Calculation of Atomic Hyperfine Structure Constants from Projected Unrestricted Hartree-Fock Functions. Constants of F^{19}

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The magnetic hyperfine constants for the $^2P_{3/2}$ and $^2P_{1/2}$ states of F^{19} are calculated from the projected unrestricted Hartree-Fock (UHF) function where the orbitals are linear combinations of analytic functions. Neglecting the nonorthogonality between the radial parts of spin α and spin β functions, the values obtained are (experimental results are given in parentheses): $a' = 2031$ Mc/sec (2010 Mc/sec), $a''' = 522$ Mc/sec (446 Mc/sec), $a'' = 9952$ Mc/sec (10 244 Mc/sec). The contribution coming from the Fermi contact operator calculated from the projected UHF function is in much better agreement with experiment than that calculated either from the UHF or configuration interaction functions.

I. INTRODUCTION

IN previous papers[1] (hereafter called Parts I and II) we have assumed that functions of the type which are generally called extended Hartree-Fock (EHF) should be suitable to calculate atomic hyperfine constants and would give satisfactory qualitative agreement with experiment. Unfortunately, as is well known, the calculation of the orbitals which minimize the energy of a multideterminant function is very difficult and has not yet been carried out except for three-electron systems.[2]

Among the different approximations to the EHF function which we have previously used we shall in this paper concentrate on the one which, from the experience which we have now collected, seems to give by far the best agreement with experiment for the atoms where the "s" orbitals are all doubly filled. This method is generally called "the projected unrestricted Hartree-Fock (PUHF) function." The approximation to the EHF function which is used here consists of using a multideterminant function which has the proper symmetry behavior and assuming that the EHF oribitals can be satisfactorily approximated by the UHF orbitals, that is to say, by those which minimize the single determinant UHF function. In this function the radial functions of orbitals of spin α are different from those of spin β.

For the calculation of the matrix elements of the hyperfine structure operators we have been forced, in view of the complexity of the form of the projected function, to introduce a reasonable approximation. We have assumed that the UHF orbitals satisfy the same normalization and orthogonality conditions as the usual Hartree-Fock orbitals with which the UHF orbitals have two-to-one correspondence.

For F^{19} this method then gives hyperfine constants which are in as good agreement with those observed as those previously calculated for B^{11}, N^{14}, and O^{17}.

II. THE PROJECTED UHF FUNCTIONS

Radford, Hughes, and Beltran-Lopez[3] measured the hyperfine constants a_J and a_J' which are often written as a' and a''' for the ground state $^2P_{3/2}$ of F^{19}. Very recently Harvey[4] has measured the constant for the state $^2P_{1/2}$ (which is ordinarily called the a'' constant).

From the experimental values it is possible to deduce quantities which are independent of J from the following equations:

$$a_{3/2} = (4\beta_n\beta_e/3I)(\langle r^{-3}\rangle - \langle r^{-3}\rangle'/5) + a_s,$$
$$a_{3/2}' = (\beta_n\beta_e/3I)(2\langle r^{-3}\rangle - \langle r^{-3}\rangle') - a_s, \qquad (1)$$
$$a_{1/2} = (8\beta_n\beta_e/3I)(\langle r^{-3}\rangle + \langle r^{-3}\rangle') - a_s.$$

The quantities $\langle r^{-3}\rangle$ and $\langle r^{-3}\rangle'$ are proportional to reduced matrix elements of operators which describe the interaction of the nuclear magnetic moment with the magnetic field associated, respectively, with the orbital and spin magnetic moments of the electrons. The quantity a_s is the contribution from the Fermi contact operator. These terms have been defined from the ground-state function; for F^{19} it is $^2P_{3/2}$ (cf. Part II).

Previously (in Part II), we have defined two different types of EHF functions: (a) the orbitals with the same values of n and l have the same radial parts for given spin; (b) the radial parts are different not only for different m_s but also for different values of m_l. Thus, in functions of type (b) in F^{19} one might expect to have five different radial parts for the $2p$ function. But even the best UHF approximation to the EHF function of type (b) cannot have five different radial parts for the $2p$ function because of certain equalities between exchange integrals. One finds, in fact, that $2p_+$ and $2p_-$ functions of α spin are solutions of the same equations. The UHF function for the $^2P_{3/2}$ state of F is

$$\psi_{\text{UHF}} = |1s\uparrow 1\bar{s}\downarrow 2s\uparrow 2\bar{s}\downarrow 2p_+\uparrow 2\bar{p}_+\uparrow 2p_0'\uparrow 2\bar{p}_0'\downarrow 2p_-\uparrow|, \quad (2)$$

where the primed orbitals are solutions of equations which are different from the equations which give the unprimed orbitals.

[1] N. Bessis, H. Lefebvre-Brion, and C. M. Moser, Phys. Rev. **124**, 1124 (1961); **128**, 213 (1962).

[2] A few calculations have been carried out on a limited basis for Li: (a) J. Kerwin and E. A. Burke, J. Chem. Phys. **36**, 2987 (1962); (b) E. Ishiguro, Y. Mizuno, and K. Kayama, in Meeting on Recent Developments in Quantum Chemistry, Hakone National Park, Japan, September 1962 (unpublished).

[3] H. E. Radford, V. W. Hughes, and V. Beltran-Lopez, Phys. Rev. **123**, 153 (1961).

[4] S. Harvey (private communication).

TABLE I. Magnetic hyperfine constants for ^2P states of F^{19} (Mc/sec).

Method[a]	$a_{3/2}$	$a_{3/2}'$	$a_{1/2}$	a_s	$\frac{4}{3}(\beta_n\beta_e/I)\langle r^{-3}\rangle$	$\frac{4}{3}(\beta_n\beta_e/I)\langle r^{-3}\rangle'$	E(a.u.)
Hartree-Fock	2030	$+634$	10 148	0	2537	2537	-99.4075
UHF	2194	$+394$	9643	221	2466	2466	-99.4090
PUHF	2031	$+522$	9952	74	2466	2547	$\cdots$
Exp.	2010.01 ± 0.02	$+446\pm10$	10 244	101[b]	2453[b]	2719[b]	-99.804

[a] Analytic basis functions are for s: $Z=8.76$, 2.13; for p: $Z_{2p}=0.7863$, 1.752, 3.068, 5.954; $Z_{3p}=4.17$. The numerical constant $2\beta_n\beta_e/I=501.6\ a_0^3$.
[b] These values are obtained with an error of about 5 Mc/sec.

In point of fact, the orbitals which minimize the energy of this determinant are only slightly different from those found from minimizing the energy of the usual UHF function where only the distinction between the radial parts of orbitals of α and β spin is introduced, which comes down in (2) to putting $2p\uparrow=2p'\uparrow$ and $2p\downarrow=2p'\downarrow$. In addition, as the constants found from the projection with respect to S^2 of this UHF function are only very slightly different from those found from the projection with respect to both S^2 and L^2 of function (2), we only give the former in Table I. We should, however, emphasize that it would be most unwise to assume a similar situation would hold with the orbitals which would minimize the EHF function.

The UHF orbitals are obtained as linear combinations of analytic functions from a program written by Nesbet and Watson. The "s" orbitals, as we have proposed in Part I, are linear combinations of two series of functions $1s$, $2s$, and $3s$ using two different values of Z for each of the three functions. The values of Z are found by minimization of the energy. The basis set for the "p" orbitals is the analytic fit given by Allen.[5]

The analytic method for calculating the orbitals appears to be somewhat more convenient than the numerical method for finding the UHF functions given by Goodings.[6] The orbitals obtained from our analytic functions appear to be very similar to those obtained numerically. In Table II we illustrate this point for the value of s orbitals at the nucleus. The contributions ρ_{2s} and ρ_{1s} to the constant a_s due to the polarization of the $2s$ and $1s$ orbitals

$$\rho_{ns}=|\varphi_{ns}\uparrow(0)|^2-|\varphi_{ns}\downarrow(0)|^2$$

are given for B^{11}, N^{14}, and F^{19} both from analytic and numerical functions in Table II. The contributions to the constants coming from the "p" orbitals are equally very close.

III. CALCULATIONS

This UHF function has the advantage of being an eigenfunction of L^2 if not of S^2. The projection operator associated with S^2 applied to this function gives a linear combination of 108 determinants which can most simply be found by generalizing a method given by Löwdin[7]

$$\psi_{PUHF}=\Omega\psi_{UHF}=\Omega T_0$$

$$=\frac{1}{30}(10T_0-2T_1+T_2-T_3+2T_4). \quad (3)$$

Here T_k designates the sum of determinants found by permuting in T_0 k functions α and β.

As these determinants are built on nonorthogonal orbitals the calculation of matrix elements of even single electron operators from (3) is, to say the least, extremely tedious. In order to make this calculation tractable we have made the following approximation for the overlap integrals:

$$\langle\varphi_i\uparrow\varphi_j\downarrow\rangle=\delta_{ij}.$$

This approximation can be readily justified. For the calculation of F we find

$$\langle 2p\uparrow 2p\downarrow\rangle\approx0.9985,$$

$$\langle 1s\uparrow 2s\downarrow\rangle=-\langle 1s\downarrow 2s\uparrow\rangle\approx0.0025.$$

This approximation leads to the following for the matrix element of a single electron operator

$$\langle\varphi_i\uparrow||\varphi_i\downarrow\rangle=\frac{1}{2}[\langle\varphi_i\uparrow||\varphi_i\uparrow\rangle+\langle\varphi_i\downarrow||\varphi_i\downarrow\rangle].$$

The approximations which we have used in Part II are equivalent to these.

One then finds the following simple relation[8]:

$$(a_s)_{PUHF}=\frac{S}{S+1}\frac{16\pi}{3}\frac{\beta_N\beta_e}{IJ}\frac{1}{2}(\rho_{2s}+\rho_{1s})=\frac{S}{S+1}(a_s)_{UHF}. \quad (4)$$

TABLE II. Core polarization results from UHF calculations (atomic units).

	Boron[a]		Nitrogen[b]		Fluorine	
	Our analytic functions	Numerical functions	Our anaytic functions	Numerical functions	Our analytic functions	Numerical functions
ρ_{2s}	0.1054	0.1085	0.9392	0.9301	0.6469	0.6411
ρ_{1s}	-0.0947	-0.0913	-0.7156	-0.7418	-0.4894	-0.5076

[a] Cf. Part II.
[b] The basis orbitals (which are slightly better than those of Part I) are s: $Z=6.9$, 1.6; p (Clementi): $Z_{2p}=0.952$, 1.2264, 1.9087, 3.8675.

[5] L. C. Allen, J. Chem. Phys. 34, 1156 (1961).
[6] D. A. Goodings, Phys. Rev. 123, 1706 (1961).
[7] P. O. Löwdin, Phys. Rev. 97, 1509 (1955).
[8] This approximation for the contribution due to the core polarization also holds for the case where the s orbitals are not all doubly filled (reference 10). Thus, for the ^2S state of Li the approximation for the constant as given by Eq. (4) is 320 Mc/sec while the rigorous projection of the function gives $a_s=\Delta E/2=323.73$ Mc/sec. [The value given in Phys. Rev. 117, 1504 (1960) is in error (private communication from Dr. Sachs).]

For fluorine

$$\langle r^{-3}\rangle_{\text{PUHF}}=\langle 2p\!\downarrow|r^{-3}|2p\!\downarrow\rangle=\langle r^{-3}\rangle_{\text{UHF}}=\langle r^{-3}\rangle'_{\text{UHF}},$$
$$\langle r^{-3}\rangle'_{\text{PUHF}}=\tfrac{1}{3}[\langle 2p\!\downarrow|r^{-3}|2p\!\downarrow\rangle+2\langle 2p\!\uparrow|r^{-3}|2p\!\uparrow\rangle].\quad(5)$$

We wish to recall (cf. Part II) that it is difficult to define the quantities $\langle r^{-3}\rangle$ and $\langle r^{-3}\rangle'$ for the UHF function which is not an eigenfunction of S^2. We have assumed here that Eqs. (1) which determine the hyperfine constants as a function of the terms $\langle r^{-3}\rangle$ and $\langle r^{-3}\rangle'$ are still valid, and we have calculated $\langle r^{-3}\rangle_{\text{UHF}}$ and $\langle r^{-3}\rangle'_{\text{UHF}}$ from the UHF function for the $^3P_{3/2}$ state which is unambiguously defined [Eq. (2)].[9]

IV. CONCLUSIONS

We give in Table III a recapitulation of the results obtained from using this method for other atoms of the second period for the calculation of a_s and in Table IV the results for the ratio $\langle r^{-3}\rangle'/\langle r^{-3}\rangle$. We should recall

TABLE III. Contact term from different methods (Mc/sec).

a_s	B^{11}	N^{14}	O^{17}	F^{19}
UHF	5.1	24	−34	221
PUHF	1.7	14	−17	74
Exp.	0.11	10.45	−18	101

that in the usual Hartree-Fock function a_s would be zero and the ratio $\langle r^{-3}\rangle'/\langle r^{-3}\rangle$ would be equal to one. In general, we feel the qualitative agreement between theory and experiment is satisfactory and much better than is found from the UHF functions themselves.

Our conclusion may appear to be in disagreement with those of several other authors. Marshall,[10] for

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[9] Our attention has been called to the fact that one would obtain other expressions for the terms $\langle r^{-3}\rangle_{\text{UHF}}$ and $\langle r^{-3}\rangle_{\text{UHF}}'$ from the equations of Goodings (reference 6) for $a_{3/2}$ and $a_{1/2}$. These are

$$\langle r^{-3}\rangle_{\text{UHF}}=9/10\langle 2p\!\downarrow|r^{-3}|2p\!\downarrow\rangle+1/10\langle 2p\!\uparrow|r^{-3}|2p\!\uparrow\rangle,$$
$$\langle r^{-3}\rangle_{\text{UHF}}'=1/2\langle 2p\!\downarrow|r^{-3}|2p\!\downarrow\rangle+1/2\langle 2p\!\uparrow|r^{-3}|2p\!\uparrow\rangle.$$

From these one finds: $a_{3/2}=2194$ Mc/sec, $a_{3/2}'=386$ Mc/sec, $a_{1/2}=9788$ Mc/sec. The difference between these formulas and Eq. (5) is that, while of course there is no difficulty for the constant $a_{3/2}$, Goodings has defined a function for the state $J=1/2$ and, as we have mentioned above, this seems to us to be a questionable procedure.

[10] W. Marshall, Proc. Phys. Soc. (London) **78**, 113 (1961).

TABLE IV. Results for $\langle r^{-3}\rangle'/\langle r^{-3}\rangle$.

$\langle r^{-3}\rangle'/\langle r^{-3}\rangle$	O^{17}	F^{19}
PUHF	1.05	1.03
Exp.	1.13	1.108

example, argues that the value obtained for the constant a_s with the UHF function should be better than that obtained with the projected UHF function because it is nearly equal to the constant that would be obtained from the EHF function. But one should not forget, as we have also shown in Part I, that this demonstration only holds to first order, that is the equivalence will no longer exist for calculations carried out with the orbitals obtained after the first iteration. The equivalence no longer holds when higher order terms are included, that is when the iterations have converged. It appears that for the atoms where the unpaired electron is s-like, there is a fortuitous cancellation of errors. In the atoms where the s orbitals are all doubly occupied, the UHF function gives very poor results both for a_s, which is too large, and for the ratio $\langle r^{-3}\rangle'/\langle r^{-3}\rangle$ which remains equal to one (cf. Table III).

Finally, we should note that the CI (configuration interaction) method given in Part I and II gives very poor results for fluorine ($a_s=-11$ Mc/sec; $\langle r^{-3}\rangle'/\langle r^{-3}\rangle=1.06$[11]). The projected UHF method, thus, seems to be a definite improvement over the usual methods. Of course, we should like to find a better agreement for $\langle r^{-3}\rangle'$. An improvement might be to use a better approximation to the EHF orbitals than those given by the UHF orbitals.

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[11] For further details see N. Bessis, Cahiers de Phys. **16**, 345 (1962).