment, is based on [for notation, see Ref 1(a)]

$$V(r)=2[-1s|-1s]+[-2s|-2s] -[-1s|1s-]-\tfrac{1}{2}[-2s|2s-]\,, \qquad (11)$$

where the exchange term has been averaged over the α and β spin directions. The leading term in $E_{\rm hfs}$ is proportional to the $2s$ radial density at the nucleus

$$E_{01} = |R_{2s}(0)|^2 ,$$

which is ~ 2.1 (of course, for the ^2P state the zeroth-order contribution would vanish). The correction first order in correlation may be shown to be identical to both (a) the first-order correction (in the spin-dependent exchange perturbation) in going from RHF to UHF and (b) the moment perturbation correction discussed below. Using method (a), Cohen *et al.*[5] have obtained $0.63a_0^{-3}$, and Gaspari, Shyu, and Das[19] have used a local approximation to the HF potential in (b), obtaining $0.59a_0^{-3}$. Thus, the RHF expansion probably converges rapidly, though as will be seen later, not any faster than the exchangeless potential used here.

Finally, we should mention that the many-body expansion,[12] which is the only perturbative calculation for the lithium atom spin density going beyond first order is also based on a restricted Ψ_0, using the nonlocal potential

$$V^{N-1}(r) = 2[-1s|-1s] - [-1s|1s-] \tag{12}$$

which contains the HF orbitals. It is formally obtained from Eq. (11) by dropping terms involving the $2s$ orbital.

The V with which we will work here is rather different from Eqs. (11) and (12), namely, the local or exchangeless potential

$$V^{\rm EL}_{(r)} = \tfrac{2}{3}\{2[-1s|-1s] + [-2s|-2s]\} , \tag{13}$$

where the orbitals need not be fully self-consistent and were arbitrarily iterated until the energy converged to 0.001 a.u. A potential of this kind is the three-electron analog of the Hartree potential for helium,[1a] but with electrons treated identically; the factor of $\frac{2}{3}$ gives correct asymptotic screening due to two electrons. Moreover, this choice of potential simplifies the perturbation problem greatly since the absence of nonlocal terms obviates an iterative solution to the pair problem.

As a summary, then, our expansions are based on

$$h_0(i) = -\tfrac{1}{2}\nabla_i^2 - 3/r_i + V(r_i) , \tag{14}$$

with $V(r_i)$ from Eq. (13) and where

$$h_0(i)ns(i) = \epsilon_i ns(i) , \quad n = 1, 2 . \tag{15}$$

We write $ns = R_{ns}Y_{00} = P_{ns}Y_{00}/r$, where P_{ns} is found by the usual Hartree-Numerov numerical finite-difference procedures. The correlation perturbation H_{10} is given by

$$H_{10} \equiv H - H_0 = \sum_{i>j} g(ij) , \tag{16}$$

where

$$g(ij) = r_{ij}^{-1} - \tfrac{1}{2}[V(r_i) + V(r_j)] .$$

B. Perturbation Expressions

By substituting the expansions for Ψ and E into the Schrödinger equation, we obtain for $E_{\rm tot}$

$$E_0 = 2\epsilon_{1s} + \epsilon_{2s} , \tag{17a}$$

$$E_{10} = \langle 0|H_{10}|0\rangle , \tag{17b}$$

$$E_{20} = \langle 0|H_{10} - E_{10}|10\rangle , \tag{17c}$$

$$E_{30} = \langle 10|H_{10} - E_{10}|10\rangle - 2\langle 0|10\rangle E_{20} , \tag{17d}$$

where the correlation-perturbed wave function Ψ_{10} is the solution to

$$(H_0 - E_0)|10\rangle = (E_{10} - H_{10})|0\rangle . \tag{18}$$

By repeated use of interchange relations we obtain for $E_{\rm hfs}$ (taking the wave functions to be real)

$$E_{01} = \langle 0|H_{01}|0\rangle = R_{2s}^2(0) , \tag{19a}$$

$$E_{11} = 2\langle 0|H_{10} - E_{10}|01\rangle = 2\langle 0|H_{01} - E_{01}|10\rangle , \tag{19b}$$

$$E_{21} = 2\langle 10|H_{10} - E_{10}|01\rangle + \langle 10|H_{01} - E_{01}|10\rangle - 2E_{11}\langle 10|0\rangle - 2E_{20}\langle 0|01\rangle . \tag{19c}$$

Here, the wave-function first order in the contact perturbation, Ψ_{01}, is the solution to

$$(H_0 - E_0)|01\rangle = (E_{01} - H_{01})|0\rangle . \tag{20}$$

From Eq. (19b) it is seen that there are two independent ways to compute E_{11}, using either Ψ_{01} (the moment perturbation method[19]) or Ψ_{10}. We will thus have a convenient check on the internal consistency of our numerical procedures. Finally, knowledge of both first-order perturbed functions enables calculation of E_{21}.

III. SOLUTION OF CONTACT PERTURBATION PROBLEM

From Eq. (20), we seek to solve

$$\Big(\sum_i h_0(i) - 2\epsilon_{1s} - \epsilon_{2s}\Big)|01\rangle = \Big(E_{01} - 2\sum_i s_{zi}\{\delta(r_i)/r_i^2\}\Big)|0\rangle . \tag{21}$$

It may be seen by direct substitution that the solution to this problem, written in terms of δ-perturbed spatial orbitals $1s'$ and $2s'$ is

$$|01\rangle = \mathcal{A}[1s'(1)1s(2)2s(3) - 1s(1)1s'(2)2s(3) + 1s(1)1s(2)2s'(3)]\alpha(1)\beta(2)\alpha(3) , \tag{22}$$

where

$$(h_0 - \epsilon_{ns})ns' = (R^2_{ns}(0) - \{\delta(r)/r^2\})ns \;, \quad n=1,\ 2 \;. \tag{23}$$

The solution Ψ_{01} is unique except for a possible additive term in Ψ_0. This we make vanish by orthogonalizing the perturbed orbitals to their unperturbed counterparts.

Solving Eq. (23) poses no difficulty so long as the δ function and the logarithmic singularities are first removed, the latter because terms such as $r\ln r$ and $r^2\ln r$ are not amenable to numerical finite-difference approximation for small r, and it is our intent to solve for the perturbed orbitals numerically rather than by basis set expansion. Thus we proceed as follows. Writing

$$ns' = -2R_{ns}(0)\phi_{ns}(r)Y_{00}/r \;, \tag{24}$$

where

$$\phi_{ns}(0) = 1 \;,$$

$$\phi_{ns}(\infty) = 0 \;,$$

and using the identity

$$\nabla^2(1/r) = -\delta(r)/r^2 \;,$$

we introduce a new δ function on substitution into Eq. (23) which identically cancels the one present.[20a] The function ϕ_{ns} is obtained by solving

$$\frac{d^2\phi_{ns}}{dr^2} + \left(\frac{6}{r} - 2V + 2\epsilon_{ns}\right)\phi_{ns} = R_{ns}(0)P_{ns}(r) \;. \tag{25}$$

That logarithmic terms are contained in ϕ_{ns} is seen in the simple example of the hydrogen atom[20b] for which

$$\phi_{1s} = (1 - 2r\ln r - 2r^2)e^{-r} \;.$$

Moreover, with an effective potential V present, ϕ_{ns} contains also terms like $r^3\ln r$ whose second derivative is rapidly varying and which should therefore also be removed. Thus, we write

$$\phi_{ns} = (1 + a_{ns}r^2 + b_{ns}r\ln r + c_{ns}r^3\ln r)e^{-3r} + y_{ns}(r) \;, \tag{26}$$

where the constants a_{ns}, b_{ns}, and c_{ns} (the factor e^{-3r} eliminates terms in $r^2\ln r$) are chosen to be

$$a_{ns} = V(0) - \epsilon_{ns} + 22.5 \;, \tag{27a}$$

$$b_{ns} = -6 \;, \tag{27b}$$

$$c_{ns} = 9 - 2[V(0) - \epsilon_{ns}] \;. \tag{27c}$$

The remaining function $y_{ns}(r)$ is then numerically well behaved and is the solution to

$$\frac{d^2y_{ns}}{dr^2} + \left(\frac{6}{r} - 2V + 2\epsilon_{ns}\right)y_{ns}(r) = g_{ns}(r) \;, \tag{28}$$

with $y(0) = y(\infty) = 0$, and $g_{ns}(r)$ containing at worst terms like $r^2\ln r$. The differential equation may be mapped onto a mesh [here $0.01a_0$ from 0 to $20a_0$], the second derivative approximated by a three-point finite-difference formula, and the resulting band matrix equation solved by successive forward and backward substitution. We have found that a better boundary condition than the requirement that the perturbed orbital vanish at large r is the assumption that $y_{n+1}/y_n = y_n/y_{n-1}$, which, in turn, equals a constant, solved for iteratively. This allows the value at the last [$(n+1)$th] point to be nonzero and is, in the spirit of the Cooley limit,[21] used to find the unperturbed orbitals.

A useful identity[22] serves as a convenient test of our computational accuracy:

$$\langle 1s' \,|\, 2s\rangle + \langle 2s' \,|\, 1s\rangle = 0 \;. \tag{29}$$

This may be obtained by substitution of the formal solution for ns in terms of $(h_0 - \epsilon_{ns})^{-1}$ into Eq. (29). We find that

$$\langle 1s' \,|\, 2s\rangle = 20.0664 \;, \qquad \langle 2s' \,|\, 1s\rangle = -20.0613 \;,$$

which sum to 0.0051, in error by only 0.03% relative to each term. The large magnitudes of these overlap integrals stem from the fact that they contain $R_{1s}(0) \sim 8.9$ and $R_{2s}(0) \sim -2.1$, and make it necessary to treat the behavior at the nucleus with great care. The appropriate procedure is to expand the numerical solution P_{ns} in a power series in r about the origin to start the outward numerical integrations. When the final solution is obtained, P_{ns}/r is extrapolated to $r = 0$.

IV. SOLUTION TO PAIR-CORRELATION PROBLEM

We have previously shown[1a] that the wave function first order in correlation, Ψ_{10}, can be written in terms of intrashell, U_{1s1s}, and intershell, U_{1s2s}, spatial pair functions:

$$\Psi_{10} = \mathcal{A}\{U_{1s1s}(12)2s(3) + (1 + P_{12})1s(1)U_{1s2s}(23)\} \times \alpha(1)\beta(2)\alpha(3) \;, \tag{30}$$

where the pair functions are solutions to

$$[h_0(1) + h_0(2) - 2\epsilon_{1s}]U_{1s1s}(12) = [C_1 - g(12)]1s(1)1s(2) \;, \tag{31a}$$

$$[h_0(1) + h_0(2) - \epsilon_{1s} - \epsilon_{2s}]U_{1s2s}(12) = [C_2 - g(12)]1s(1)2s(2) + C_3 1s(2)2s(1) \;. \tag{31b}$$

Here, the constants C_1, C_2, and C_3 are required to make the inhomogeneity orthogonal to the homogeneous solutions and are given by

$$C_1 = \langle 1s(1)1s(2) \,|\, g(12) \,|\, 1s(1)1s(2)\rangle \;, \tag{32a}$$

$$C_2 = \langle 1s(1)2s(2) \,|\, g(12) \,|\, 1s(1)2s(2)\rangle \;, \tag{32b}$$

$$C_3 = \langle 1s(1)2s(2) \,|\, g(12)2s(1)1s(2)\rangle \;. \tag{32c}$$

To correlate the $1s$-$2s$ pair only one U_{1s2s} pair function is required, however, if desired the usual singlet and triplet pairs may be projected from it as discussed in Ref. 1(a).

When the expansions of the pair functions in spherical harmonics,

$$U_{1sns}(12)=\sum_l [(2l+1)/4\pi]U^l_{1sns}(r_1, r_2)P_l(\cos\theta_{12})/(r_1r_2)\ , \qquad n=1,\,2 \tag{33}$$

and the Neumann expansion of r_{12}^{-1} are substituted into Eq. (31) the equations for the U^l decouple. For example, for the U_{1s1s} pair we obtain the equations

$$\left[(1+P_{12})\left(-\frac{1}{2}\,\frac{\partial^2}{\partial r_1^2}-\frac{3}{r_1}+\frac{l(l+1)}{2r_1^2}+V(r_1)\right)-2\epsilon_{1s}\right]U^l_{1s1s}$$

$$=\left(\delta_{l0}\{C_1+\tfrac{1}{2}[V(r_1)+V(r_2)]\}-\frac{1}{2l+1}\,\frac{r_<^l}{r_>^{l+1}}\right)\times P_{1s}(r_1)P_{1s}(r_2)\ . \tag{34}$$

To effect solution of Eqs. (34) and their analogs for the U_{1s2s} case, the square in r_1-r_2 space from 0 to $20a_0$ in each direction is divided into four regions. An inner square extends from the origin to $4a_0$ along both r_1 and r_2 and is partitioned by a mesh $(0.1\times 0.1)a_0$. On the sides of this square are two rectangles, each $(4\times 16)a_0$ which are sectioned by rectangular meshes $(0.1\times 0.4)a_0$; finally, the remaining large $(16\times 16)a_0$ square contains a square mesh of $(0.4\times 0.4)a_0$. The reason the outer regions can be treated by a coarse mesh is that the pair functions die off rather rapidly outside the inner square and therefore these outer regions make relatively small contributions to the perturbation terms. (An exception is the term E_{21} in which approximately 30% of the value is obtained outside the inner square; however, this term is sufficiently small already that large errors in it are tolerable.)

In each region the differential equation is mapped onto the relevant grid, using a five-point finite-difference formula to approximate the two radial second derivatives. The resulting algebraic equation involves a banded supermatrix of the form shown in Fig. 1 of Ref. 1(a).[23] The solution to this equation is obtained in the following way. Working first with an inner $(5\times 5)a_0$ square we impose the boundary condition $U_{j+1}/U_j=U_j/U_{j-1}$, the analog of that used in the one-dimensional case, Eq. (28). Now the limiting ratio varies somewhat around the periphery since j symbolizes a pair of r_1-r_2 coordinates, but values of U on an inner $(4\times 4)a_0$ square remain constant to at least eight decimal places, no matter which ratio is chosen. Thus the solution on the inner 4×4 square is known and its values on the periphery then serve as inner boundary conditions for the three outer regions. Notice, of course, that whenever r_1 or r_2 equals zero there is no difficulty with boundary values since U then vanishes.

There are a number of independent checks on the validity of these procedures and we mention only one at this time. In analogy with the one-particle identity, Eq. (29), we may show that

$$\langle 1s(1)1s(2)\,|\,U_{1s2s}(12)\rangle+\langle 1s(1)2s(2)\,|\,U_{1s1s}(12)\rangle=0\ . \tag{35}$$

This follows since, from Eq. (31a), we have

$$\langle 1s(1)2s(2)\,|\,U_{1s1s}(12)\rangle=\langle 1s(1)2s(2)\,|\,[h_0(1)+h_0(2)-2\epsilon_{1s}]^{-1}[C_1-g(12)]1s(1)1s(2)\rangle$$

$$=(\epsilon_{1s}-\epsilon_{2s})^{-1}\langle 1s(1)2s(2)\,|\,g(12)\,|\,1s(1)1s(2)\rangle\ ,$$

and an analogous result with opposite sign is obtained from the second term of Eq. (35) and the formal solution for U_{1s2s}. We find that

$$\langle 1s(1)1s(2)\,|\,U_{1s2s}(12)\rangle=-0.028\,08\ ,$$

$$\langle 1s(1)2s(2)\,|\,U_{1s1s}(12)\rangle=0.028\,73\ ,$$

which give a difference of 0.000 65, in error by only 2%. This error is, of course, larger than that for the perturbed orbitals which are obtained on the much smaller one-dimensional mesh.

V. EVALUATION OF TOTAL ENERGY

A. Energy Through First Order

We evaluate the energy through first order using Ψ_0 in Sec. V A and through third order using Ψ_{10} in Sec. V B. From the orbital energies (in a.u.)

$$\epsilon_{1s}=-2.0469\ ,\quad \epsilon_{2s}=-0.2376\ ,$$

we obtain E_0 as

$$E_0=2\epsilon_{1s}+\epsilon_{2s}=-4.3314\ .$$

This result is rather different from the RHF E_0 equal to $-5.151\,82$ obtained, in turn, from $\epsilon_{1s}=-2.477\,75$ and $\epsilon_{2s}=-0.196\,32$. The difference stems largely from the fact that the exchangeless $1s$ orbital sees a greater $1s$ Coulomb potential than the HF $1s$ orbital ($\frac{4}{3}$ vs 1 electron), while the exchangeless $2s$ orbital experiences a lesser $1s$ potential than its HF counterpart ($\frac{4}{3}$ vs 2 electrons).

Values of E_0 differing from the HF result are also obtained in the V^{N-1} and bare nucleus expansions.

To obtain E_{10} we use Eq. (17b) and find that

$$E_{10} = [1s1s\,|\,1s1s] + 2[1s2s\,|\,1s2s] - [1s2s\,|\,2s1s] - 2\langle 1s\,|\,V\,|\,1s\rangle - \langle 2s\,|\,V\,|\,2s\rangle \ ,$$

where the order of the electrons is implied by the order of the orbitals: $|\,abc\rangle \equiv |\,a(1)b(2)c(3)\rangle$. Evaluation of these integrals by trapezoidal rule on a mesh of $0.001a_0$ furnishes, to four-decimal accuracy,

$$E_{10} = -3.0818 \ ,$$

$$E_0 + E_{10} = -7.4132 \ ,$$

which is in good agreement with the RHF energy, $-7.432\,73$.[12]

B. Second- and Third-Order Energies

The evaluation of E_{20} and E_{30} is considerably more complex, involving large numbers of two- and three-electron integrals. We compute E_{20} from Eq. (17c) as

$$E_{20} = \langle (1-P_{13})1s1s2s\,|\,\sum_{i>j} r_{ij}^{-1} - \sum_i V(r_i) - E_{10}\,| \times\{U_{1s1s}(12)2s(3) + (1+P_{12})1s(1)U_{1s2s}(23)\}\rangle \ . \tag{36}$$

Since the pair functions contribute additively to E_{20} and, in turn, the contribution from each pair is the sum of contributions from each l [cf. Eq. (55) of Ref. 1(a)], we may write, in obvious notation,

$$E_{20} = \textstyle\sum_l E_{20}(1s,1s;l) + \sum_l E_{20}(1s,2s;l) \ .$$

Values for the individual terms were obtained by numerical integrations and are given in Table I. Convergence in l is extremely rapid and requires only values of $l \le 3$ for three-decimal accuracy. Also, as seen from the values in parentheses for $l = 0$, 1 which give the contributions from the inner $(4\times 4)a_0$ square alone, the exterior three regions need not be considered for $l > 1$.

TABLE I. Second-order energies of ^2S Li (a.u.).

l	$E_{20}(1s,1s;l)$	$E_{20}(1s,2s;l)$
0	$-0.003\,78(-0.003\,40)^{\rm a}$	$-0.035\,22(-0.031\,08)^{\rm a}$
1	$-0.026\,39(-0.026\,39)^{\rm a}$	$-0.003\,32(-0.003\,31)^{\rm a}$
2	$-0.004\,10^{\rm a}$	$-0.000\,36^{\rm a}$
3	$-0.001\,22^{\rm a}$	$-0.000\,09^{\rm a}$
$\sum_{l=0}^{3}$	$-0.035\,49$	$-0.038\,99$
Total	$-0.074\,48 \left\{\begin{array}{l}+0.\\ -0.0015^{\rm b}\end{array}\right.$	$-0.069\,95^{\rm a}$

[a] Values obtained solely from the inner $(4\times 4)a_0$ square. For $l = 2, 3$ the exterior regions make negligible contributions. The total second-order energy computed on the inner square is 94% of the total.

[b] Error estimates are obtained by extrapolation to zero mesh as described in the text. The second-order energy is in error by 2% at most.

Summing $E_{20}(1s,1s;l)$ and $E_{20}(1s,2s;l)$ we find that the two pair functions make approximately equal contributions to E_{20} of $-0.035\,49$ and $-0.038\,99$, respectively, giving a total E_{20} of $-0.074\,48$. The accuracy of this number can be assessed by the following argument. Since 94% of E_{20} comes from the innermost square (mesh, $h = 0.10$) only this region need be studied in detail. By recalculating the inner square for the mesh $h = 0.11$ and assuming an even power-series expansion in h of E_{20},[3]

$$E_{20}(h) = E_{20}\big|_{h=0} + h^2 E_{20}''\big|_{h=0} + O(h^4) \ ,$$

we obtain $E_{20}(h=0) = -0.075\,98$. Thus we may reexpress our result in terms of a symmetric error bound as

$$E_{20} = -0.0752 \pm 0.0008 \ ,$$

$$E_0 + E_{10} + E_{20} = -7.4884 \pm 0.0008 \text{ a.u.}$$

The error is approximately 2% and is consistent both with that found for Eq. (35) and also with the spin-density results given in Sec. VI.

Finally, E_{30} may be computed from Eqs. (17d) and (33) as

$$\begin{aligned} E_{30} = {} & \langle \textstyle\sum_l \{U_{1s1s}^{l}(12)2s(3) + (1+P_{12})1s(1)U_{1s2s}^{l}(23)\}\,|\,\sum r_{ij}^{-1} - \sum V(r_i) - E_{10}\,| \\ & \times (1-P_{13}) \textstyle\sum_{l'} \{U_{1s1s}^{l'}(12)2s(3) + (1+P_{12})1s(1)U_{1s2s}^{l'}(23)\}\rangle \\ & - 2E_{20}\langle (1-P_{13})1s(1)1s(2)2s(3)\,|\textstyle\sum_l \{U_{1s1s}^{l}(12)2s(3) + (1+P_{12})1s(1)U_{1s2s}^{l}(23)\}\rangle \ . \end{aligned} \tag{37}$$

Pairwise additivity is no longer present in E_{30}; however, the contributions to E_{30}, obtained from expressions analogous to Eq. (58) of Ref. 1a can be indexed in the following manner. We define $E_{30}(l)$ as the sum of all contributions to the third-order energy obtained from using pair functions up to and including angular momentum l, minus the sum of all contributions obtained using pairs good through

TABLE II. Contributions to E_{30} and E_{21} indexed by l value.

l	$E_{30}(l)$(a.u.)	$E_{21}(l)(a_0^{-3})$
0	-0.0086	-0.151
1	0.0130	-0.147
2	0.0032	$+0.000$
3	0.0015	-0.001
Total	0.0091	-0.299

$l-1$. For example, $E_{30}(0)$ is the sum of all terms resulting from U_{1s1s}^0 and U_{1s2s}^0 in Eq. (37), whereas $E_{30}(1)$ is the sum of all terms resulting from U_{1s1s}^0, U_{1s2s}^0, U_{1s1s}^1, and U_{1s2s}^1, minus $E_{30}(0)$. By definition, the $E_{30}(l)$ sum to E_{30}. Using the values given in Table II we obtain

$$E_{30}=\sum_l E_{30}(l)=0.0091 .$$

The convergence in l is again rapid, indicating that $l \leq 3$ is sufficient for an accurate value of E_{30}. Again, also, the bulk of E_{30} (80%) comes from the inner $(4\times 4)a_0$ square and calculation on the outer square is unnecessary for $l>1$. From examination of the dependence of the total value of E_{30} on h we can give a conservative error bound of ± 0.003. Thus, the total energy is given as

$$E_{\text{tot}}=E_0+E_{10}+E_{20}+E_{30}=-7.4793\pm 0.0038 \text{ a.u.},$$

which is in excellent agreement with the accurate nonrelativistic value, $-7.478\,07$.[14]

VI. EVALUATION OF SPIN-DENSITY AT NUCLEUS

A. Density Through First Order

From Eq. (19a) we evaluate E_{01} as

$$E_{01}=R_{2s}^2(0)=4.497a_0^{-3} .$$

This result is rather far both from experiment, 2.9096, and also the RHF value, 2.065-2.097, and is probably due, in part, to the absence of exchange terms from V. It is not, however, much further off than the RHF.

Using the first equality of Eq. (19b) we may obtain E_{11} using Ψ_{01} as

$$E_{11}=2\langle(1-P_{13})1s1s2s\,|\sum r_{ij}^{-1}-\sum V(r_i)-E_{10}|\times(1s'1s-1s1s')2s+1s1s2s'\rangle , \qquad (38)$$

or expanding further

$$E_{11}=4[1s2s\,|\,1s2s']-2[1s2s\,|\,2s'1s]-2[1s2s\,|\,2s1s'] -2\langle 2s|\,V\,|2s'\rangle+2\{\langle 1s\,|\,2s'\rangle+\langle 2s\,|\,1s'\rangle\} \times\{\langle 1s|\,V\,|2s\rangle-[1s1s\,|\,2s1s]\} . \qquad (39)$$

Here, terms containing the factor $\{\langle 1s\,|\,2s'\rangle+\langle 1s'\,|\,2s\rangle\}$ which result from the expansion of Eq. (38) would vanish identically from Eq. (29) for the exact $1s$ and $2s$ functions and, in fact, make negligible contributions to E_{11}. Notice also that only the $l=0$ term in the expansion of r_{12}^{-1} contributes.

The total value for E_{11}, obtained by numerical integration on a mesh of $0.01a_0$, equals $-1.346a_0^{-3}$, of which -1.631 is the contribution from the $1s$ orbital. Since the perturbed orbitals are known only at a single mesh value, we cannot improve our results by extrapolation. However, the high accuracy of the test of Eq. (29) and the smallness of the mesh suggest a conservative error estimate of 1%, giving

$$E_{11}=(-1.346\pm 0.013)a_0^{-3} ,$$

$$E_{01}+E_{11}=(3.151\pm 0.013)a_0^{-3} .$$

Turning now to the alternate calculation of E_{11} via Ψ_{10} we obtain

$$E_{11}=4\langle 1s2s\,|\,\delta(r_2)/r_2^2|\,U_{1s2s}\rangle-2\langle 2s1s\,|\,\delta(r_1)/r_1^2+\delta(r_2)/r_2^2|\,U_{1s2s}\rangle+2\langle 1s\,|\,\delta/r^2|\,1s\rangle\langle 2s1s\,|\,U_{1s2s}\rangle -2E_{01}\{2\langle 1s2s\,|\,U_{1s2s}\rangle-\langle 2s1s\,|\,U_{1s2s}\rangle\}-2\langle 1s\,|\,\delta/r^2|\,2s\rangle\{\langle 2s1s\,|\,U_{1s1s}\rangle+\langle 1s1s\,|\,U_{1s2s}\rangle\} . \qquad (40)$$

Since U_{1s2s} has not been orthogonalized to $1s(1)2s(2)$ or $1s(2)2s(1)$, their overlaps enter, as do the approximately cancelling "mixed" overlaps of Eq. (35). Notice that aside from the latter, U_{1s1s} does not contribute to E_{11} for the obvious reason that the correlation perturbation treats $1s\alpha$ and $1s\beta$ symmetrically. The value of E_{11} is somewhat more difficult to obtain accurately in this second formalism due to the necessity of evaluating δ-function expectation values of pair functions, known only on a sparce grid. The appropriate method to use is best shown by the following. For the integral

$$\langle 1s(1)2s(2)\,|\,\delta(r_2)/r_2\,|\,U_{1s2s}(12)\rangle$$

$$=\lim_{r_2\to 0}\{[R_{2s}(r_2)/r_2^2]\int dr_1 P_{1s}(r_1)U_{1s2s}^0(r_1,r_2)]\},$$

the function (of r_2) in curly brackets approaches $r_2=0$ with a cusp and the desired limit should therefore be obtained by Aitken's interpolation and extrapolation algorithm.[24]

When all the integrals of Eq. (40) are evaluated there still remains the usual numerical error contained both in the pair functions and in the normal (non-δ-function) integrations. These can be taken into account by h^2 extrapolation as in previous sections. Our value for $h=0.1a_0$, $-1.364a_0^{-3}$, extrapolates to $-1.337a_0^{-3}$, giving a symmetrical average

TABLE III. Comparison of perturbative ^2S Li total energies (a.u.).[a]

	Exchangeless	Many body[b]	Z expansion[c]
E_0	−4.3314(42%)[d]	−5.7823(22%)	−10.1250(−35%)
$E^{(1)}$	−7.4132(1%)	−7.432 23(0.6%)	−7.056 585(−6%)
$E^{(2)}$	−7.4884(−0.1%)	−7.474 19(0.05%)	−7.464 93(−0.17%)
$E^{(3)}$	−7.4793(−0.02%)	−7.478 78(0.01%)	−7.472 61(−0.07%)

[a] The partial sum $E^{(n)}$ is defined as $\sum_{i=0}^{n}$.

[b] Reference 12.

[c] Reference 13.

[d] Percent errors are given in parentheses.

of 1.350 ± 0.014, in very good agreement with the previous values $(-1.346 \pm 0.013)a_0^{-3}$, confirming explicitly the interchange theorem and validating the accuracy of our numerical procedures for the hyperfine problem.

B. Second-Order Spin Density

Employing Ψ_{01} and Ψ_{10}, determined above, and Eq. (19c), we may obtain E_{21}. Although the complete expression is rather lengthy, it may be summarized by the values

$$\langle 10 | H_{01} - E_{01} | 10 \rangle = 0.539 \ ,$$

$$2\langle 10 | H_{10} - E_{10} | 01 \rangle = -0.218 \ ,$$

$$2E_{11}\langle 0 | 10 \rangle = 0.620 \ ,$$

where the term $E_{20}\langle 0 | 01 \rangle$ vanishes by the orthogonality previously mentioned. In Table II, the contributions from each l value are given and, again, convergence in l is seen to be rapid. The final value of E_{21} obtained is $0.299a_0^{-3}$, with a conservative error estimate of 0.06 or 20%. The error is rather large because for E_{21}, unlike the previous terms, a significant contribution (~33%) comes from the outer regions of coarser mesh. The total spin density is thus

$$E_{01} + E_{11} + E_{21} = (2.850 \pm 0.076)a_0^{-3} \ ,$$

in good agreement with the experimental value 2.9096.[18]

VII. DISCUSSION

The most interesting feature of the two perturbation expansions considered in this work is their rapid convergence to very accurate values despite rather poor starting points. Thus, while the total energy is in error by 42% in zeroth order, the error through first order is only 1% and through third order it has converged to within 0.001 hartree (−0.02%) of "experiment." The fact that the energy obtained lies below the accurate value is in no contradiction since there is no lower bound to the sum through E_{30}. An upper bound to the ground-state energy may be found from Ψ_0 and Ψ_{10} by minimizing

$$\frac{\langle \Psi_0 + \alpha\Psi_{10} | H_0 + H_{10} | \Psi_0 + \alpha\Psi_{10} \rangle}{\langle \Psi_0 + \alpha\Psi_{10} | \Psi_0 + \alpha\Psi_{10} \rangle}$$

with respect to the variable parameter α. The result obtained is −7.4779 a.u. for $\alpha = 0.875$, based on a Ψ_{10} orthogonalized to Ψ_0.

It is interesting to compare the perturbation expansion for the total energy in the exchangeless potential with the many-body and Z exapnsions given in Table III. Through first order this and the many-body treatments are quite similar, being in error by 1% and 0.6%, respectively. The second-order energies are rather different, however, both in magnitude and in composition; that is, we find comparable contributions from correlating the $1s$-$1s$ and $1s$-$2s$ pairs, whereas the many-body treatment furnishes them in the ratio 25:1. In addition, the exchangeless potential leads to convergence from below while the many-body V^{N-1} treatment converges from above.

Notice that in Table III we present a many-body "third-order energy" whereas technically that method computes an infinite-order energy, obtained, in this instance, by laddering the $1s$-$1s$ pair. The total result of the laddering is to change the $1s$-$1s$ pair energy from −0.039 413 to −0.044.[12] As we have previously shown,[25] it is often possible to apply a geometric approximation to whole orders of perturbation theory as opposed to individual diagonal diagrams. Thus, writing

$$-0.044 = -0.039\,413(1 + x + x^2 + \cdots) \ ,$$

we obtain $x = 0.104$ and a fourth-order term of only ~0.0004. This implies that essentially all the higher correlation energy, at least to the accuracy reported, is contained in E_{30}. The many-body (V^{N-1}) and Rayleigh-Schrödinger (exchangeless) calculations are thus comparable. The error in each order for the former case seems to be uniformly half that found for the latter. A more slowly convergent series than these is the Z expansion also given in Table III, for $Z = 3$, in error by ~0.005 a.u. through third order. Thus, unlike the Z expansion for helium which converges more rapidly than the Hartree and HF expansions, for three electrons the use of effective potentials enhances convergence, at least through third order.

Turning now to the results for the spin density we find again rapid convergence. The three partial sums determined here are 4.497(54%), 3.149(8.2%), and 2.850(−1.9%) compared with the accurate value 2.9096. The rather poor starting point is perhaps due in part to lack of exchange potentials, but in any case, the result through first order is superior to that obtained in the HF expansion through first

TABLE IV. Comparison of perturbation treatments of ^2S Li hyperfine interaction (a_0^{-3}).

	RS(V^{EL})	Many body (V^{N-1})[a]	RHF
E_{01}	4.497		2.065[a]
E_{11}	-1.348[b]		0.63[c]
$E_{01}+E_{11}$	3.149	2.578	2.695
E_{21}	-0.299	0.270	
$E_{01}+E_{11}+E_{21}$	2.850	2.848[d]	
E_{31} + higher orders		0.042[c]	
Total[e]	2.850	2.890	

[a] Reference 12.

[b] The average of the values obtained from Ψ_{10} and Ψ_{01} is given here.

[c] Reference 5.

[d] Estimated by geometric approximation as discussed in the text.

[e] The experimental value is 2.9096.

order, 2.70($-$7%). Thus, important physical effects may be very rapidly picked up in higher orders.

It is useful to compare our results for the hyperfine problem with those of the many-body treatment (Table IV), though now the separation of the latter into orders of perturbation is somewhat more difficult. The many-body E_{01} is the HF value 2.065 (in that calculation), and the sum through first order ($E_{11}=0.513$) is $2.578a_0^{-3}$ or in error by -11%, slightly worse than the RHF and exchangeless expansions. Of the remaining contribution, 0.312, part comes from E_{21} and part from laddering EPV diagrams. Using the geometric approximation described previously, we estimate that 0.270 is from E_{21} and 0.042 from E_{31} and higher terms. If this assessment is correct, then the V^{N-1} potential gives $2.848a_0^{-3}$ through second order, essentially the same value obtained in this work. Again, we find similar rates of convergence between the expansion based on V^{N-1}, chosen by physical intuition and V^{EL}, chosen for mathematical convenience, vindicating use of this unorthodox potential and reaffirming that little is known about the choice of effective V for rapid convergence.

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