PHYSICAL REVIEW VOLUME 188, NUMBER 1 5 DECEMBER 1969

Atomic Hyperfine Structure. III.
Excited States of C,N, and O

Henry F. Schaefer III* and Richard A. Klemm
Department of Chemistry, Stanford University, Stanford, California 94305

(Received 22 May 1969)

Using restricted Hartree-Fock (RHF) wave functions and two previously defined types of configuration-interaction (CI) wave functions – the polarization wave function and the first-order wave function – we have made *ab initio* calculations of the hyperfine structure (hfs) of ^1D C, ^2D N, ^2P N, and ^1D O. The hyperfine parameters of these excited states exhibit some interesting effects not encountered in the hfs of the ground states of first-row atoms. In particular, both ^2D N and ^2P N show no electric-quadrupole hfs in the RHF approximation. However, both the polarization and first-order wave functions predict a small electric-quadrupole hfs for these states of N^{14}. Radford and Evenson have experimentally studied the hfs of ^2D N, and our CI results are in good agreement (usually within experimental error) with their hfs constants. As was found previously for the ground states of N, O, and F, the polarization wave function gives better agreement with the experimental hfs than does the first-order wave function. The present results also indicate that the hfs parameters $|\psi(0)|^2$, $\langle r_l^{-3}\rangle$, $\langle r_s^{-3}\rangle$, and $\langle r_q^{-3}\rangle$ are not usually transferable between different states of the same atom.

INTRODUCTION

The purpose of this series of papers[1] is to study, using configuration interaction (CI) wave functions, the hyperfine structure (hfs) of first-row atoms. In papers I and II, we introduced two types of limited CI wave functions, the polarization wave function[1a] and the first-order wave function.[1b] The polarization wave function includes the restricted Hartree-Fock (RHF) configuration plus all configurations corresponding to polarizations of the core and valence RHF orbitals. The first-order wave function[2] contains the RHF configuration plus all configurations which do not correspond to true correlation effects.[3] Polarization and, to a lesser degree, first-order wave functions, yielded hfs parameters for the ground states of N, O, and F in better agreement with experiment[4,5] than previously used[6–14] theoretical approaches. In particular, polarization wave functions resulted in spin densities between 25 and 45% too small, and other hfs parameters were within 2% of experiment. We note that previous calculations of the spin density $|\psi(0)|^2$ had given highly erratic results for these atoms, sometimes even differing in sign from the experimental spin density.

Since the submission of paper I, highly successful calculations of the spin densities of the ground states of oxygen,[15] nitrogen,[16] and phosphorous[17] have been reported using the Brueckner-Goldstone many-body perturbation theory (MBPT),[18,19] as developed for atoms by Kelly.[20] MBPT calculations have also been reported by Das and co-workers on the ground and first excited states of lithium.[21] Related spin-density calculations, using pair correlation approaches, were performed earlier by Nesbet[22] and by Schaefer and Kaldor.[23] It remains to be explained why MBPT gives such excellent results but the related pair correlation methods,[22,23] which involve the summation of contributions from single and pair excitations, give poor agreement with experiment. In another related work, Sandars[24] has discussed the use of perturbation theory in the calculation of hfs.

Many fewer *ab initio* investigations have been made of that part of the hfs resulting from the operators

$$\sum_i \frac{\vec{l}_i}{r_i^3}\;\sum_i \left(\frac{3\vec{s}_i\cdot\vec{r}_i}{r_i^5}\vec{r}_i-\frac{\vec{s}_i}{r_i^3}\right),$$

$$\text{and}\quad \sum_i \frac{C_i^{(2)}}{r_i^3}\;.$$

With these operators can be associated different effective values of $\langle r^{-3}\rangle$, namely, $\langle r_l^{-3}\rangle$, $\langle r_s^{-3}\rangle$, and $\langle r_q^{-3}\rangle$. Papers I and II of this series,[1] using polarization and first-order wave functions, reported calculations of effective values of $\langle r^{-3}\rangle$ for the ground states of first-row atoms. Other work includes that of Judd,[25] who has qualitatively discussed the effects of different configurations on the different values of $\langle r^{-3}\rangle$. In a very recent paper, the first MBPT calculation of $\langle r_l^{-3}\rangle$, $\langle r_S^{-3}\rangle$, and $\langle r_q^{-3}\rangle$ for an atom with more than three electrons has been performed by Kelly[26] on the oxygen atom. In another paper now in press, Goddard[27] has presented a complete discussion of the hfs of the ground states of B, C, N, O, and F using unrestricted[28] and spin-extended[29] Hartree-Fock wave functions.

To date, very little theoretical work has been done on the hfs of excited states. Apparently, the lithium atom is the largest atom for which excited state hfs calculations have been carried out. A number of calculations on ^2P Li have been reported, including a 45-term CI calculation,[30] spin-extended Hartree-Fock calculations,[10b] an MBPT study,[21b] and the use of the spin-optimized SCF function by Kaldor and Harris.[31] The fact that all of these approaches give good agreement with experiment indicates the relative simplicity of the electronic structure of ^2P Li. Using spin-extended Hartree-Fock wave functions, Goddard[10b] has an addition studied the hfs of the 3^2S, 3^2P, and 3^2D states of lithium.

This study concerns itself with the lowest-multiplet excited states of C, N, and O. In the RHF approximation, these states arise from the orbital occupancies $1s^22s^22p^n$, where $n = 2, 3, 4$. These states, ^1D C, ^1S C, ^2D N, ^2P N, ^1D O, and ^1S O, are of particular interest because of their relationship to the ground states of C, N, and O. Since ^1S states have no hfs, the ^1S states of carbon and oxygen will not be discussed hereafter. The ^2D state of nitrogen is of particular interest because its hfs has been experimentally investigated by Radford and Evenson.[32] In this paper, we use RHF, polarization, and first-order wave functions to discuss the hfs of these lowest-lying excited states of carbon, nitrogen, and oxygen.

TABLE I. Orbital occupancies, separated into three types, for polarization and first-order wave functions. The polarization wave function includes only configurations of type (1), whereas the first-order wave function includes configurations of all three types. *X* is an orbital in the Hartree-Fock wave function, and *Y* is an orbital not occupied in the Hartree-Fock approximation. In general, there is more than one configuration of the proper symmetry corresponding to each orbital occupancy. The number *n* of $2p$ electrons goes from two for carbon to four for oxygen.

Notation:

$s_i = \{s_1, s_2, s_3, s_4, s_5, s_6\}$
$p_i = \{p_1, p_2, p_3, p_4, p_5, p_6\}$
$d_i = \{d_1, d_2, d_3, d_4, d_5, d_6\}$
$f_i = \{f_1, f_2, f_3, f_4\}$

(1) $X_i \to Y_i$
$1s \to s_i$; $1ss_i2s^22p^n$
$1s \to d_i$; $1sd_i2s^22p^n$
$2s \to s_i$; $1s^22ss_i2p^n$
$2s \to d_i$; $1s^22sd_i2p^n$
$2p \to p_i$; $1s^22s^22p^{n-1}p_i$
$2p \to f_i$; $1s^22s^22p^{n-1}f_i$

(2) $X_iX_j \to X_kX_l$
$1s^2 \to 2p^2$; $2s^22p^{n+2}$
$2s^2 \to 2p^2$; $1s^22p^{n+2}$
$1s2s \to 2p^2$; $1s2s2p^{n+2}$

(3) $X_iX_j \to X_kY_i$
$1s^2 \to 2pp_i$; $2s^22p^{n+1}p_i$
$1s^2 \to 2pf_i$; $2s^22p^{n+1}f_i$
$2s^2 \to 2pp_i$; $1s^22p^{n+1}p_i$
$2s^2 \to 2pf_i$; $1s^22p^{n+1}f_i$
$1s2s \to 2pp_i$; $1s2s2p^{n+1}p_i$
$1s2s \to 2pf_i$; $1s2s2p^{n+1}f_i$

WAVE FUNCTIONS

Reference 1a contains a discussion of the properties of polarization wave functions. First-order wave functions are discussed in Refs. 1b and 2, and more thoroughly in a recent paper[33] concerning the electron affinities of first-row atoms. Table I lists the types of configurations used in polarization and first-order wave functions for first-row atoms whose RHF function has the orbital occupancy $1s^22s^22p^n$

To be more specific, polarization wave functions for the states of interest here are composed of 59 (^1D C), 105 (^2D N), 95 (^2P N), and 69 (^1D O) configurations. The differences in numbers of configurations do not indicate that calculations on some states used larger basis sets than others; all calculations used the same *size* basis sets and differences in numbers of configurations are due to the symmetry properties of the different states. The first-order wave functions for these states consisted of 142 (^1D C), 195 (^2D N), 193 (^2P N), and 109 (^1D O) configurations. One of the most complicated of these wave functions, the first-order wave function for ^2P N, was constructed from 3334 Slater determinants, 979 of which were distinct. Owing to the fact[34] that more than one *L-S* eigenfunction of the proper symmetry can result from most orbital occupancies, many determinants are included in more than one configuration. A more complete discussion of the L-S eigenfunction problem is given in Ref. 34.

In all calculations, our first configuration was the accurate RHF function of Clementi, Roothaan, and Yoshimine[35] for the particular state. These RHF functions[35] appear to be within 0.0001 hartree of the energy of the exact RHF function. In addition six s, six p, six d, and four f Slater-type orbitals (STO) were added to the RHF basis to form an equal number of atomic orbitals for the CI calculations. The additional STO's were chosen as described in paper I, and the energies of the resulting polarization and first-order wave functions are believed[1] to be within about 0.0001 hartree of the exact polarization and first-order energies. The actual basis sets used are given in Ref. 33.

The CI calculations were performed as described previously.[34,36] Documentation of the computer programs, including actual listings of the programs, is contained in the thesis[37] of one of the authors. The first-order wave functions used here were described previously.[33] The polarization functions were computed specifically for the present research.

The energies of the polarization and first-order wave functions for ^1D C, ^2D N, ^2P N, and ^1D O are given in Table II. For comparison, the RHF energies of Clementi, Roothaan, and Yoshimine[35] and the experimental energies of Veillard and Clementi[38] are included in Table II.

REVIEW OF HFS THEORY

The most general original presentation of hfs theory for the many-electron atom is that of Trees.[39] However, Trees's work[39] was published in 1953, before the start of efforts to obtain *ab initio* wave functions beyond the RHF level of approximation. Therefore, Trees's work was intended for use either in conjunction with RHF functions or for the analysis of experimental hfs data. In paper I [Ref. 1(a)], we extended Trees's analysis[39] in order to evaluated atomic hfs using expectation values determined from the more general CI wave functions. Here we summarize the detailed analysis contained in paper I.

The hyperfine energy levels W_F are given by the formula

$$W_F = \tfrac{1}{2} AK + BK(K+1), \qquad (1)$$

where $K = F(F+1) - I(I+1) - J(J+1)$. (2)

In Eq. (1), A arises from the magnetic-dipole interaction and B from the electric-quadrupole interaction between the nucleus and the electrons.

In the L-S coupling scheme, neglecting relativistic effects

$$A = (2\mu_B \mu_I \mu_N / I)(\lambda_l \alpha_l + \lambda_d \alpha_d + \lambda_s \alpha_s), \qquad (3)$$

$$B = [3e^2 Q / 2I(2I-1)] \lambda_q \alpha_q \,, \qquad (4)$$

where μ_B is the Bohr magneton, μ_I is the nuclear magnetic-dipole moment in nuclear magnetons, μ_N is the nuclear magneton, e is the electron charge, and Q is the nuclear electric-quadrupole moment (usually given in barns). Since units can be very confusing in hfs calculations, we note that[40]

$$\frac{2\mu_B \mu_I \mu_N}{I} = 95.4096 \frac{\mu_I}{I} \text{ MHz};$$
$$\frac{3e^2 Q}{2I(2I-1)} = \frac{704.922\,Q}{2I(2I-1)} \text{ MHz} . \qquad (5)$$

if μ_I is given in nuclear magnetons, and Q is given in barns. The quantities λ_l, λ_d, λ_s, and λ_q are rather complicated algebraic functions of L, S, and J, while α_l, α_d, α_s, and α_q are the reduced matrix elements[41]

$$\alpha_l = \langle LS \| \textstyle\sum_i \dfrac{\vec{l}_i}{r_i^3} \| LS \rangle , \qquad (6)$$

$$\alpha_d = \langle LS \| \textstyle\sum_i \dfrac{3\vec{s}_i \cdot \vec{r}_i}{r_i^5} \vec{r}_i - \dfrac{\vec{s}_i}{r_i^3} \| LS \rangle , \qquad (7)$$

$$\alpha_s = \langle LS \| \textstyle\sum_i \dfrac{8\pi}{3} \delta(\vec{r}_i) \vec{s}_i \| LS \rangle , \qquad (8)$$

TABLE II. Energies of different wave functions for pertinent excited states of C, N, and O.

	^1D C	^2D N	^2P N	^1D O
RHF[a]	−37.63132	−54.29615	−54.22809	−74.72921
Polarization, this work	−37.67294	−54.35012	−54.25525	−74.77482
First order[b]	−37.69543	−54.35547	−54.29421	−74.77831
Experiment[c]	−37.809	−54.525	−54.481	−75.038

[a] Reference 35.
[b] Reference 33.
[c] Reference 38.

$$\alpha_q = \langle LS \,\|\, \sum_i \frac{C_i^{(2)}}{r_i^3} \,\|\, LS \rangle . \qquad (9)$$

In Eq. (9), $C_i^{(2)}$ is the tensor of rank two introduced by Racah.[42] Paper I contains explicit formulas for the λ's and relates the reduced matrix elements α to expectation values calculated for wave functions with definite values of L, S, M_L, and M_S.

TEST OF THE TWO-PARAMETER THEORY

Using RHF wave functions for atoms with open $2p$ shells, the reduced matrix elements α_l, α_d, and α_q can all be expressed in terms of the single parameters $\langle r^{-3}\rangle = \langle 2p \mid r^{-3} \mid 2p\rangle$. If these relationships were rigorously true, then all of hfs for atoms could be explained in terms of the two parameters $\mid\psi(0)\mid^2$ and $\langle r^{-3}\rangle$; and it would be possible to deduce experimental values of spin densities using only two independent magnetic hfs constants plus the magnetic-dipole moment of the nucleus being considered. In fact, the "experimental" spin densities of ^2P B and ^3P C were deduced[7, 8] in this manner by Bessis *et al.*

However, as shown theoretically by Trees[39] and experimentally by Harvey,[5] there are three independent parameters needed to describe the magnetic-dipole hfs of an atom with an open $2p$ shell; and an additional independent parameter is needed to determine the electric-quadrupole hfs. The four-parameter theory is necessary because the operator $\langle r^{-3}\rangle$ appears in three different environments: l_z, $(3\cos^2\Theta-1)s_z$, and $(3\cos^2\Theta-1)$, in the expectation values which determine α_l, α_d, and α_q. Therefore, in paper I, we stated that the previously deduced spin densities of B and C were unreliable, and that there was not sufficient experimental hfs data available to deduce the true spin densities of B and C.

In order to quantitatively test the validity of the use the two-parameter theory in deducing spin densities from experiment, Karplus,[43] has suggested that this theory be used to deduce the (experimentally known) spin densities of ^3P O and ^2P F. We have carried out this procedure, and for ^3P O^{17} the pertinent equations are

$$A_2 = -36.1354\,\langle r_l^{-3}\rangle - 7.2271\,\langle r_s^{-3}\rangle - 151.364\,|\psi(0)|^2 = -218.569 \text{ MHz}, \qquad (10)$$

$$A_1 = -36.1354\,\langle r_l^{-3}\rangle + 36.1354\,\langle r_s^{-3}\rangle - 151.364\,|\psi(0)|^2 = 4.738 \text{ MHz}, \qquad (11)$$

where the experimental values on the right-hand side are those of Harvey.[5] If one assumes $\langle r_l^{-3}\rangle = \langle r_s^{-3}\rangle$, one obtains $\langle r^{-3}\rangle = 5.150$ and $\mid\psi(0)\mid^2 = -0.0313$. For comparison, $\langle r^{-3}\rangle_{\text{RHF}} = 4.973$, and the true spin density[5] of oxygen is $+0.1138$. Similarly, for ^2P F^{19}, the pertinent equations are

$$A_{3/2} = 334.404\,\langle r_l^{-3}\rangle - 66.881\,\langle r_s^{-3}\rangle + 1400.75\,|\psi(0)|^2 = 2009.99 \text{ MHz}, \qquad (12)$$

$$A_{1/2} = 668.809\,\langle r_l^{-3}\rangle + 668.809\,\langle r_s^{-3}\rangle - 1400.75\,|\psi(0)|^2 = 10244.21 \text{ MHz}, \qquad (13)$$

where the experimental value of $A_{3/2}$ is that of Radford, Hughes, and Beltran-Lopez[44] and the experimental value of $A_{1/2}$ is that of Harvey.[5] Assuming again that $\langle r_l^{-3}\rangle = \langle r_s^{-3}\rangle = \langle r^{-3}\rangle$, one obtains $\langle r^{-3}\rangle = 7.634$ and $\mid\psi(0)\mid^2 = -0.0231$. For comparison, $\langle r^{-3}\rangle_{\text{RHF}} = 7.545$ and the exact value of $\mid\psi(0)\mid^2$ is $+0.0717$ a. u.[5]

It was not to be expected that the two-parameter theory would give exact agreement with the true spin densities. However, it was surprising to find above that for both oxygen and fluorine, the spin density deduced from experiment using the two-parameter theory was of the wrong sign. These results certainly justify our earlier assumption[1] that spin densities deduced from experiment using the two-parameter theory should not be considered the experimental values.

RESULTS

Table III contains all the expectation values and reduced matrix elements required for an analysis of the hfs of ^1D C, ^2D N, ^2P N, and ^1D O. Included in Table III are values computed from RHF,[35] polarization, and first-order wave functions.

In order to compute the constants A and B given in Eq. (1), we must assume values of the appropriate nuclear moments. Table IV contains the nuclear moments assumed in this work. With a few exceptions, we have adopted the nuclear moments tabulated recently by Fuller and Cohen.[45] For C^{11}, we have used the magnetic-dipole and electric-quadrupole moments deduced in paper I. O'Konski and Ha[46] have recently completed a study of the determination of the electric-quadrupole moment of N^{14} using *ab initio* molecular wave functions and experimental molecular quadrupole coupling constants. Their work is based in part on the calculations of McLean and Yoshimine[47] and seems to provide the best value to date, 0.0156 b, for $Q\,(N^{14})$. Finally, we use the value deduced in paper I for $Q\,(O^{17})$.

The calculated hfs constants A and B are listed in Tables V and VI, respectively. These tables also include the experimental values of Radford

TABLE III. Calculated hfs parameters in a.u. For each parameter and each atomic state, three values are given. In descending order, the three values are those computed from (1) RHF wave functions; (2) polarization wave functions; and (3) first-order wave functions.

	^1D C	^2D N	^2P N	^1D O
$\langle J=L+S, M_J=J \left\| \sum_i \frac{l_{zi}}{r_i^3} \right\| J=L+S, M_J=J \rangle$	3.263101 3.218629 3.190964	6.040068 5.899598 5.866205	2.968033 2.954445 2.939389	9.849068 9.845345 9.803776
$\langle J=L+S, M_J=J \left\| \sum_i \frac{(3\cos^2\theta_i - 1)s_{zi}}{r_i^3} \right\| J=L+S, M_J=J \rangle$	0.0 0.0 0.0	1.208014 1.282213 1.275435	−0.593606 −0.646699 −0.641475	0.0 0.0 0.0
$\langle J=L+S, M_J=J \left\| \sum_i \frac{8\pi}{3} \delta(\vec{r}_i) s_{zi} \right\| J=L+S, M_J=J \rangle$	0.0 0.0 0.0	0.0 0.126435 0.121759	0.0 0.131181 0.114765	0.0 0.0 0.0
$\langle J=L+S, M_J=J \left\| \sum_i \frac{(3\cos^2\theta_i - 1)}{r_i^3} \right\| J=L+S, M_J=J \rangle$	−1.305241 −1.253256 −1.172333	0.0 0.095721 0.096885	0.0 −0.116132 −0.049084	3.939627 3.672473 3.688620
$\alpha_l = \langle LS \left\| \sum_i \frac{\vec{l}_i}{r_i^3} \right\| LS \rangle$	8.936371 8.814578 8.738814	16.54141 16.15671 16.06526	7.270167 7.236882 7.200004	26.97278 26.96259 26.84875
$\alpha_d = \langle LS \left\| \sum_i \frac{3\vec{s}_i \cdot \vec{r}_i}{r_i^5} \vec{r}_i - \frac{\vec{s}_i}{r_i^3} \right\| LS \rangle$	0.0 0.0 0.0	−19.57206 −20.77423 −20.66441	12.59230 13.71857 13.60773	0.0 0.0 0.0
$\alpha_s = \langle LS \left\| \sum_i \frac{8\pi}{3} \delta(\vec{r}_i) \vec{s}_i \right. LS \rangle$	0.0 0.0 0.0	0.0 0.309701 0.298248	0.0 0.321327 0.281116	0.0 0.0 0.0
$\alpha_q = \langle LS \left\| \sum_i \frac{C_i^{(2)}}{r_i^3} \right\| LS \rangle$	−2.730106 −2.621373 −2.452111	0.0 0.200215 0.202650	0.0 −0.318041 −0.134423	8.240321 7.681528 7.715303

TABLE IV. Nuclear moments used in this work. I is the nuclear spin, μ is the nuclear magnetic-dipole moment in nuclear magnetons, and Q is the nuclear electric-quadrupole moment in barns. Note that nuclei with spin-$\frac{1}{2}$ have no quadrupole moment. Unless indicated, these nuclear moments are from Fuller and Cohen, Ref. 45.

Nucleus	I	μ	Q
C^{11}	$\frac{3}{2}$	± 0.997[a]	± 0.0322[a]
C^{13}	$\frac{1}{2}$	+0.7024	...
N^{13}	$\frac{1}{2}$	± 0.3221	...
N^{14}	1	+0.4036	+0.0156[b]
N^{15}	$\frac{1}{2}$	−0.2831	...
O^{15}	$\frac{1}{2}$	± 0.7189	...
O^{17}	$\frac{5}{2}$	−1.8937	−0.0256[a]

[a] Reference 1a.
[b] Reference 46.

and Evenson[32] for ^2D N.

Using Eq. (1) and the calculated hfs constants A and B, hyperfine energy-level diagrams can be predicted. Figure 1 illustrates such a predicted energy-level diagram for ^1D O^{17}, using the polarization wave function. This ^1D state of oxygen differs from the previously studied ground-state atoms in that there is no contribution to the hfs from either the spin-dipolar (α_d) or contact (α_s) parts of the hfs Hamiltonian. In addition, there is no experimental hfs information available for ^1D O^{17}.

COMPARISON WITH EXPERIMENT

From the paramagnetic-resonance spectrum of ^2D N^{14}, Radford and Evenson[32] were able to measure $A_{5/2}$, $A_{3/2}$, $B_{5/2}$, and $B_{3/2}$. Their results are compared with our calculated values in

TABLE V. Calculated magnetic hyperfine constants A in MHz. The nuclear magnetic-dipole moments used are those given in Table IV.

	^1D C			^1D O		
	A_2 C^{11}	A_2 C^{13}		A_2 O^{15}	A_2 O^{17}	
Hartree-Fock	1.62666	1.14600		3.54025	−9.32559	
Polarization	1.60449	1.13038		3.53891	−9.32207	
First-order	1.59070	1.12067		3.52397	−9.28271	
				^2D N		
	$A_{5/2}$ N^{13}	$A_{3/2}$ N^{13}	$A_{5/2}$ N^{14}	$A_{3/2}$ N^{14}	$A_{5/2}$ N^{15}	$A_{3/2}$ N^{15}
Hartree-Fock	178.1952	118.7968	111.6417	74.4278	−156.6193	−104.4128
Polarization	179.6744	104.1234	112.5684	65.2347	−157.9193	−91.5161
First-order	178.5718	103.5902	111.8776	64.9006	−156.9502	−91.0474
Experiment[a]	...	...	114.69 ± 0.07	65.3 ± 0.2	...	...
				^2P N		
	$A_{3/2}$ N^{13}	$A_{1/2}$ N^{13}	$A_{3/2}$ N^{14}	$A_{1/2}$ N^{14}	$A_{3/2}$ N^{15}	$A_{1/2}$ N^{15}
Hartree-Fock	97.2927	486.4637	60.9552	304.7761	−85.5125	−427.5625
Polarization	99.9356	501.7299	62.6110	314.3406	−87.8354	−440.9802
First-order	98.8602	499.0279	61.9372	312.6477	−86.8901	−438.6054

[a] Reference 32.

TABLE VI. Calculated electric-quadrupole hyperfine constants B in MHz. For the definition of B, see Eq. (4). The nuclear electric-quadrupole moments used are those given in Table IV.

	^1D C^{11}	^2D N^{14}		^2P N^{14}	^1D O^{17}
	B_2	$B_{5/2}$	$B_{3/2}$	$B_{3/2}$	B_2
Hartree-Fock	0.20574	0.0	0.0	0.0	0.14811
Polarization	0.19755	−0.01316	−0.03070	0.05321	0.13807
First-order	0.18479	−0.01332	−0.03107	0.02249	0.13868
Experiment[a]	...	−0.0150 ± 0.0075	−0.0375 ± 0.0250	...	...

[a] Reference 32.

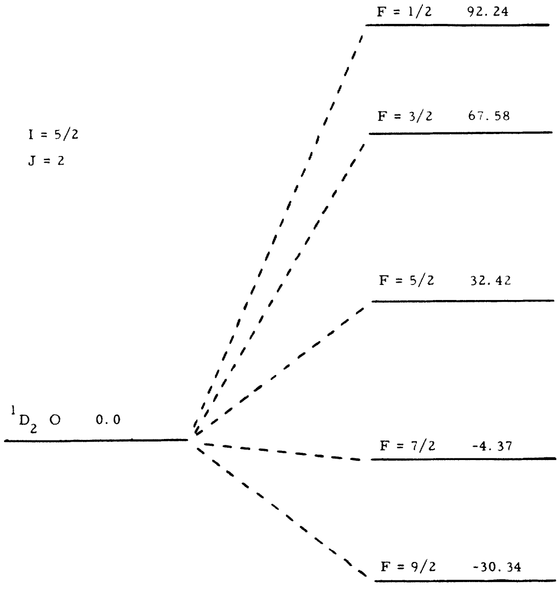

FIG. 1. Predicted hyperfine energy-level diagram for ^1D O^{17}. Here we use the O^{17} nuclear moments given in Table IV and expectation values calculated from polarization wave functions. Energies are in MHz.

Tables V and VI. It is seen that, using both polarization and first-order wave functions, the three constants $A_{3/2}$, $B_{5/2}$, and $B_{3/2}$ are predicted within the limits of experimental error established by Radford and Evenson.[32] In fact, the close agreement for $B_{5/2}$ and $B_{3/2}$ may indicate that the error limits established there by Radford and Evenson are unnecessarily large. For the fourth constant $A_{5/2}$, the polarization function value differs by 1.9% and the first-order value by 2.5% from experiment. On the other hand, the RHF approximation fails to give agreement to within experimental error for any of the four hfs constants.

An interesting feature of the hfs theory of ^2D N is that the RHF approximation predicts an identically zero electric field gradient at the nitrogen nucleus. This is also true for ^2P N, and thus, the RHF approximation is inherently incapable of preducting any electric-quadrupole hfs for these two states. This property of RHF functions is analogous to the better-known inability of the RHF approximation to predict a nonvanishing spin density for states with closed inner shells and an open p shell in the RHF approximation.

The comparison with experiment in Table V bears out previous statements[1] on the accuracy and relative accuracy of polarization and first-order wave functions in describing atomic hfs. In paper I, it was stated that, if an experimental hfs constant is not dominated by the contribution from the spin density, the polarization function should provide agreement to within 2%; and in paper II, it was stated that, in general, polarization functions provide better agreement with experimental hfs data than do first-order wave functions.

DISCUSSION

In order to deduce the values of $\langle r_l^{-3} \rangle$, $\langle r_S^{-3} \rangle$, and $|\psi(0)|^2$, it is necessary[5] to experimentally determine the values of at least three independent magnetic hfs constants. Although Radford and Evenson[32] were able to measure three independent magnetic hfs constants, they considered the third $(a_{5/2,\ 3/2})$ of these to be subject to 5.3% experimental uncertainty. For this reason, they[32] did not attempt to directly deduce the three parameters $\langle r_l^{-3} \rangle$, $\langle r_S^{-3} \rangle$, and $|\psi(0)|^2$ from experiment. The approach adopted by Radford and Evenson was to assume that the spin density of ^2D N was identical to the experimentally determined[4] spin density of ^4S N. After postulating the spin density, they used their accurate values of $A_{5/2}$ and $A_{3/2}$ to deduce values of $\langle r_l^{-3} \rangle$ and $\langle r_S^{-3} \rangle$ for ^2D N.

We have defined the spin density as[1]

$$|\psi(0)|^2 = 2\langle J = L + S,$$

$$M_J = |\textstyle\sum_i \delta(\vec{r}_i) s_{zi} |J = L + S, M_J = J\rangle . \qquad (14)$$

However, Radford and Evenson[32] have used Harvey's definition[5] of the spin density. As defined by Harvey,[5] the spin density is equal to[48] $2S^{-1}$ times our spin density as given by Eq. (14).

Our calculated spin densities, which are given in Table VII, can be used to discuss the assumption of Radford and Evenson[32] that the spin density of ^2D N is the same as that of ^4S N. It is seen in Table VII that, using our definition of $|\psi(0)|^2$, the calculated values for ^2D N and ^4S N are very different. However, following the procedure of Radford and Evenson and using the definition of Harvey,[5] the polarization function spin density for ^2D N is 24% larger than that for ^4S N. And first-order wave functions yield a spin density for ^2D N which is 22% larger than that calculated for ^4S N. Since papers I and II showed that spin densities computed with polarization and first-order wave functions were always between 25 and 45% less than experiment, we can reasonably conclude that the true spin density of ^2D N is on the order of 25% larger than that of ^4S N.

Our calculations thus indicate that Radford and Evenson's assumption concerning the spin density of ^2D N leads to an error on the order of 25% in $|\psi(0)|^2$. However, the spin density is a much smaller contributor to the hfs than are the two parameters $\langle r_l^{-3} \rangle$ and $\langle r_S^{-3} \rangle$. Therefore, Radford and Evenson's deduced values of $\langle r^{-3} \rangle$

TABLE VII. Spin densities $|\psi(0)|^2$ for different states of the nitrogen atom. We define $|\psi(0)|^2 = 2\langle J=L+S, M_J = J|\Sigma_i \delta(\vec{r}_i)s_{zi}|J=L+S, M_J=J\rangle$. Harvey has defined a spin density which differs from ours by a factor of $1/2S$. For ^4S N, the spin densities according to the definition of Harvey are given in parentheses.

	^4S N	^2D N	^2P N
RHF	0.0 (0.0)	0.0	0.0
Polarization function	0.0730 (0.0243)[a]	0.0302	0.0313
First-order function	0.0714 (0.0238)[b]	0.0291	0.0274
Experiment	0.0972 (0.0324)[c]	...	...

[a] Reference 1a.

[b] Reference 1b.

[c] Reference 4.

may be quite close to the exact values.

The calculated values of $\langle r^{-3}\rangle$ for ^1D C, ^2D N, ^2P N, and ^1D O are given in Table VIII. Radford and Evenson's values[32] were 2.995 a.u. for $\langle r_l^{-3}\rangle$ and 3.293 a.u. for $\langle r_s^{-3}\rangle$. We expect our polarization function values of $\langle r_l^{-3}\rangle$ and $\langle r_s^{-3}\rangle$ to be the most accurate of the calculated values. From Table VIII, it is seen that our polarization function values 2.950 and 3.206 differ by 1.5 and 2.7% from the $\langle r_l^{-3}\rangle$ and $\langle r_s^{-3}\rangle$ values of Radford and Evenson. Since comparison with experiment in Paper I indicated that values calculated from polarization functions were within 2% of experiment, it is probable that the values given by Radford and Evenson[32] are close to the exact values. It is not clear to the present authors whether the calculated polarization function values or the values deduced by Radford and Evenson[32] represent the most reliable predictions of $\langle r_l^{-3}\rangle$ and $\langle r_s^{-3}\rangle$.

Table VIII also shows that it is unwise to attempt to transfer values of $\langle r^{-3}\rangle$ between different states of the same atom. For example, for the ^3P and ^1D states of oxygen, the difference between calculated values of $\langle r_l^{-3}\rangle$ is about 0.3 a. u. But this difference is comparable to the variations between $\langle r_l^{-3}\rangle$, $\langle r_s^{-3}\rangle$, and $\langle r_q^{-3}\rangle$ for the ^3P state of oxygen. An exception to this nontransferability of parameters is provided by the ^2D and ^2P states of nitrogen. The calculated values of $|\psi(0)|^2$, $\langle r_l^{-3}\rangle$, and $\langle r_s^{-3}\rangle$ are nearly the same for the ^2D state as for the ^2P state.

ACKNOWLEDGMENT

We wish to express our sincere gratitude to Professor Frank E. Harris, who sponsored this research, for many helpful discussions.

TABLE VIII. Calculated values of $\langle r^{-3}\rangle$ in a.u. For each entry, polarization function values are given above those obtained from first-order wave functions. The abbreviation NA indicates that an $\langle r^{-3}\rangle$ analysis is not applicable to a particular entry. For ^3P O, the experimental values of Harvey (Ref. 5) are given in parentheses. Calculated values for ^3P C and ^3P O are from Ref. 1. All other results are from the present research.

	$\langle r_l^{-3}\rangle$	$\langle r_s^{-3}\rangle$	$\langle r_q^{-3}\rangle$	$\langle r^{-3}\rangle_{\text{RHF}}$
^3P C	1.679	1.782	1.637	1.692
	1.663	1.769	1.537	
^1D C	1.609	NA	1.567	1.632
	1.595		1.465	
^2D N	2.950	3.206	NA	3.020
	2.933	3.189		
^2P N	2.954	3.233	NA	2.968
	2.939	3.207		
^3P O	4.613 (4.58)	5.125 (5.19)	4.334	4.973
	4.570	5.100	4.307	
^1D O	4.923	NA	4.591	4.925
	4.902		4.611	

[*] National Defense Education Act Title-IV predoctoral Fellow. Present address: Department of Chemistry, University of California, Berkeley, Calif. 94720.

[1] H. F. Schaefer, R. A. Klemm, and F. E. Harris, Phys. Rev. (a) 176, 49 (1968); (b) 181, 137 (1969).

[2] H. F. Schaefer and F. E. Harris, Phys. Rev. Letters 21, 1561 (1968).

[3] H. J. Silverstone and O. Sinanoglu, J. Chem. Phys. 44, 1899 (1966); 44, 3608 (1966).

[4] W. W. Holloway, E. Luscher, and R. Novick, Phys. Rev. 136, B27 (1964).

[5] J. S. M. Harvey, Proc. Roy. Soc. (London) A285, 581 (1965).

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

[7] N. Bessis, H. Lefebvre-Brion, and C. M. Moser, Phys. Rev. 124, 1124 (1962); 128, 213 (1962); 130, 1441 (1963).

[8] N. Bessis, H. Lefebvre-Brion, and C. M. Moser, Rev. Mod. Phys. 35, 1441 (1963).

[9] G. Malli and S. Fraga, Theoret. Chim. Acta 6, 54, 278 (1966); 7, 75 (1967).

[10] W. A. Goddard, Phys. Rev. (a) 157, 93 (1967); (b) 176, 106 (1968).

[11] B. Liu and P. S. Bagus (unpublished). Numerical UHF calculations for first-row atoms.

[12] U. Kaldor, J. Chem. Phys. 48, 835 (1968); 49, 6 (1968).

[13] U. Kaldor, Phys. Rev. 176, 19 (1968); 176, 71 (1968).

[14] U. Kaldor, H. F. Schaefer, and F. E. Harris, Intern. J. Quantum Chem. 2S, 13 (1968).

[15] H. P. Kelly, Phys. Rev. 173, 142 (1968).

[16] N. C. Dutta, C. Matsubara, R. T. Pu, and T. P. Das, Phys. Rev. 177, 33 (1969).

[17] N. C. Dutta, C. Matsubara, R. T. Pu, and T. P. Das, Phys. Rev. Letters 21, 1139 (1968).

[18] K. A. Brueckner, Phys. Rev. 97, 1353 (1955); 100, 36 (1955).

[19] J. Goldstone, Proc. Roy. Soc. (London) A239, 267 (1957).

[20] H. P. Kelly, Phys. Rev. 131, 684 (1963); 136, B896 (1964); 144, 39 (1966).

[21] (a) E. S. Chang, R. T. Pu, and T. P. Das, Phys. Rev. 174, 1 (1968); (b) J. D. Lyons, R. T. Pu, and T. P. Das, *ibid.* 178, 103 (1969).

[22] R. K. Nesbet, Colloq. Intern. Centre Natl. Rech. Sci. (Paris) 164, 87 (1967). In more recent (1968) unpublished work on the ground states of B, C, N, O, and F, Nesbet found that his Bethe-Goldstone procedure, including one- and two-particle correlations, resulted in erratic spin densities. For nitrogen, however, inclusion of three particle terms gave good agreement with experiment.

[23] H. F. Schaefer and U. Kaldor, J. Chem. Phys. 49, 469 (1968).

[24] P. G. H. Sandars, Colloq. Intern. Centre Natl. Rech. Sci. (Paris) 164, 111 (1967).

[25] B. R. Judd, Colloq. Intern. Centre Natl. Rech. Sci. (Paris) 164, 311 (1967).

[26] H. P. Kelly, Phys. Rev. 180, 55 (1969).

[27] W. A. Goddard, Phys. Rev. (to be published).

[28] J. A. Pople and R. K. Nesbet, J. Chem. Phys. 22, 571 (1954).

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

[30] R. W. B. Ardill and A. L. Stewart, Proc. Phys. Soc. (London) 92, 296 (1968).

[31] U. Kaldor and F. E. Harris, Phys. Rev. (to be published).

[32] H. E. Radford and K. M. Evenson, Phys. Rev. 168, 70 (1968).

[33] H. F. Schaefer, R. A. Klemm, and F. E. Harris, J. Chem. Phys. (to be published).

[34] H. F. Schaefer and F. E. Harris, J. Comput. Phys. 3, 217 (1968).

[35] E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. 127, 1618 (1962).

[36] H. F. Schaefer and F. E. Harris, Phys. Rev. 167, 67 (1968); 170, 108 (1968).

[37] H. F. Schaefer, Ph. D. thesis, Stanford University, 1969 (unpublished).

[38] A. Veillard and E. Clementi, J. Chem. Phys. 49, 2415 (1968).

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

[40] Using the most recent tabulation of the fundamental constants, E. R. Cohen and J. W. DuMond, Rev. Mod. Phys. 37, 537 (1965).

[41] For a discussion of reduced matrix elements, see M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

[42] G. Racah, Phys. Rev. 62, 438 (1942).

[43] M. Karplus (private communication). We wish to thank Professor Karplus for this suggestion.

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

[45] G. H. Fuller and V. W. Cohen, Nucl. Data Tables, U.S. At. Energy Comm. A5, 433 (1969).

[46] C. T. O'Konski and T.-K. Ha, J. Chem. Phys. 49, 5354 (1968).

[47] A. D. McLean and M. Yoshimine, Bull. Am. Phys. Soc. 13, 373 (1968).

[48] J. S. M. Harvey (private communication).