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Calculation of the Hyperfine Constants for B^{11} and O^{17}†

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The hyperfine constants for B^{11} and O^{17} have been calculated using a configuration interaction (CI) function based on the usual Hartree-Fock (HF) representation (where the orbitals are expressed as linear combinations of analytic functions) plus singly excited $s\rightarrow s'$ functions and, for oxygen, singly excited $p\rightarrow p'$ functions. The s functions are made up of two second-degree polynomials, each multiplied by a different exponential function. The p functions are linear combinations of several $2p$ analytic orbitals. The energies were minimized with respect to the exponents of s functions. The values obtained are (experimental results are given in parentheses): for the ^2P state of B^{11}, $a_{3/2}=67$ Mc/sec (73.3 Mc/sec); $a_{1/2}=360.5$ Mc/sec (366.5 Mc/sec); $Q=0.039$ b (deduced from $b_{3/2}=2.695$ Mc/sec); for the ^3P state of O^{17}: $a_2=-216$ Mc/sec (-218.57 Mc/sec) $a_2'=-132$ Mc/sec (-126.6 Mc/sec), $a_1=-3.8$ Mc/sec (4.74 Mc/sec), $a_1'=-113$ Mc/sec (-91.8 Mc/sec), $Q=-0.024$ b (deduced from $b_2=-10.4$ Mc/sec). For oxygen, the CI calculation where each excited $p\rightarrow p'$ configuration is represented by three independent functions is shown to be an approximation to the most general formulation of what Löwdin has called the extended Hartree-Fock (EHF) functions. The unrestricted Hartree-Fock (UHF) functions have also been calculated. As the UHF functions are not eigenfunctions of J^2, there is no unambiguous way to define functions for states corresponding to definite values of J. For both boron and oxygen the values of the Fermi contact term obtained from projection of the UHF functions are in better agreement with experiment than the values calculated from the UHF functions.

I. INTRODUCTION

In a previous paper[1] arguments were given to show that the multideterminant function which Löwdin[2] has called the extended Hartree-Fock (EHF) function is suitable to calculate the magnetic hyperfine constant for the $^4S_{3/2}$ state of N^{14}. Since the EHF function cannot now be determined, we calculated the hyperfine constant using three different procedures to approximate the EHF functions: (I) a configuration interaction (CI) function built on the usual Hartree-Fock (HF) single determinant representation (where the orbitals are linear combinations of analytic functions) plus singly excited $s\rightarrow s'$ functions; (II) an unrestricted Hartree-Fock (UHF) calculation (which is sometimes called "spin-polarized" calculation) where the radial parts of s orbitals with α spin are different from those of β spin (this function is not, of course, an eigenfunction of S^2); (III) the projection of this UHF function to obtain the function corresponding to the correct spectroscopic state.

In this paper we shall apply these three procedures to two first-row atoms of the periodic table, B^{11} and O^{17}, where p orbitals play an important role in the hyperfine spectra. We will calculate the electric and magnetic constants for the $^2P_{3/2}$ and $^2P_{1/2}$ states of B^{11} and the $^3P_2$ and $^3P_1$ states of O^{17}.

It is straightforward to calculate the constants for different values of J using procedures (I) and (III). For oxygen, (II) gives functions which are not eigenfunctions of S^2 and in certain cases not eigenfunctions of L^2 either. Consequently, there seems to be no unambiguous way of defining these functions for different values of J. Goodings[3] has calculated the magnetic hyperfine constants for the $^2P_{1/2}$ state of B^{11} using numerical HF and UHF functions, but as far as we can tell no previous work using analytic functions has been published for either B^{11} and O^{17}.

II. GENERAL CONSIDERATIONS

When the electronic wave functions of an atom are written in Russell-Saunders (LS) coupling, the matrix element of the magnetic hyperfine operator has the general form[4]:

$$A(J,J')=2\beta_n\beta_e\{\lambda_l(J,J')\alpha_l+\lambda_d(J,J')\alpha_d+\lambda_s(J,J')\alpha_s\},\tag{1}$$

where β_n and β_e are the nuclear and electronic magnetic moments. The reduced matrix elements α_l, α_d, α_s, which are independent of J and J', are defined as follows:

$$\alpha_l=\left\langle LS\left\|\sum_i\frac{\mathbf{l}_i}{r_i^3}\right\|LS\right\rangle,\tag{2}$$

$$\alpha_d=-\left\langle LS\left\|\sum_i\left(\frac{\mathbf{s}_i}{r_i^3}-\frac{3\mathbf{r}_i(\mathbf{s}_i\cdot\mathbf{r}_i)}{r_i^5}\right)\right\|LS\right\rangle,\tag{3}$$

$$\alpha_s=\frac{8\pi}{3}\langle LS\|\sum_i\delta(\mathbf{r}_i)\mathbf{s}_i\|LS\rangle.\tag{4}$$

α_l is the contribution to the field created by the orbital motion of electron i, which is situated at a distance r_i from the nucleus, $\mathbf{l}_i$ being the angular orbital moment; α_d is the contribution due to the magnetic moment of electron i of spin $\mathbf{s}_i$; α_s is the contribution due to the

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

[2] P. O. Löwdin, Phys. Rev. **97**, 1474 (1955).

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

[4] R. E. Trees, Phys. Rev. **92**, 308 (1953).

Table I. Wigner coefficients for ^3P states.

J	J'	λ_l	λ_d	λ_s	λ_q
2	2	$1/\sqrt{6}$	$-1/15\sqrt{2}$	$1/\sqrt{6}$	$4/\sqrt{30}$
	1	$1/2\sqrt{6}$	$-1/15\sqrt{2}$	$-1/2\sqrt{6}$	
1	1	$1/2\sqrt{6}$	$1/6\sqrt{2}$	$1/2\sqrt{6}$	$-2/\sqrt{30}$
	0	$1/3$	$1/6\sqrt{3}$	$-1/3$	

Fermi contact operator. The electric quadrupole hyperfine constant is

$$b_J=-e^2Q\lambda_q(J,J)\alpha_q, \tag{5}$$

where Q is the nuclear electric quadrupole moment and

$$\alpha_q=\left\langle LS\left\|\sum_i\frac{3\cos^2\theta_i-1}{r_i^3}\right\|LS\right\rangle. \tag{6}$$

The values of the λ's for ^2P states are given in the literature[5] and for ^3P states are given in Table I.

The constants a_J:

$$a_J=(IJ)^{-1}A(J,J), \tag{7}$$

$$a'_J=I^{-1}(2J-1)^{-\frac{1}{2}}A(J,J-1), \tag{8}$$

and b_J have been determined from atomic beam experiments for both the[6] $^2P_{3/2}$ and[7] $^2P_{1/2}$ of B^{11}. Recent paramagnetic resonance measurements[8] of O^{17} have confirmed earlier work[9] for the $^3P_2$ state and have also given the constants a_J, a_J', and b_J for the $^3P_1$ state.

It is by now well known that the HF function, for atomic states with filled s shells makes a zero contribution to α_s [Eq. (4)]. To have a nonzero value, it is necessary to use a wave function where the s orbitals are in some way "polarized." In the $^4S_{3/2}$ state of N^{14} which we have examined before,[1] the p orbitals are all singly occupied, and thus our function only needed to introduce s polarization. Boron in its $^2P_{3/2}$ ground state has only a single p electron; polarization of only the s orbitals also needs only to be considered here. In oxygen the contributions α_l and α_d [Eqs. (2) and (3)] to the magnetic constant are themselves not properly explained by a one-determinant HF function. Using such a function, it can readily be shown that the value of a_1 for oxygen should be zero when experimentally one finds it to be about +5 Mc/sec. This nonzero value cannot only be the result of s orbital "polarization," for if this were true, then it could easily be demonstrated that the value of a_1 should be about -18 Mc/sec. If we are to account for the observed value, "polarization" of the p orbitals is also necessary.

The single-determinant representation for oxygen in the $^3P_2$ ground state has p orbitals, both singly and doubly occupied:

$$\Psi_0=|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\psi_0(m_1)\bar{\psi}_0(m_1)\psi_0(m_2)\psi_0(m_3)|, \tag{9}$$

where the φ's are orbitals of symmetry s $(l=0)$ and the ψ's the orbitals of symmetry p $(l=1)$. All the orbitals of p symmetry have the same radial part and differ only in their angular part, which can be characterized by the magnetic quantum numbers m_i. In oxygen the function with maximum projection of M_L $(M_L=L=1)$ corresponds to the values

$$m_1=+1,\quad m_2=0,\quad m_3=-1.$$

In the usual or "restricted" HF function (among other requirements) spin orbitals with the same n and l values but with different spins or with different magnetic quantum numbers all have the same radial parts.[10] If these restrictions are not imposed, then we can write an "unrestricted" Hartree-Fock (UHF) function of the form

$$\Psi_{\mathrm{uHF}}=|\phi_1\bar{\phi}_1'\phi_2\bar{\phi}_2'\chi_1(m_1)\bar{\chi}_1'(m_1)\chi_2(m_2)\chi_3(m_3)|. \tag{10}$$

In this function the ϕ's are of s symmetry, the χ's of p symmetry. The primed and unprimed orbitals are solutions of different HF equations and correspond to different projections of spin. The radial parts of the χ's which correspond to different values of m_i *may* all be different.

The function of type (10) is not an eigenfunction of either S^2 or L^2. It cannot be used to calculated quantities which correspond to different eigenfunctions of J^2 unless (a) one transforms this function into one which is an eigenfunction of S^2 and L^2; or (b) a number of simplifying assumptions are made in order to be able to calculate these quantities.

A function which would have the correct symmetry properties would be a generalized (or extended) Hartree-Fock (EHF) function which *can be defined* as

$$\Psi_{\mathrm{EHF}}=\Omega\Psi_{\mathrm{UHF}}, \tag{11}$$

where Ω indicates the projection operator for both S^2 and L^2. The EHF function is a linear combination of Slater determinants built on nonorthogonal orbitals and, as we have mentioned before, there is at present no way of finding the orbitals which minimize the energy of Eq. (11). We will have to use approximations to these orbitals.

Previously we have shown[1] that first-order corrections to orbitals of s symmetry can be obtained from a CI function built on a one-determinant function and all singly excited $s \longrightarrow s'$ functions. We shall show that the first-order corrections to the p orbitals can also be obtained from a CI function which includes all single excited $p \longrightarrow p'$ configurations.

The simplest approximation will be to represent each

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[5] See, e.g., G. Breit and W. A. Wills, Phys. Rev. **44**, 470 (1933).

[6] G. Wessel, Phys. Rev. **92**, 1581 (1953).

[7] H. Lew and R. S. Title, Can. J. Phys. **38**, 868 (1960).

[8] S. Harvey (private communication).

[9] R. A. Kamper, K. R. Lea, and C. D. Lustig, Proc. Phys. Soc. **B70**, 897 (1957).

[10] For a discussion of the restrictions to the HF functions, see, e.g., R. E. Watson and A. J. Freeman, Phys. Rev. **120**, 1125 (1960); R. K. Nesbet, Revs. Modern Phys. **32**, 355 (1961).

χ_i^e (the superscript e refers to the fact that these orbitals now are those which minimize the EHF function) by the orbital ψ_0 plus a series of q other orbitals of p symmetry (ψ_n) to give a complete set of functions. Thus,

$$\begin{aligned} \chi_i^e(m_i) &= \psi_0(m_i) + \sum_{n=1}^{q} a_{in}\psi_n(m_i), \\ \chi_i'^e(m_i) &= \psi_0(m_i) + \sum_{n=1}^{q} a_{in}'\psi_n(m_i). \end{aligned} \tag{12}$$

If the expansions of Eq. (12) are put back into Eq. (11) and if we assume that the coefficients a_{in} are sufficiently small so that terms in $a_{in}^2\cdots$ can be neglected, then the EHF function takes the form

$$\begin{aligned} \Psi_{\mathrm{EHF}} = \Psi_0 + \sum_{n=1}^{q} \{ & a_{1n}\Omega|\cdots\psi_n(m_1)\bar{\psi}_0(m_1)\psi_0(m_2)\psi_0(m_3)| \\ & + a_{2n}\Omega|\cdots\psi_0(m_1)\bar{\psi}_0(m_1)\psi_n(m_2)\psi_0(m_3)| \\ & + a_{3n}\Omega|\cdots\psi_0(m_1)\bar{\psi}_0(m_1)\psi_0(m_2)\psi_n(m_3)| \\ & + a_{1n}'\Omega|\cdots\psi_0(m_1)\bar{\psi}_n(m_1)\psi_0(m_2)\psi_0(m_3)| \}. \end{aligned} \tag{13}$$

It is known[11] that the minimization of the energy of such a function comes down, to first order, to the calculation of a CI function between the one determinant function and single excited functions. In this case the excited functions are $p \longrightarrow p'$. In this procedure corrections due to doubly-excited configurations are neglected.

However, the configuration p^3p' gives rise to only *three* independent functions of ^3P symmetry and these must be used to determine a maximum of *four* corrections [a_{in} ($i=1, 2, 3$) and a_{1n}']. As the starting ψ_0 orbitals all have the same radial parts, the EHF χ^e orbitals cannot all be determined to be different and we must impose some equalities on the radial parts of these orbitals.

(1) If we assume that the χ^e orbitals have all the same radial part, then this implies that all the a_{in}'s and a_{1n}' are equal to a single parameter μ_n and we find again the usual condition for self-consistence, that is to say, the matrix element of the electrostatic Hamiltonian between the function Ψ_0 and one of the independent functions (Φ_{1n}) which belongs to the configuration p^3p' must be zero. If the function Ψ_0 is chosen to be the HF function, then $\mu_n=0$. Thus for boron where the configuration p' gives rise to only one function of ^2P symmetry, one cannot obtain, by first order correction, a p orbital different from the one determined by the usual Hartree-Fock equations.

(2) We can assume that the p orbitals of α spin will have different radial parts from the orbital of β spin. This formulation is equivalent to removing the restriction on the HF function which Watson and Freeman[10] and Goodings[3] have done to form UHF functions. The corresponding EHF function has the form:

$$\underset{\text{Type I}}{\Psi_{\mathrm{EHF}}} = \Omega'|\phi_1^e\bar{\phi}_1'^e\phi_2^e\bar{\phi}_2'^e\chi_1^e(m_1)\bar{\chi}_1'^e(m_1)\chi_1^e(m_2)\chi_1^e(m_3)|, \tag{14}$$

where Ω' indicates that the projection is only to be carried out for S^2. Using an expansion similar to Eq. (12) one finds a first-order equivalence between the function (14) and a CI function where each $p \longrightarrow p'$ excitation is represented by two independent functions. If the orbitals ψ_0 are the HF orbitals, then it is possible to show that $a_n'=3a_n$ and in the CI function each $p \longrightarrow p'$ excitation can be represented only by one independent function (Φ_{2n}). (We shall call this calculation an approximation to EHF function of type I.)

(3) Instead of having all α orbitals with the same radial part, one can arrange for the α orbitals which are singly occupied in the HF representation to have a different radial part from the doubly occupied orbitals. Thus,

$$\begin{aligned} \underset{\text{Type IIa}}{\Psi_{\mathrm{EHF}}} = \Omega|\phi_1^e\bar{\phi}_1'^e\phi_2^e\bar{\phi}_2'^e & \\ \times\chi_1^e(m_1)\bar{\chi}_1'^e(m_1)\chi_2^e(m_2)\chi_2^e(m_3)|, & \end{aligned} \tag{15}$$

where radial part of $\chi_1^e \neq$ radial part of $\chi_2^e \neq$ radial part of $\chi_1^{e\prime}$. Or we can arrange that α orbitals with the same $|m_i|$ values, i.e., which have the same exchange integrals with the third α orbital, have the same radial part. Thus

$$\begin{aligned} \underset{\text{Type IIb}}{\Psi_{\mathrm{EHF}}} = \Omega|\phi_1^e\bar{\phi}_1'^e\phi_2^e\bar{\phi}_2'^e & \\ \times\chi_1^e(m_1)\bar{\chi}_1'^e(m_1)\chi_2^e(m_2)\chi_1^e(m_3)|. & \end{aligned} \tag{16}$$

The CI calculation where each single excitation $p \longrightarrow p'$ is represented by three independent functions Φ_{1n}, Φ_{2n}, Φ_{3n} can be considered to be equivalent, to first order, to formulations IIa or IIb to the EHF functions. As the forms of Φ_{1n}, Φ_{2n} and Φ_{3n} are a particular choice, they are given explicitly in the Appendix.

III. CALCULATIONS

We have used a program written by R. K. Nesbet and R. E. Watson for the IBM 704 to calculate the self-consistent field orbitals for the atomic functions as a linear combination of analytic functions. This program can be used to calculate both HF and UHF orbitals. For the s orbitals we have used two polynomials each containing three terms multiplied by different exponential functions. For the p orbitals we have used several different analytic fits. The energies of the CI functions have been carefully minimized with respect to the two exponents of the s functions.

Three types of functions have been used to calculate the hyperfine constants:

(I) The CI function was built from the HF function plus all singly excited $s \longrightarrow s'$ functions and, for oxygen,

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[11] R. Lefebvre, Cahiers phys. 381, 1 (1959).

TABLE II. Magnetic hyperfine constants for ^2P states of B^{11} (Mc/sec).[a]

	Analytical (1) HF function	Numerical[b] HF function	CI (1) function	Analytic (1) UHF function	Analytic (2) UHF function	Numerical[b] UHF function	Projected (1) UHF function	Projected (2) UHF function	Exp.[c]
a_s	0	0	−3.8	5.1	−5.9	8.2	1.7	−1.97	0.11
a_p	70.8	70.74	70.8	71.25	71.22	71.31	71.25	71.22	73.24
$a_{3/2}$	70.8	70.74	67.	76.35	65.32	79.5	72.95	69.25	73.35
$a_{1/2}$	354.0	353.6	357.8	351.15	362.0	348.35	354.55	358.07	366.09
E (a.u.)	−24.5285	−24.53	−24.529	−24.529	−24.529				−24.66

[a] Analytic basis functions are for $2p$ ($Z=0.8662$; 1.3946; 2.7692; 7.3539) from the fit of A. Dalgarno (private communication). The "s" basis orbitals are (1) $1s, 2s, 3s$ ($Z=5.0$; 1, 14); (2) $1s$ ($Z=3.9469$; 4.3308; 7.605), $2s$ ($Z=1.1571$; 2.0887; 8.682). The numerical constant $2\beta_n\beta_e/I=171.0118a_0^3$ Mc/sec.

[b] See reference 3.

[c] See reference 6.

singly excited $p\rightarrow p'$ functions. As in the case of nitrogen, each $s\rightarrow s'$ single excitation gives rise to two independent functions. We have chosen one of the functions which has zero matrix element both with the electrostatic and hyperfine Hamiltonians, so that this function can be neglected without any change in the results. In oxygen, when we have used all three functions which correspond to the configuration p^3p' this is the approximation to EHF functions of type II (a or b). When we have used only one function chosen in a special way, this is the approximation to EHF function of type I.

(II) UHF functions have been widely used to study the hyperfine splitting in paramagnetic atoms and ions[12]; it is certainly of interest to study their use for boron and oxygen. When the HF representation for the atomic state is a single determinant, there is no difficulty in writing down the corresponding UHF function. This is so for the state $J=2$ of oxygen. But, unfortunately, there is no unambiguous way of defining functions for $J=1$ and $J=0$. As we must be arbitrary, we have calculated the hyperfine constant a_1, a_2', a_1' from the values of α_l, α_d, and α_s obtained from the state $J=2$ and we have assumed that the ratios given in Table I are still valid. This procedure has at least the merit to avoid both the difficulties of defining excited state functions and the manipulation of determinants built on nonorthogonal orbitals. In the UHF functions we have used for the s orbitals the exponents determined in (I).

(III) We will also wish to calculate the constants obtained from projecting out the ^2P function for boron and the ^3P function for oxygen from the corresponding UHF functions. Even for the paramagnetic atoms and ions this has not been rigorously done, as far as we know, except for Li^7.[13] In general, an exact treatment would be very tedious as there are in the projected functions a multitude of determinants built on a series of nonorthogonal orbitals.

For practical reasons we have limited our calculation for oxygen to a first-order development of the projection of the UHF function analogous to the expansion Eq. (13). The contribution of the Fermi contact operator in this approximation is then simply obtained by multiplying the value obtained from the UHF function by a constant factor.[14,15] These constants[16] are, respectively, 1/3 for B^{11} and 1/2 for O^{17}. In boron, of course, only the contribution from the Fermi contact operator will be changed on projection of the UHF function.

For the other contributions in the case of O^{17} the following first-order development can be made for the integrals $\langle r^{-3}\rangle$ starting from Eq. (12):

$$\langle \chi_i|r^{-3}|\chi_i\rangle=\langle\psi_0|r^{-3}|\psi_0\rangle+2\sum_{n=1}^{q} a_{in}\langle\psi_0|r^{-3}|\psi_n\rangle. \quad (17)$$

The left-hand side of this equation is calculated from the UHF orbitals. For the right side, the integrals $\langle\psi_0|r^{-3}|\psi_0\rangle$ are obtained from the corresponding HF calculation and the remaining term is obtained by substraction. The projection of the UHF function is carried from Eq. (13) and the invariant quantities which one needs can be expressed as a function of the corrections which are just the second term on the right-hand side of Eq. (17).

IV. RESULTS

A. Boron

As boron has only one p electron outside the s shell the calculations are much simpler than for oxygen. From the hyperfine spectra for the $^2P_{3/2}$ [6] and $^2P_{1/2}$ [7] states the contributions to the magnetic constant coming from the p electron (a_p) and from the polarization of the s orbitals (a_s) can be deduced. There are the relations:

$$\begin{aligned} a_{3/2}&=a_p+a_s,\\ a_{1/2}&=5a_p-a_s. \end{aligned} \quad (18)$$

The constants are collected in Table II.

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[12] See, for example, R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961) where an extensive bibliography is given.

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

[14] Compare Appendix II of reference 1.

[15] From recent work of A. J. Freeman and R. E. Watson [Quarterly Progress Report, Solid State and Molecular Physics Group, Massachusetts Institute of Technology, April 15, 1961 (unpublished)] it appears that this approximation introduces an error of only about 5% for N^{14}.

[16] R. K. Nesbet, Ann. Phys. (New York) **3**, 397 (1958).

As the value of a_s is extremely sensitive to the basis set of s orbitals,[1] the constants obtained from the functions marked a in Table II have been calculated by carefully minimizing the energy of the CI function with respect to the two s exponents (Z's). On the contrary, the value of a_p is hardly sensitive to the choice of parameters that one uses, provided the basis set is sufficient to represent the numerical $2p$ HF orbital.

We have calculated UHF functions using (1) the same s parameters as those which minimized the energy of the CI function and (2) an analytic fit to the numerical $1s$ and $2s$ HF orbitals using three analytic $1s$ and three $2s$ functions.[17] Although the energies are essentially identical from both functions, the values of a_s are very different and we find it interesting that the value obtained from the polynomial function is much closer to the a_s obtained from the numerical UHF function than is the one of fit. In addition, we have calculated the constants obtained from the projection of the UHF functions.

Finally, the value of Q for B^{11} has been calculated using Eq. (5) where α_q has been calculated using the CI function given in Table II and the experimental value $b_{3/2}=2.695$ Mc/sec.[6] We have found

$$Q\ (B^{11})=0.039\ \text{b}. \tag{18}$$

Previously, the value proposed was 0.036 b.[6]

B. Oxygen

The magnetic constants are collected in Table III. In all cases there are two parameters for the s basis functions.

In addition to calculating the quantities $a(J,J')$ the results could also be expressed in terms of the quantities α_l, α_d, and α_s which are independent of J and J'. But we have preferred to give the values of parameters which have been frequently used by experimentalists and are defined as follows:

$$\begin{aligned}\langle r^{-3}\rangle &= \lambda_l(2.2)\alpha_l,\\ \langle r^{-3}\rangle' &= 5\lambda_d(2.2)\alpha_d,\\ \langle r^{-3}\rangle'' &= -\tfrac{5}{2}\lambda_q(2.2)\alpha_q,\\ a_s &= (\beta_n\beta_e/I)\lambda_s(2.2)\alpha_s.\end{aligned} \tag{19}$$

In the HF representation the integrals $\langle r^{-3}\rangle$, $\langle r^{-3}\rangle'$, and $\langle r^{-3}\rangle''$ are all equal to $\langle p|r^{-3}|p\rangle$ where p is the HF orbital.[18] It should be particularly noted that the contribution a_s obtained from projecting UHF function of types I and II is in much better agreement with experiment than the values determined from the unprojected

TABLE III. Hyperfine constants for ^3P states of O^{17}.[a]

	Analytic HF function	UHF only s spin-polarized	Approximations EHF, Type I UHF	Proj. UHF	CI	Approximations EHF, Type II UHF type IIa	Proj. UHF type IIa	UHF type IIb	Proj. UHF type IIb	CI	Exp.[b]
a_2 (Mc/sec)	−251.7	−235.7	−235.3	−220	−212	−234.2	−218.8	−236.5	−219.8	−216.1	−218.569±0.003
a_2' (Mc/sec)	−145.3	−134.3	−115.9	−127.6	−129.4	−115.4	−126.9	−117.3	−127.5	−131.9	−126.6 ±1.4
a_1 (Mc/sec)	0	−19.5	−34.1	−9.2	−2.4	−34.1	−8.1	−28.3	−8.6	−3.8	4.739±0.009
a_1' (Mc/sec)	−146.8	−115.2	−81.2	−102.7	−109.4	−77.9	−101.1	−76.8	−102.	−113.1	−91.8 ±1.4
E (a.u.)	−74.8083	−74.8096	−74.8117		−74.8129	−74.8117		−74.8118		−74.8132	−75.105
$\langle r^{-3}\rangle$ (10^{25} cm^{-3})	3.36	3.36	3.13	3.13	3.10	3.11	3.11	3.13	3.13	3.16	3.06
$\langle r^{-3}\rangle'$ (10^{25} cm^{-3})	3.36	3.36	3.13	3.28	3.26	3.16	3.28	3.24	3.29	3.30	3.46
$\langle r^{-3}\rangle''$ (10^{25} cm^{-3})	3.36	3.36	3.13	3.13	3.10	3.11	3.13	3.03	3.12	3.08	?
a_s (Mc/sec)	0	−19.5	−34.1	−17.1	−11.4	−34.1	−17.1	−34	−17	−11.5	−18

[a] Analytic basis functions are for $2p$ ($Z=1.4107$; 2.7489; 5.9169) and for s ($Z=7.8$; 1.9). The numerical constant $2\beta_n\beta_e/I=-72.24938a_0^3$ Mc/sec.

[b] See reference 8.

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[17] A. Dalgarno (private communication).

[18] If the experimental value of a_s is obtained from the values of a_2, a_2', and a_1 and this put back into the equation for a_1 with the experimental values of $\langle r^{-3}\rangle$ and $\langle r^{-3}\rangle'$ we find $a_1'=-90.2$ Mc/sec which is, within experimental error, the value originally obtained. Thus we can rely on the equations which relate the $a(J,J')$'s to different transitions in the resonance spectra (communication from S. Harvey).

function. This is not true for the UHF function where only the s orbitals are spin polarized.

If Q is deduced from $\langle r^{-3}\rangle''$ using the complete CI function for α_q and the experimental value $b_2=-10.44$ Mc/sec,[8] we find

$$Q=-0.024 \text{ b}. \tag{20}$$

Previously the value -0.0265 b has been proposed.[9,19]

V. CONCLUSIONS

The functions which we have used in this paper seem adequate to give a qualitative basis for understanding the experimental results, but, of course, there can be no claim for high accuracy. The results that would be obtained from the final iteration of the EHF functions are difficult to predict but one can hope they might be in even better agreement with experiment.

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APPENDIX

The functions Φ_{1n}, Φ_{2n}, and Φ_{3n} for oxygen are

$$\Phi_{1n}=\tfrac{1}{2}\{X_1+X_2+X_3+X_4\},$$

$$\Phi_{2n}=(1/2\sqrt{2})\{-2X_2+X_3+X_4-X_5-X_6\},$$

$$\Phi_{3n}=(1/2\sqrt{10})\{2X_1+X_4-3X_3-3X_5+X_6+4X_7\},$$

where

$$X_1=\det|1s\ \bar{1}\bar{s}\ 2s\ \bar{2}\bar{s}\ np_+\ \bar{2}\bar{p}_+\ 2p_-\ 2p_0|,$$

$$X_2=\det|1s\ \bar{1}\bar{s}\ 2s\ \bar{2}\bar{s}\ 2p_+\ \bar{n}\bar{p}_+\ 2p_-\ 2p_0|,$$

$$X_3=\det|1s\ \bar{1}\bar{s}\ 2s\ \bar{2}\bar{s}\ 2p_+\ \bar{2}\bar{p}_+\ np_-\ 2p_0|,$$

$$X_4=\det|1s\ \bar{1}\bar{s}\ 2s\ \bar{2}\bar{s}\ 2p_+\ \bar{2}\bar{p}_+\ 2p_-\ np_0|,$$

$$X_5=\det|1s\ \bar{1}\bar{s}\ 2s\ \bar{2}\bar{s}\ np_+\ 2p_+\ \bar{2}\bar{p}_-\ 2p_0|,$$

$$X_6=\det|1s\ \bar{1}\bar{s}\ 2s\ \bar{2}\bar{s}\ np_+\ 2p_+\ 2p_-\ \bar{2}\bar{p}_0|,$$

$$X_7=\det|1s\ \bar{1}\bar{s}\ 2s\ \bar{2}\bar{s}\ 2p_+\ \bar{2}\bar{p}_0\ np_0\ 2p_0|.$$

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[19] M. J. Stevenson and C. H. Townes, Phys. Rev. **107**, 635 (1957).