then we proceed as in (ii) except that we know that $O_{ii}\Phi'=0$ for any Φ' with the same orbital more than twice.

This is all quite easy to visualize in Hilbert space; since R must leave all scalar products invariant, the vectors must all move together under R, but since $G_i\Phi\chi$ is transformed essentially into itself, we can at most allow rotations within the space spanned by these vectors. Thus, the set of GI orbitals in Φ form a basis for a reducible representation of $\mathcal{G}$. The reason that we cannot completely reduce this representation is that the GI orbitals are not all eigenfunctions of the same one-electron Hamiltonian (as in the Hartree-Fock method).

Magnetic Hyperfine Structure of Lithium

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(Received 19 October 1966)

For the first time a spin-polarized extended Hartree-Fock calculation on a three-electron system, Li, is reported. The calculations are discussed with primary emphasis on the hyperfine splitting spectrum which is determined by the spin density at the nucleus, $Q(0) = \langle \psi | \sum_i \hat{s}_z(i) \delta(r_i) | \psi \rangle / S$. We calculate $Q(0)$ for the ground state to be 0.2403, as compared with the experimental value of 0.2313.

INTRODUCTION

THERE has been a great deal of interest in constructing electronic wave functions for atoms accurate enough to predict the effective magnetic field at the nucleus due to the electrons.[1-4] The difficulty has been in obtaining accurate values for the part of the field due to the Fermi contact term[1-4]

$$H_c = (8\pi/3)g\mu_0 Q(0)\mathbf{S},$$

where

$$Q(0) = \langle \psi | \sum_i \hat{s}_z(i) \delta(r_i) | \psi \rangle / S \qquad (1)$$

is called the spin-density at the nucleus. For example, for the ground states of N and Mn^{++} the Hartree-Fock wave function leads to $H_c=0$ in flagrant disagreement with experiment.[3,5] Similarly, the large negative magnetic fields at the nuclei of some transition-metal atoms, as observed by Mössbauer experiments on metals, are inconsistent with the predictons using Hartree-Fock wave functions.[1,2]

Probably the most widely used method to improve upon the Hartree-Fock method for this property has been the unrestricted Hartree-Fock (UHF) method.[4,6-9]

This method has had some success[8] but does not seem to account for the H_c in B^{10}, N^{11}, O^{10}, F^{12}, P^{13}, or in the transition element atoms in metals.[2] In the UHF method the wave function is approximated by a single Slater determinant, as in the Hartree-Fock method, but we now allow different orbitals for the different spins. Since the inner-shell or core states are not exactly spin paired, they can contribute to the spin density at the nucleus, $Q(0)$. A glaring flaw in this approach[3,7,10-15] is that the UHF wave function is not an eigenfunction of S^2. One could, of course, project out from the UHF wave function the components of incorrect multiplicity, but although the UHF orbitals are optimum for the Slater determinant, they will not be optimum for the projected wave function.[15]

It has long been known that the proper solution is to optimize the orbitals *after* the projection rather than *before*.[1,3,11,15,16] Unfortunately, this procedure, the spin-

[1] A. J. Freeman and R. E. Watson, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. IIA, p. 167.

[2] V. Heine, Phys. Rev. **107**, 1002 (1957); D. A. Goodings and V. Heine, Phys. Rev. Letters **5**, 370 (1960); A. J. Freeman and R. E. Watson, *ibid.* **5**, 498 (1960); R. E. Watson and A. J. Freeman, J. Appl. Phys. Suppl. **32**, 118S (1961); Phys. Rev. **123**, 2017 (1961).

[3] S. M. Blinder, Advan. Quant. Chem. **2**, 47 (1965).

[4] D. A. Goodings, Phys. Rev. **123**, 1706 (1961).

[5] L. W. Anderson, F. M. Pipkin, and J. C. Baird, Phys. Rev. **116**, 87 (1959).

[6] J. A. Pople and R. K. Nesbet, J. Chem. Phys. **22**, 571 (1954); J. C. Slater, Phys. Rev. **82**, 538 (1951); R. K. Nesbet, Proc. Roy. Soc. (London) A230, 312 (1955); A. T. Amos and G. G. Hall, *ibid.* A263, 483 (1961); R. E. Watson and A. J. Freeman, Phys. Rev. **120**, 1125 (1960); R. K. Nesbet, Rev. Mod. Phys. **33**, 28 (1961); R. K. Nesbet and R. E. Watson, Ann. Phys. (N.Y.) **9**, 260 (1960).

[7] G. W. Pratt, Phys. Rev. **102**, 1303 (1956).

[8] L. M. Sachs, Phys. Rev. **117**, 1504 (1960).

[9] This method is often referred to as the spin-polarized Hartree-Fock (SPHF) method.

[10] N. Bessis, H. Lefebvre-Brion, and C. M. Moser, Phys. Rev. **128**, 213 (1962).

[11] N. Bessis, H. Lefebvre-Brion, and C. M. Moser, Phys. Rev. **124**, 1124 (1961).

[12] N. Bessis, H. Lefebvre-Brion, and C. M. Moser, Phys. Rev. **130**, 1441 (1963).

[13] N. Bessis, H. Lefebvre-Brion, C. M. Moser, A. J. Freeman, R. K. Nesbet, and R. E. Watson, Phys. Rev. **135**, A588 (1964).

[14] W. Marshall, Proc. Phys. Soc. (London) **78**, 113 (1961); J. Phys. Soc. Japan **17**, Suppl. B-I20 (1962).

[15] P.-O. Löwdin, Advan. Chem. Phys. **2**, 207 (1959).

[16] P.-O. Löwdin, Phys. Rev. **97**, 1509 (1955).

polarized extended Hartree-Fock method,[1,3,15-17] has been too difficult to actually carry out in the past—even for the case of Li.[1,3,10,11,15,18] This difficulty has been overcome by the GF method,[19,20] which yields wave functions equivalent to those which would be obtained by the spin-polarized extended Hartree-Fock method. The essence of this method is sketched below.

Since most of the past calculations comparing the efficacy of the various methods for predicting H_c have been for the lithium atom, we will present the results from some GF calculations for this atom and compare them with some of the past results. We find that the GF wave function for Li does indeed yield a good value for $Q(0)$.

THE METHOD AND CALCULATIONS ON Li

The Hartree-Fock and UHF wave functions can be written as $\mathcal{Q}\Phi\chi$, where Φ is a product of orbitals (one-electron spatial functions), χ is a product of one-electron spin functions, $\mathcal{Q}$ is the antisymmetrizer, $\sum_\tau \zeta_\tau \tau$, and ζ_τ is the parity of the permutation τ. The GF wave function is written as $G_f\Phi\chi$, where Φ and χ are again products of orbitals and spin functions, respectively, and G_f is an operator involving permutations on spatial and spin coordinates (see Refs. 19 and 20 for detailed discussions of this operator). The G_f operator has the property that $G_f\Phi\chi$ satisfies Pauli's principle (the $\mathcal{Q}$ ensures this property for the UHF wave function) and is an eigenfunction of $\hat{S}^2$ (not generally possible for the UHF wave function). In the UHF method the orbitals in Φ are required to be the best possible ones, i.e., the energy must be stationary with respect to variations in these orbitals. In the same way in the GF method we require that the orbitals in Φ be the best possible ones. In both cases we obtain a set of pseudo-eigenvalue equations for the best orbitals and thus an independent-particle scheme.

In the case of Li,

$$\Phi = \phi_{1a}(1)\phi_{2a}(2)\phi_{1b}(3) \quad \text{and} \quad \chi = \alpha(1)\alpha(2)\beta(3), \quad (2)$$

where ϕ_{1a} and ϕ_{2a} are orthogonal. The GF function can be expanded in terms of Slater determinants as

$$G_f\Phi\chi = (2/3)[2\,\mathcal{Q}\phi_{1a}\phi_{2a}\phi_{1b}\alpha\alpha\beta$$
$$+ \mathcal{Q}\phi_{1a}\phi_{1b}\phi_{2a}\alpha\alpha\beta + \mathcal{Q}\phi_{1b}\phi_{2a}\phi_{1a}\alpha\alpha\beta],$$

but we must emphasize that we do not use this expanded form to derive the equations for the best ϕ_i. The success of the GF method in obtaining equations which can be derived explicitly and solved depends crucially on the form of the G_f operator which allows

[17] Unfortunately the same name, extended Hartree-Fock, is also used for a much different procedure; e.g., see P.-O. Löwdin, Phys. Rev. **97**, 1474 (1955); and G. Das and A. C. Wahl, J.Chem. Phys. **44**, 87 (1966).

[18] P.-O. Löwdin, Rev. Mod. Phys. **35**, 640 (1963).

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[20] W. A. Goddard, preceding paper, Phys. Rev. **157**, 81 (1957).

TABLE I. Expansion coefficients for the lithium atom GF orbitals.[a]

Basis function	ϕ_{1a}	ϕ_{1b}	ϕ_{2a}
$1s(4.5)$	0.02741	−0.00219	−0.038890
$2s(3.95)$	−0.07473	−0.10517	−0.017857
$1s(2.65)$	1.02249	1.07104	−0.089226
$2s(2.05)$	0.03650	0.04883	−0.115170
$1s(0.7)$	−0.00314	−0.00525	0.074766
$2s(0.664)$	0.00169	0.00023	0.994502

[a] The orbital exponents for the basis functions are in parentheses.

many simplifications. These equations are solved in the same way as are the Hartree-Fock equations,[21] i.e., by expanding each unknown orbital in terms of a set of basis functions $\{X_\mu\}$,

$$\phi_i = \sum_\mu X_\mu C_{\mu i},$$

and solving for the $C_{\mu i}$.

We report here a calculation on the ground state (^2S) of Li using six Slater-type basis functions for which all of the orbital exponents have been optimized. The expansion coefficients for the various orbitals are shown in Table I. The amplitudes of the orbitals at the nucleus for the Hartree-Fock,[22] UHF,[8] and GF wave functions are given in Table II. The $2s$ orbital has not changed too much but the splitting in the $1s$ orbitals for the GF function is about $3\frac{1}{2}$ times the splitting for the UHF orbitals. In Table III we show the $Q(0)$ for the various functions. We see that the GF wave function yields a fairly good value for $Q(0)$ as does the UHF wave function in this case. Some other properties of the GF wave functions are discussed in Appendix A.

COMPARISON WITH OTHER CALCULATIONS

There have been several attempts to find ways of approximating the GF or spin-polarized extended Hartree-Fock wave function. This is not so important now since we can carry out the calculations exactly, but is still of interest. Bessis et al.[11] show that to first order the GF method is equivalent to a configuration interaction between the Hartree-Fock wave function and all singly excited configurations. In addition, if certain integrals are neglected, they show that the $Q(0)$ from GF and UHF calculations are the same to first order. From Table III we see that this is approximately true although the difference between $Q(0)_{GF}$ and $Q(0)_{UHF}$

TABLE II. The amplitude at the nucleus for the orbitals of Li.

	HF[a]	UHF[b]	GF
$\phi_{1a}(0)$	2.6129	2.6189	2.6352
$\phi_{1b}(0)$	2.6129	2.6073	2.5932
$\phi_{2a}(0)$	−0.4082	−0.4048	−0.4019

[a] Roothaan, Sachs, and Weiss, Ref. 22.
[b] Sachs, Ref. 8.

[21] C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951).

[22] C. C. J. Roothaan, L. Sachs, and A. W. Weiss, Rev. Mod. Phys. **32**, 186 (1960).

	$Q(0)$	$4\pi Q(0)$	absolute percent error of $Q(0)$	Energy (a.u.)
HF[a]	0.1666	2.094	28.0	−7.432727
UHF[b]	0.2248	2.825	2.8	−7.432751
Proj. UHF[b,c]	0.1866	2.345	19.3	−7.432768
GF	0.2403	3.020	3.9	−7.432813
CI, no r_{ij}[d]	0.2065	2.595	10.7	−7.47710
CI, r_{ij}[e]	0.2249	2.826	2.8	−7.4779
Exper	0.2313[f]	2.906	0.0	−7.4780[g]

[a] Roothaan, Sachs, and Weiss, Ref. 22.
[b] Sachs, Ref. 9.
[c] Proj. UHF is spin-projected UHF.
[d] Weiss, Ref. 23.
[e] Burke, Ref. 24.
[f] P. Kusch and H. Taub, Phys. **75**, 1477 (1949); a conversion factor of 3474.4 was used to convert Mc/sec to atomic units.
[g] Moore, Ref. 28.

is about one-fourth the difference between $Q(0)_{\exp}$ and $Q(0)_{HF}$. Marshall[14] considered first-order perturbations on the Li ^2S state and obtained $Q(0)_{UHF}=0.224$ and $Q(0)_{GF}=0.216$. The UHF result is close but the first-order perturbation yields a rather poor approximation to the $Q(0)_{GF}$; this is another indication[4] that straightforward perturbation schemes may not be useful for $Q(0)$.

Bessis et al.[12] have noted that for a projected determinant the contribution to $Q(0)$ from the orbitals which are spin-paired in the Hartree-Fock wave function is approximately given by $S/(S+1)$ times the contribution these orbitals would make to $Q(0)$ for a single determinant. Since the GF wave function can be written as a spin-projected Slater determinant, we can use this relation and the amplitudes at the nucleus in Table II to approximate $Q(0)_{GF}$. The result is $Q(0)_{GF}\approx0.2347$ which is in fair agreement with the exact result.

So far we have considered only independent-particle wave functions, HF, UHF, and GF. There have also been several configuration interaction (CI) calculations carried out on Li. Weiss[23] has considered configuration interaction wave functions with up to 45 configurations and no r_{ij} coordinates. The best wave function yielded a very good energy but a $Q(0)$ of 0.2065. Burke[24] has used wave functions with interelectronic coordinates r_{12}, r_{13}, and r_{23} and obtained an even better energy and a $Q(0)$ of 0.2249 while Berggren and Wood[25] using the same type of wave function obtained a slightly worse energy, −7.47630, but a better $Q(0)$, 0.2285. A small basis set with nonoptimized orbitals was used by Nesbet[26] for a CI calculation yielding a very good $Q(0)$. This same basis set yields a $Q(0)_{HF}$ which is 0.014 higher than the exact $Q(0)_{HF}$, and Marshall[14] has suggested that the same error in $Q(0)$ may occur for the

TABLE IV. $Q(0)$ and E for Nesbet's basis set.

	$Q(0)$	E (a.u.)
HF[a]	0.1805	−7.431765
CI[a]	0.2284	−7.431849
GF	0.2587	−7.431881

[a] Nesbet, Ref. 26.

other wave functions using this basis set. In fact, Nesbet's value for $Q(0)_{CI}$ is 0.022 higher than that obtained by Weiss[23] with a much more optimized basis set, and the GF calculations with Nesbet's basis set yield a $Q(0)_{GF}$ which is 0.018 higher[27] (see Table IV) than that for the accurate GF wave function which supports Marshall's suggestion that the good value of $Q(0)_{CI}$ is due to the particular nonoptimized basis set which was used.

The calculations using interelectronic coordinates yield good results for Li but such calculations may be extremely difficult for larger atoms. On the other hand, conventional configuration interaction, although yielding good energies, leads to rather poor values of $Q(0)$ for Li. Thus on the basis of calculations on Li, the UHF and GF methods would appear to be the likely candidates for predicting $Q(0)$ for larger atoms. As mentioned above, the UHF method has had some successes and many failures in this regard but does not yield eigenfunctions of S^2. GF calculations have been carried out on several systems including the Li ^2P state and the N ^4S state, and in every case the GF orbitals are split much more than are the UHF orbitals. Thus the values of $Q(0)$ from GF calculations may differ considerably from the UHF values, and there is hope that the GF method can improve upon the fair to poor values of $Q(0)$ obtained by the UHF method for transition metal ions in metals, and for P, B, N, O, and F.

SUMMARY AND CONCLUSION

The spin-polarized extended Hartree-Fock wave function for Li has been determined by the GF method. As expected this leads to a good value of spin density at the nucleus, $Q(0)$; however, the $Q(0)$ differs from the UHF value by more than has been previously suggested. It appears that this method may be useful for studying the magnetic field at the nucleus in large atoms.

APPENDIX

Here we discuss some properties of the GF wave functions for Li as given in Table I. The ratio of potential energy to twice the total energy is 1.000001 which is quite close to the value, 1.0, demanded by the virial theorem. The orbital energies are −2.49872, −2.46385, and −0.196490; thus, we would predict a first ionization

[23] A. W. Weiss, Phys. Rev. **122**, 1826 (1961).
[24] E. A. Burke, Phys. Rev. **130**, 1871 (1963); **135**, A621 (1964).
[25] K. F. Berggren and R. F. Wood, Phys. Rev. **130**, 198 (1963).
[26] R. K. Nesbet, Phys. Rev. **118**, 681 (1960); Quarterly Progress Report, Solid State and Molecular Theory Group, Massachusetts Institute of Technology, 1956, pp. 3, 47 (unpublished).

[27] Note that the GF energy is actually *lower* than the CI energy. This is probably because the CI calculation was by second-order perturbation methods.

energy of 0.1965 which is 0.8% from the correct value of 0.1981.[28] The cusps[29] for the orbitals are -3.0136, -3.0156, and -3.0131 as compared to a value of -3.0 for the exact orbitals.

Now consider a one-electron operator, $F = \sum_i f(i)$, which does not depend on spin coordinates. For a GF wave function the expectation value of F is given by

$$\langle F \rangle = (1/D) \sum_{i,j=1}^{3} \langle \phi_i | f | \phi_j \rangle D_j{}^i , \qquad (A1)$$

where the $D_j{}^i$ form a Hermitian matrix called the spatial density matrix and D is a normalization constant.

For Li these quantities are given by

$$D_{1a}{}^{1a} = 1 + \tfrac{1}{2} | \langle 2a | 1b \rangle |^2 ,$$

$$D_{2a}{}^{1a} = -\tfrac{1}{2} \langle 2a | 1b \rangle \langle 1b | 1a \rangle ,$$

$$D_{1b}{}^{1a} = \tfrac{1}{2} \langle 1b | 1a \rangle ,$$

$$D_{2a}{}^{2a} = 1 + \tfrac{1}{2} | \langle 1a | 1b \rangle |^2 , \qquad (A2)$$

$$D_{1b}{}^{2a} = \tfrac{1}{2} \langle 1b | 2a \rangle ,$$

$$D_{1b}{}^{1b} = 1.0 ,$$

$$D = 1 + \tfrac{1}{2} | \langle 1a | 1b \rangle |^2 + \tfrac{1}{2} | \langle 2a | 1b \rangle |^2 ,$$

where $\langle i | j \rangle$ is the overlap between orbital i and orbital j. For the orbitals in Table I the quantities in (A2) are 1.0000068, -0.0018452597, 0.49994523, 1.4998905,

TABLE V. Expectation values of $\sum_i r_i{}^n$ for Li.[a]

n	$\langle \sum_i r_i{}^n \rangle$
-2	30.21526
-1	5.715620
$+1$	5.015984
$+2$	18.58901
$+4$	562.4982

[a] The GF orbitals in Table I were used.

0.0018454618, 1.0, and 1.4998973, respectively. With these numbers we can evaluate the expectation value for any F if the values for $\langle i | f | j \rangle$ are available. Table V contains the expectation values of $\sum_i r_i{}^n$ for $n = -2$, -1, 1, 2, and 4. These values are within 0.1% of the values given by Hartree-Fock wave functions.[22] For the electron density at the nucleus, $\sum_i \delta(r_i)$, the GF wave function yields 13.830 as compared to a value of 13.827 for the Hartree-Fock wave function.[22] Thus, the GF and Hartree-Fock wave functions agree quite closely for the expectation values of spatial one-electron operators.

Consider a one-electron operator involving spin, $M = \sum_i m(i) \hat{s}_z(i)$, where m depends only on spatial coordinates.

Then for Li

$$\langle M \rangle = \tfrac{1}{2} \langle \sum_i m(i) \rangle - (2/3D) [\tfrac{1}{4} \langle 1a | m | 1a \rangle (1 - \langle 1b | 2a \rangle^2) + \tfrac{1}{4} \langle 2a | m | 2a \rangle (1 - \langle 1b | 1a \rangle^2)$$
$$+ \tfrac{1}{2} \langle 2a | m | 1a \rangle \langle 1a | 1b \rangle \langle 1b | 2a \rangle + \langle 1a | m | 1b \rangle \langle 1b | 1a \rangle + \langle 2a | m | 1b \rangle \langle 1b | 2a \rangle + \langle 1b | m | 1b \rangle]$$
$$= (1/12D) [\langle 1a | m | 1a \rangle (4 + 5 \langle 1b | 2a \rangle^2) + \langle 2a | m | 2a \rangle (4 + 5 \langle 1b | 1a \rangle^2)$$
$$- 10 \langle 2a | m | 1a \rangle \langle 1a | 1b \rangle \langle 1b | 2a \rangle - 2 \langle 1a | m | 1b \rangle \langle 1b | 1a \rangle - 2 \langle 2a | m | 1b \rangle \langle 1b | 2a \rangle - 2 \langle 1b | m | 1b \rangle], \qquad (A3)$$

where D is given in (4) and the orbitals are taken as real. For the orbitals in Table I, $\langle 1b | 1a \rangle = 0.99989046$ and $\langle 1b | 2a \rangle = 0.0036909236$. To find $Q(0)$ we let m be the delta function, and using the above overlaps, (A3), and the values in Table II we find a $Q(0)$ of 0.2403.

[28] *Atomic Energy Levels*, edited by C. E. Moore, Nat. Bur. Std. Circ. No. 467 (U. S. Government Printing and Publishing Office, Washington, D. C., 1949).

[29] The logarithmic derivative of the radial part of the orbital evaluated at the nucleus. For the exact orbital this is $-Z/(l+1)$, where Z is the nuclear charge and l is the orbital-angular-momentum quantum number.