only up to the $n=3$ He$^+$ level. We used an n^{-3} law in extrapolating to $n=4$. Also shown in Fig. 5 are our results in transforming the line cross sections into $n=4$ cross sections.

It would seem that fair agreement is being reached at the higher energies where the Born approximation is expected to hold. Both estimates are rough, however.

VI. EXCITATION OF THE $4\,^1D \rightarrow 2\,^1P$ (λ4922Å) LINE

This line is pressure-dependent with the apparent cross section increasing with pressure. Population mechanisms include collisional transfer, $n\,^1P \rightarrow n\,^1F$ with subsequent $n\,^1F$ ($n>4$) cascade to $4\,^1D$, and also $4\,^1P \rightarrow 4\,^1D$ collisional transfer. Figure 6 is an excitation curve to this line at 4 μ pressure.

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Validity of the Concept of the Core Polarization Effect in Hyperfine Structure

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The core polarization effect in hyperfine structure is discussed by a semiempirical evaluation of 16 recently calculated values of the Fermi contact term for the ground state of lithium. The analysis proceeds by an investigation of the manner in which the various wave functions approximate eigenfunctions of $\mathbf{S}^2$, in conjunction with an examination of the one-electron orbitals employed. The concept of core polarization by non-*s* electrons is shown to be valid, while if the polarizing electron is an *s* electron, no definite conclusion concerning core polarization can be made. Finally, it is proposed that for all cases of a single polarizing electron, the following many-electron, approximate unrestricted Hartree-Fock wave function may be used:

$$\phi=A_p\{B_1[\prod_i U_{n(i)l(i)}\alpha U_{n'(i)l(i)}\beta]U_{N,L}\alpha+B_2[U_{N,L}\alpha\prod_i U_{n(i)l(i)}\beta U_{n'(i)l(i)}\alpha]\},$$

where N, L are the quantum numbers of the polarizing electron and $B_1=-B_2$ if $L=0$. Two tests of the validity of this wave-function approximation are proposed.

INTRODUCTION

Recently, many approximate wave functions of the ground state of lithium have been reported.[1–9] For all of these, the Fermi[10] contact term in hyperfine structure has also been calculated. The calculation of the contact term is of interest since it has been predicted by Pratt[11] that one should expect a contribution to the contact term from the core, 1*s* electrons in an open-shell configuration due to the spin polarization of the core, in this case by the outer, unpaired 2*s* electron. This effect is called the core polarization effect and has been applied[12] to cases for which the polarizing electron is not an *s* electron. The hyperfine fields thereby calculated are at least of the same order as those observed experimentally and have not been predicted by any other theory.

The lithium atom in its ground state represents the simplest test of the validity of the core polarization hypothesis. One expects for hyperfine structure a large contribution from the 2*s* valence orbitals and a smaller contribution from the core orbitals provided that the latter orbitals are represented by an open-shell configuration.[11] Recent hyperfine structure calculations,[1–9] however, show several inconsistencies. In the first place, there seems to be little correlation between the "goodness" (as determined by calculated total energy) of a wave function and the "goodness" (as determined by deviation of experimental and calculated values) of the contact term. Of greater significance are the results using nearly exact wave functions which show that the value of the contact term with and without open-shell orbitals changes only slightly. This result has been interpreted[5] as casting serious doubt on the physically simple and highly useful concept of core polarization.

It is the purpose of this paper to investigate these inconsistencies. For the energy versus contact term correlation it will be shown that the energy value (known to be a poor criterion of "goodness") must be considered in conjunction with the structure of the wave function before any comparisons with hyperfine structure calculations can be made. By this analysis one is able to show a correlation between the ground state energy and the contact term. Furthermore, one may then predict the best form of a wave function for more complicated physical situations. On the question of core

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polarization it will be shown that (1) one cannot unequivocally state that the core contribution is negligible when the polarizing electron is in an s state and (2) if the polarizing electron is not in an s state then one will obtain a large core contribution (spin-polarized core) to the contact term in hyperfine structure.

FORMULATION

Fermi[10] showed that for s electrons the Hamiltonian of the hyperfine energy, the so-called contact term, is given by

$$H=(8\pi/3)\mu_0\mu_I[(2I+1)/I](\langle f\rangle/4\pi), \qquad (1)$$

where

$$f=\sum_{i=1}^{N}\frac{2\delta(r_i)}{r_i^2}\sigma_{z_i} \qquad (2)$$

and $\int_0^\infty 2\delta(r)dr=1$. From Eq. (2) it follows that the quantity $\langle f\rangle/4\pi=Q(0)$, the electron spin density at the nucleus.

For purposes of comparison all of the calculations of $\langle f\rangle$ may be considered in the manner which the wave functions used approximate eigenfunctions of $\mathbf{S}^2$. Thus a general description can begin with the exact eigenfunctions and then consider in turn the various approximations. The first discussion of this type was given by Pratt[11] in which the value of $\langle f\rangle$ was given by[13]

$$\begin{aligned}\langle f\rangle=N\{&A_1^2U_{2s}^2(0)\\&+A_2^2[2U_{1s}^2(0)+2U_{1's}^2(0)-2U_{2s}^2(0)]\\&+2A_1A_2[U_{1's}^2(0)-U_{1s}^2(0)]\}\\&\qquad+\text{terms due to nonorthogonality}. \qquad (3)\end{aligned}$$

It is assumed here for convenience that all quantities are real. The normalization and other constants are included in N; A_1 and A_2 are variational parameters associated with the two linearly independent spin functions which are eigenfunctions of $\mathbf{S}^2$; the U's are the one-electron orbitals (here evaluated at the nucleus, $r=0$). A glance at Eq. (3) clearly shows core asymmetry in the A_1A_2 term. One might suspect that core polarization effects arise from this term. All calculations, however, have shown that the A_2 parameter is negligibly small in energy calculations and has often been neglected in calculating $\langle f\rangle$. As a matter of fact the values of $\langle f\rangle$ closest to experimental values have ignored A_2. Thus a more thorough investigation must include those terms due to the nonorthogonality of the U's.

A wave function which is an eigenfunction of $\mathbf{S}^2$ for the doublet ground state of a three-electron atom is[14]

$$\begin{aligned}6^{\frac{1}{2}}\phi=A_p\{&A_1[U_{1s}\alpha U_{1's}\beta U_{2s}\alpha-U_{1s}\beta U_{1's}\alpha U_{2s}\alpha]\\&+A_2[2U_{1s}\alpha U_{1's}\alpha U_{2s}\beta-U_{1s}\alpha U_{1's}\beta U_{2s}\alpha\\&\qquad-U_{1s}\beta U_{1's}\alpha U_{2s}\alpha]\}. \qquad (4)\end{aligned}$$

In Eq. (4) A_p is the antisymmetrizing operator, A_1 and A_2 have the same meaning as in Eq. (3), and the electrons 1, 2, and 3 are represented, in that order, in the product of one-electron functions. The antisymmetrizing operator can, of course, be replaced by a determinant wave function. For the present case the wave function can be considered as the linear combination of three determinants. In order to investigate the nonorthogonal terms in Eq. (3) we wish to orthogonalize where possible. Thus in the determinant derived from $A_pU_{1s}\alpha U_{1's}\beta U_{2s}\alpha$ we may only orthogonalize U_{1s} and U_{2s}, etc. Let us construct $U_{2s,1s}$ and $U_{2s,1's}$ which are U_{2s} orbitals orthogonal to U_{1s} and $U_{1's}$ orbitals, respectively. Hence,

$$U_{2s,1s}=U_{2s}-S_{2s,1s}U_{1s} \qquad (5)$$

and

$$U_{2s,1's}=U_{2s}-S_{2s,1's}U_{1's}, \qquad (6)$$

where $S_{2s,1s}$ and $S_{2s,1's}$ are overlap integrals between the subscripted orbitals. It is not necessary (nor desirable on account of symmetry) to orthogonalize the core orbitals with each other.

The formula for $\langle f\rangle$ using the wave function of Eq. (4) may be written, similar to Eq. (3), as products of A_1^2, A_1A_2, and A_2^2. Since, as already noted, A_2 plays an insignificant role in the energy calculation and since it has also been observed[6] that the A_2^2 contribution is negligible in computing $\langle f\rangle$, we will neglect the A_2^2 contributions. Thus,

$$\begin{aligned}\langle f\rangle\sim 4\pi A_1^2[&U_{1s}^2(0)(S_{1's,2s}^2-S_{1s,2s}^2)+U_{1's}^2(0)(S_{1s,2s}^2-S_{1's,2s}^2)+2U_{1s}(0)U_{1's}(0)(S_{1s,2s}S_{1's,2s}\\&-S_{1s,1's}S_{1's,2s}^2-S_{1s,1's}S_{1s,2s}^2+S_{1s,2s}S_{1's,2s}S_{1s,1's}^2)+U_{2s,1s}^2(0)+U_{2s,1's}^2(0)+2U_{2s,1s}(0)U_{2s,1's}(0)S_{1s,1's}^2\\&-2U_{1s}(0)U_{2s,1's}(0)S_{1s,1's}(S_{2s,1's}-S_{1s,1's}S_{2s,1s})-2U_{1's}(0)U_{2s,1s}(0)S_{1s,1's}(S_{2s,1s}-S_{1s,1's}S_{2s,1's})]\\&+8\pi A_1A_2[-U_{1s}^2(0)(2-S_{2s,1s}^2+S_{2s,1's}^2-2S_{1s,1's}S_{2s,1's}S_{2s,1s})+U_{1's}^2(0)(2-S_{2s,1's}^2\\&+S_{2s,1s}^2-2S_{1s,1's}S_{2s,1's}S_{2s,1s})-U_{2s,1s}^2(0)+U_{2s,1's}^2(0)+2U_{1s}(0)U_{2s,1s}(0)S_{1s,1's}S_{2s,1's}\\&\qquad-2U_{1's}(0)U_{2s,1s}(0)S_{2s,1's}-2U_{1's}(0)U_{2s,1's}(0)S_{1s,1's}S_{2s,1s}+2U_{1s}(0)U_{2s,1's}(0)S_{2s,1s}]. \qquad (7)\end{aligned}$$

Equation (7) may be further simplified. Since $A_1\gg A_2$, let us drop those terms in A_1A_2 which are of order equal to or less than the lowest order terms in A_1^2. Order here is determined by power of core-valence overlap integrals and these are quadratic, to lowest order, in the A_1^2 term. Hence

$$\langle f\rangle\sim 4\pi A_1^2B+8\pi A_1A_2C, \qquad (8)$$

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[13] The notation 1s, 1's is used instead of the more usual 1s, 1s' since it is the principal quantum number that is slightly altered and not the orbital angular momentum quantum number.

[14] E. A. Burke and J. F. Mulligan, J. Chem. Phys. 28, 995 (1958).

TABLE I. Comparison of energy and hyperfine splitting calculations for lithium.

Ref.	Wave function[a]	$-E$(a.u.)	$\langle f\rangle(a_0^{-3})$	Absolute percent difference of $\langle f\rangle$ from experiment
1	35-term configuration interaction	7.41792	3.989	37.2
2	Two-determinant, open-shell, Slater-type orbitals	7.4436	3.772	29.8
2	Closed-shell, Slater-type orbitals	7.41792	2.093	27.9
3	Closed-shell, Hartree-Fock	7.43273	2.095	27.9
3	One-determinant, open-shell, Hartree-Fock with $\langle f\rangle$ projected	7.43275	2.337[b]	19.6
1	41-term configuration interaction	7.47622	2.580	11.2
1	45-term configuration interaction	7.47710	2.595	10.7
4	One-determinant open-shell, Slater-type orbitals	7.41795	3.233	10.1
5	Closed shell, r_{ij} core	7.47476	2.648	8.9
6	Three-determinant, open-shell, Slater-type orbitals	7.4437	3.038	4.5
7	Two-determinant open-shell, Slater-type core orbitals with expanded valence-orbital	7.4450	2.802	3.6
3	One-determinant open-shell, Hartree-Fock	7.43275	2.825	2.8
8	Closed-shell, r_{ij} core, r_{ij} core-valence	7.4779	2.826	2.8
9	Six-term configuration interaction	7.4319	2.872	1.2
5	Closed-shell, r_{ij} core, r_{ij} core-valence	7.47630	2.872	1.2
5	Two-determinant, open-shell, r_{ij} core, r_{ij} core-valence	7.47631	2.883	0.8
	Experiment	7.47805[c]	2.9062[d]	0.0

[a] An unrestricted Hartree-Fock wave function is denoted here as open-shell Hartree-Fock. This facilitates comparisons.
[b] This value differs from that in the reference and has been privately communicated to the author by Lester M. Sachs.
[c] Charles W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev. **127**, 830 (1962).
[d] P. Kusch and H. Taub, Phys. Rev. **75**, 1477 (1949).

where

$$\begin{aligned} C\sim &-2U_{1s}^2(0)+2U_{1's}^2(0)\\ &+2U_{1s}(0)U_{2s}(0)(2S_{1s,2s}+S_{1s,1's}S_{2s,1's})\\ &-2U_{1's}(0)U_{2s}(0)(2S_{2s,1's}+S_{1s,1's}S_{2s,1s}) \end{aligned} \tag{9}$$

and B may be obtained from Eq. (7). Equation (9) has been obtained by dropping the orthogonal orbitals which will not be needed in the discussion of the A_1A_2 term. As an empirical check of the approximation $\langle f\rangle$ has been calculated using an open-shell wave function composed of Slater-type orbitals[6] with the result that the approximate formula for $\langle f\rangle$ yields a value which deviates by less than 1% from the value obtained by using the complete formula. We may now proceed to discuss the various wave functions used in the computation of $\langle f\rangle$.

DISCUSSION

Wave functions and associated energies along with the computed values of $\langle f\rangle$ and the absolute percentage deviation of the computed values of $\langle f\rangle$ are listed in Table I. Table II classifies the various wave functions in terms of the number of determinants, core configuration, and type of 2*s* orbital employed.

Three-Determinant Functions

One might expect that a three-determinant function for which $\phi_{2s}(0)$ is not zero would be closer to the experimental value than the three-determinant function for which $\phi_{2s}(0)=0$. By reference to the tables we see that this is not the case. However, the former wave function is a 45-term configuration interaction of which only four terms are of the three-determinant type. It must be remembered, both here and in what follows, that in considering $\langle f\rangle$ and in analyzing the various contributions to $\langle f\rangle$ we are actually considering the matrix elements of $\langle f\rangle$, i.e., $\langle f\rangle_{ij}$. Thus $\langle f\rangle=\Sigma_{ij}c_ic_j\langle f\rangle_{ij}$ and the c's are the eigenvectors of the wave function. Apparently there is insufficient mixing of three-determinant configurations in the 45-term configuration-interaction wave function[1] to compensate for the inadequacies

TABLE II. Composition of wave functions employed in hyperfine splitting calculations for lithium.

Configuration			
Determinants	Core configuration	$\phi_{2s}(0)$[a]	References
3	open	zero	6
3	open	nonzero	1
2	open	zero	1, 2
2	open	nonzero	1, 7, 5
1	open	zero	4
1	open	nonzero	3[b]
1	closed	zero	3
1	closed	nonzero	3, 5, 8, 9, 5

[a] A wave function is classified here as a nonzero $\phi_{2s}(0)$ type if any matrix element of $\langle f\rangle$ is of this type.
[b] Although the projected value of $\langle f\rangle$ may be considered as a two-determinant representation, it is simpler to compare it to single-determinant results.

(which will be discussed) inherent in the one- and two-determinant approximations.

Two-Determinant Functions

By reference to Table II we note that the poorest values and the best value of $\langle f\rangle$ have been obtained with two-determinant approximations. The 35-term configuration-interaction function of Martin and Weiss[1] is part of the 45-term function discussed earlier. It is apparently quite important to include nonzero $\phi_{2s}(0)$ terms, not included in the 35-term function, in two-determinant functions. This surmise is further substantiated by the 41-term function by the same authors yielding a significant improvement in $\langle f\rangle$ by the inclusion of nonzero $\phi_{2s}(0)$ terms. It is also in agreement with the results of Hurst, *et al.*[2] who used Slater-type orbitals for which $\phi_{2s}(0)=0$. Furthermore, it will be noted that both the 35-term configuration-interaction function[1] and the Slater-type-orbitals[2] function yield values of $\langle f\rangle$ greater than the experiment. As a matter of fact, all open-shell calculations of $\langle f\rangle$ for which $\phi_{2s}(0)=0$ yield values greater than experimental values and this fact will prove to be quite significant in discussions of core polarization.

An interesting comparison exists between the results of Hurst *et al.*,[2] and Kerwin and Burke.[6] Both wave functions are identical in every respect except that the latter is three-determinant, i.e., uses A_1 and A_2 variational parameters of Eq. (4). In this case then it is certainly important to keep the A_2 parameter. The difficulty is apparently surmounted by the wave function of Ritter *et al.*[7] This wave function differs from the former two only in the valence-orbital representation which is nonzero at the nucleus. The apparent effect is to reduce the significance of the A_1A_2 term in $\langle f\rangle$. This can be seen from Eq. (9) if we regard the four terms there as $1s$, $1's$, $1s$–$2s$, and $1's$–$2s$ contributions. Note that in going from a zero to a nonzero $\phi_{2s}(0)$ the $1s$ contribution increases (if we include $1s$–$2s$ in the $1s$ contribution) while the difference in $1s$ and $1's$ contributions become smaller and from the results of Ritter *et al.*[7] becomes very small. The two-determinant function of Berggren and Wood[5] will be discussed in conjunction with single-determinant functions.

ONE-DETERMINANT FUNCTIONS

Before comparing the single-determinant results in detail we should examine the analytic form of $\langle f\rangle$ in a single-determinant representation. Thus

$$\langle f\rangle=4\pi\left[U_{1s}^2(0)-U_{1's}^2(0)+\frac{U_{1s,2s}^2(0)}{1-S_{1s,2s}^2}\right]. \tag{10}$$

It is interesting and informative to apply this to simple Slater-type orbitals with

$$U_{1s}(r)=(a^3/\pi)^{1/2}e^{-ar},$$

$$U_{1's}(r)=(b^3/\pi)^{1/2}e^{-br}, \quad\text{and}\quad U_{2s}(r)=(c^5/3\pi)^{1/2}re^{-cr}.$$

Let us assume, unless disproven, that $a\sim b$ so that $a=d+\Delta$ and $b=d-\Delta$ with $\Delta\ll1$. With this assumption the third term in the square bracket of Eq. (10) should remain practically unaltered in going from a closed-shell to an open-shell representation and thus the first two terms represent the core contribution, $\langle f\rangle_{\text{core}}$. Hence, using the Slater-type orbitals we find

$$\langle f\rangle_{\text{core}}\sim4[(d+\Delta)^3-(d-\Delta)^3]\sim24d^2\Delta. \tag{11}$$

Let us allow the best possible value of $\langle f\rangle_{\text{core}}$, i.e., let it be the difference between the experimental value (see Table I) and the value calculated with closed-shell Slater-type orbitals.[2] One finds $\Delta\sim0.0005$ which satisfies the condition $\Delta\ll1$. It is well known[15] that the energy value varies in the fifth decimal place with a variation of Δ in the fourth decimal place so that this value of Δ gives an energy which is practically unchanged, but a value of $\langle f\rangle$ equal to the experimental value! One cannot argue that this value of Δ will greatly affect the contribution of the $2s$ electron since the third term in the square bracket of Eq. (10) is virtually unaffected and, by the converse of the conclusion drawn by James and Coolidge,[16] one does not expect a great effect on the valence orbitals representation due to an improvement of the core representation. This effect is not inconsistent with the closed-[2] and open-shell[4] Slater-orbitals results for which the energies are -7.41792 and -7.41795, respectively, with associated values of $\langle f\rangle$ of 2.093 and 3.233. The latter value of $\langle f\rangle$ deviates from the experimental value since one cannot expect the variationally determined Δ to be the same as that required for $\langle f\rangle$. Similarly the closed- and open-shell Hartree-Fock results[3] yield respective energy values of -7.43273 and -7.43275 with respective $\langle f\rangle$ values of 2.095 and 2.825 (as compared to the experimental value of 2.906).

Therefore, the defect in single-determinant, open-shell configurations is that the shells are hardly open at all. Thus errors which occur in lithium calculations can be expected to multiply many times over in hfs calculations for atoms involving many more electrons. Although wave-function parameters could be properly adjusted to account for hfs they would probably not be useful for the description of other physical phenomena. An example would be the antiferromagnetic effect.[17] This effect can supposedly be explained by an improved representation of the exchange-integral representation on account of the slight change in the core orbitals. On account of this it is also difficult to rationalize the

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[15] E. A. Burke, Ph.D. thesis, Fordham University, 1959 (unpublished).

[16] H. M. James and A. S. Coolidge, Phys. Rev. 49, 688 (1936).

[17] J. C. Slater, Phys. Rev. 81, 385 (1951).

title "exchange polarization effect" associated with the UHF formulation.

It has been shown[3] and discussed[18] that attempts to remedy the defects in the wave function with projection operators[19] fails, and only serves to emphasize the inadequate representation afforded by single-determinant, open-shell configurations. As a further indication of the relative ease of parameter adjustment required to give a value of $\langle f\rangle$ close to experiment is the six-term configuration-interaction wavefunction used by Nesbet.[9] For despite the fact that closed-shell orbitals were used the $2s$ orbitals were predominantly of the nonzero $\phi_{2s}(0)$ type producing one of the best values of $\langle f\rangle$ calculated so far.

The wavefunctions which have not yet been considered are all of the James and Coolidge[16] type involving the explicit use of interelectronic, r_{ij}, coordinates. From Table I we see that the addition of core-valence terms to a correlated core for a single-determinant approximation[5] produces a significant improvement in the calculation of hfs. As expected then, well-correlated wave functions are quite important in hyperfine structure calculations.[20] The f values calculated with the correlated core and core-valence, closed-shell functions of Burke[8] and of Berggren and Wood[5] are inconsistent with their energy values. This is not too surprising since the energy is known to be a rather crude measure of goodness. Also these wave functions, though similar, differ in some respects. That calculated by the present writer[8] used noninteger exponents throughout and the secular equation was solvable to the tenth order only. To that order the $\langle f\rangle$ values are the same as those of Berggren and Wood.[5]

Perhaps the most interesting comparison is that between the two best values of Berggren and Wood. Both of these use interelectronic separation coordinates between all orbitals but the former is a closed-shell (hence proper eigenfunction of $\mathbf{S}^2$) calculation while the latter is a two-determinant approximation to an open-shell calculation. From the previous discussion we saw that the calculations of Ritter *et al.*[7] indicate that the A_1A_2 term in Eq. (7) is negligible in a two determinant approximation when the $2s$ orbital is nonvanishing at the nucleus. Hence here we need only regard the A_1^2 terms of Eq. (7) from which it will be observed that in going from an open- to a closed-shell representation only three terms do not cancel. These terms are

$$U_{2s,1s}^2(0)+U_{2s,1's}^2(0)+2U_{2s,1s}(0)U_{2s,1's}(0)S_{1s,1's}^2.$$

In a closed-shell representation these terms combine into $4U_{2s,1s}^2(0)$. It will be observed that the core orbital contributions enter in the same way, i.e., there is no $1s$, $1's$ asymmetry here. On the assumption of only a slight effect on the valence orbital due to a splitting of the core orbitals and since the three noncancelling terms represent core contribution symmetrically, these terms should practically equal the closed-shell contribution. A calculation on the relatively simple wave function of Kerwin and Burke[6] substantiated the hypothesis in that case. Thus the remaining A_1^2 terms of Eq. (7) must nearly cancel. Hence if there is to be any core polarization by the $2s$ electron the remaining terms must lessen the valence electrons contribution to $\langle f\rangle$. The $2s$ electron contributes to $\langle f\rangle$ in the terms

$$-2U_{1s}(0)U_{2s,1's}(0)S_{1s,1's}(S_{2s,1's}-S_{1s,1's}S_{2s,1s})$$
$$-2U_{1's}(0)U_{2s,1s}(0)S_{1s,1's}(S_{2s,1s}-S_{1s,1's}S_{2s,1's}).$$

In order to facilitate the investigation consider the following equalities:

$$S_{1s,1's}=1-\delta_1,\quad S_{2s,1s}=S-\delta_2,\quad \text{and}\quad S_{2s,1's}=S+\delta_2.$$

Now δ_1 and δ_2 are at least of the same order so for simplicity let $\delta_1=\delta_2=\delta$. Let us ignore powers of δ higher than unity and let us drop the orthogonal orbitals. Then all that remains is

$$\{4S^2\delta U_{1s}(0)U_{1's}(0)\}$$
$$-\{2\delta U_{2s}(0)[(2+S)U_{1s}(0)-(2-S)U_{1's}(0)]\}.$$

Each of the curly brackets is positive since $S<1$, and with this wave function $U_{1s}(0)>U_{1's}(0)$. We are unable to say definitely that the difference in the curly brackets is negative and thus are unable to say whether an open-shell representation reduces the contribution to $\langle f\rangle$ so that the core contribution is not negligibly small. If the latter statement were true of course we would be able to state that core polarization does indeed contribute to hfs. One might speculate, however, that since the second of the curly brackets is the only term of those added to an open-shell representation which contains $\phi_{2s}(0)$ terms, there is some lowering of the valence-orbitals contribution to $\langle f\rangle$ due to the minus sign in front of the curly bracket and therefore a core polarization effect.

In what has preceded we were unable to state whether or not the $2s$ electron (or for that matter any unpaired s electron) can polarize the core electrons. It is perhaps unnecessary, in any case, to know the precise mechanism when the valence electron is an s electron. It would be more meaningful to be able to state that core polarization is produced by a non-s electron for here hyperfine fields are experimentally observed[21] which cannot be attributed to the valence electron alone. Reconsider Eq. (7). Let the unpaired electron be in an n, l state with $n\neq 1$ and $l\neq 0$. The terms $U_{nl,1's}^2(0)+U_{nl,1s}^2(0)+U_{nl,1's}(0)\,U_{nl,1s}(0)S_{1s,1's}$ should remain relatively unchanged in going from a closed- to an open-shell representation on account of the symmetric manner in which the core electrons contribute. The remaining terms of Eq. (7) will be the same for the general n, l case, except

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[19] P. O. Lowdin, Phys. Rev. **97**, 1509 (1955).

[20] G. G. Hall, Rept. Progr. Phys. 22, 1 (1959).

[21] An excellent bibliography of experimental results may be found in Ref. 19.

that the term $2\delta U_{n,l}(0)[(2+S)U_{1s}(0)-(2-S)U_{1's}(0)]$ will no longer be included since $U_{nl}(0)=0$ for the n, l assumed here. Since the terms introduced in an open-shell representation are apparently negligible for a $2s$ valence electron, then with the exclusion of the $U_{n,l}(0)$ term we might expect a measureable change in the value of $\langle f\rangle$ from those terms arising from an open-shell representation or a core polarization for a non-s unpaired electron. To further substantiate the hypothesis compare the wave functions of Ritter *et al.*,[7] and Hurst *et al.*[2] The difference between the two is in the $2s$ representation. The $2s$ orbital employed by Hurst *et al.* is zero at the nucleus and to that extent resembles a non-s electron. By reference to Table I we see that the calculated value of $\langle f\rangle$ is quite different for these two functions which can be likened to core polarization by a non-s electron. Of renewed interest now is the comparison of the wave functions employed by Kerwin and Burke[6] with those of Hurst *et al.*[2] When the polarizing electron is not an s electron, or equivalently, when the $2s$ orbital vanishes at the nucleus, it is necessary to include the A_1A_2 term of Eq. (7), for from Table I we see that $\langle f\rangle$ as calculated by Kerwin and Burke[6] is much closer to the experimental value than that calculated in Ref. 2.

SUMMARY AND CONCLUSIONS

In the calculation of hyperfine structure for the case for which the unpaired electron is an s electron, well-correlated, closed-shell wave functions which contain many terms for which the valence electron's orbital is nonvanishing at the nucleus serve very well. Thus, configuration-interaction wave functions which contain many such closed-shell configurations for which $\phi_{2s}(0)=0$ cannot be expected to yield significantly good values of $\langle f\rangle$. Similarly, restricted-Hartree-Fock (RHF) functions which do not contain very much correlation will also fail to yield a significantly good value of $\langle f\rangle$.

Single-determinant open-shell representations are fortuitously good for calculations of the Fermi contact term in hyperfine structure. Fortuitous because the "shells" are hardly "open" at all so that applications to other physical situations will be no better than closed-shell wave functions. Since it already is a task to calculate wave functions for many-electron atoms it would seem far preferable to have functions which are more generally useful. Furthermore it is predicted that errors inherent in a single-determinant approximation for three electrons will multiply many times over in passing to calculations involving many electron atoms.

A two-determinant, open-shell wave function for which $\phi_{2s}(0)$ is not zero gives a reasonably good result for hfs when the unpaired electron is in an s state and the calculation is significantly improved with well-correlated wave functions. However, if the unpaired electron is not in an s state, then the two-determinant approximation is no longer useful in the computation of the contact term.

Thus it seems that an exact eigenfunction of $\mathbf{S}^2$, viz., a three-determinant wave function is required for hfs calculations. However, an examination of the approximation of $\langle f\rangle$ in Eqs. (7), (8), and (9) shows that none of the terms of the determinant arising from $A_pU_{1s}\alpha U_{1's}\alpha U_{2s}\beta$ of Eq. (4) enters into $\langle f\rangle$ when the $2s$ orbital vanishes at the nucleus. Hence this determinant may be dropped when the unpaired electron is not an s electron. For a many-electron atom one could then write

$$\phi=A_p\{B_1[\prod_i U_{n(i)l(i)}\alpha U_{n'(i)l(i)}\beta]U_{N,L}\alpha + B_2[U_{N,L}\alpha \prod_i U_{n(i)l(i)}\beta U_{n'(i)l(i)}\alpha]\}, \quad (12)$$

where there is a single unpaired electron with principal and orbital angular momentum quantum numbers of N and L. Note that all determinants which would allow identical spin for orbits which differ only in the n, n' quantum numbers are not included. This approximation proved valid for lithium provided that all s orbitals had nonvanishing contributions at the nucleus.

Equation (12) may be considered as a revised base for unrestricted Hartree-Fock (UHF) calculations since it is the Hartree-Fock method and particularly the analytic approximations[22] to the method which are more generally useful. For the case of $L=0$ in Eq. (12) let $B_1=-B_2$; otherwise there is no simple relation between the two parameters. As a test of the hypothesis it is proposed that a UHF calculation, based on Eq. (12), of lithium be performed. It is not expected that the value of $\langle f\rangle$ will improve greatly but that the energy will be significantly improved indicating, in general, a better representation of the system. Also it is proposed that improved (i.e., similar to functions of Ritter *et al.*[7]) Slater-type functions be used in conjunction with Eq. (12) on the ground state of the boron atom, with its p electron polarizing the core s electrons. This latter test will also enable us to ascertain the validity of the two-determinant approximation of Eq. (12).

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[22] C. A. Coulson, Proc. Cambridge Phil. Soc. **34**, 204 (1938); C. C. J. Roothan, Rev. Mod. Phys. **23**, 69 (1951); and R. K. Nesbet, Rev. Mod. Phys. (to be published).