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Evaluation of the Orbit-Dependent Hyperfine Constants of the $2p$-Series Atoms from Multiconfiguration Hartree-Fock Wave Functions

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The values of the orbit-dependent hyperfine-structure constants are given for the ground-state terms of the atoms B, C, O, and F. These values are obtained from multiconfiguration Hartree-Fock wave functions using a very limited number of excited terms. The excited terms are chosen from guidelines based on second-order perturbation theory. The results are in satisfactory agreement with available experimental data and accurate many-body perturbation-theory calculations for O. A physical explanation, in terms of the configuration-interaction model, is presented for the essential importance of non-core-polarization contributions to the Fermi contact term for these atoms.

I. INTRODUCTION

The accurate *ab initio* calculation of the hyperfine-structure (hfs) constants of the ground-state terms of the $2p$-series atoms is of considerable current interest.[1-5] In fact, the determination of their values has been a challenging problem since Harvey[6] measured very accurately the hfs of the ground ^3P term of O^{17} and the ground ^2P term of F^{19}.

The magnetic and electric quadrupole hfs Hamiltonian may be written, in a nonrelativistic approximation, as

$$H_{\mathrm{hfs}} = \frac{2\mu_I\mu_B\mu_N}{I}\vec{\mathrm{I}}^{(1)} \times \sum_i \left[\frac{\vec{l}_i}{r_i^3} - (10)^{1/2}\frac{\{\vec{\mathrm{s}}^{(1)}\vec{\mathrm{C}}^{(2)}\}_i^{(1)}}{r_i^3} + \frac{8\pi}{3}\delta(\vec{\mathrm{r}}_i)\vec{\mathrm{s}}_i^{(1)}\right] - \left(\frac{3}{2}\right)^{1/2}\frac{e^2Q}{I(2I-1)}\{\vec{\mathrm{I}}^{(1)}\vec{\mathrm{I}}^{(1)}\}^{(2)}\cdot\sum_i\left[\frac{\vec{\mathrm{C}}_i^{(2)}}{r_i^3}\right], \qquad (1)$$

where μ_I is the nuclear magnetic moment in units of μ_N. Harvey[6] showed that, for pure L-S coupling (taking into account small departures from this coupling for 0), three parameters were required for the magnetic and one for the electric quadrupole parts of the hfs Hamiltonian to explain the observed hfs. The parameters are denoted as (1) the core-polarization quantity $|\psi(0)|^2$, with its angular coefficient proportional to $(g_{\alpha J}-1)$, where $g_{\alpha J}$ is the Lande factor of the level αJ considered[7]; (2) instead of the usual single radial integral $\langle r^{-3}\rangle$ for the $2p$ electron, two different ones, denoted $\langle r_l^{-3}\rangle_{2p}$ and $\langle r_{sC}^{-3}\rangle_{2p}$, to be used, respectively, in the matrix elements of the $l^{(1)}$ and the $\{s^{(1)}C^{(2)}\}^{(1)}$ parts of H_{hfs}; and (3) a parameter $\langle r_Q^{-3}\rangle_{2p}$ to be used in the electric quadrupole part of H_{hfs}. In particular, he showed that $\langle r_l^{-3}\rangle_{2p}$ and $\langle r_{sC}^{-3}\rangle_{2p}$ are different by more than 10% for both O^{17} and F^{19}. Shortly afterward, Judd[8] interpreted the difference between $\langle r_l^{-3}\rangle$ and $\langle r_{sC}^{-3}\rangle$ in terms of far-configuration interactions. Moreover, he showed that the third radial quantity, $\langle r_Q^{-3}\rangle$, used for the derivation of the nuclear quadrupole moment Q from the electric-quadrupole experimental constants, must be different from the other two.

Our aim in the present work is to find to which accuracy a simple multiconfigurational Hartree-Fock (MCHF) computation can interpret the values of $\langle r_l^{-3}\rangle_{2p}$, $\langle r_{sC}^{-3}\rangle_{2p}$, and $\langle r_Q^{-3}\rangle_{2p}$ in the ground-state terms of the $2p$-series atoms. We first give the principles of our computations, then the results, and finally discuss the achievements and the shortcomings of the MCHF method for the problem considered. Information is also presented concerning the quantity $|\psi(0)|^2$.

II. PRINCIPLES

A. MCHF Method

The principle of the MCHF method is well known from the work of Hartree *et al.*[9] It can be sketched in the following way: once a given set of Russell-Saunders (RS) terms from various configurations is assumed to contribute appreciably to the wave function ψ of a state, the MCHF method yields the radial orbital functions and the weights of the terms which make the total electronic energy E of that state stationary. (Of course, for the lowest state of a given symmetry this energy is minimized.) The electronic Hamiltonian is the usual electrostatic fixed nucleus Hamiltonian given in atomic units (a.u.) by

$$H_{\mathrm{elec}} = -\tfrac{1}{2}\sum_i \nabla_i^2 - \sum_i Z/r_i + \sum_{i>j} 1/r_{ij}. \qquad (2)$$

In the following, we shall call its three parts, respectively, the kinetic, central-field, and Coulomb operators. We shall also use atomic units for energy and length; the conversion factors[10] to eV and Å are

$$1 \text{ a.u.} = 27.2117 \text{ eV}, \; 1 \text{ Bohr} = 1a_0 = 0.529\,177 \text{ Å}.$$

For all the wave-function calculations, we have used a MCHF program developed and written by Froese-Fischer[11] and modified by one of us (P.S.B.). This program solves for the radial wave functions by direct numerical integration of the MCHF integro-differential equations. Thus we avoid the problem of optimizing the nonlinear parameters of basis functions which arises in analytic expansion approaches[12] to the solution of these equations.

B. Choice of Configurations

We are interested only in the ground-state terms of boron (B), carbon (C), oxygen (O), and fluorine (F). Indeed, the nitrogen ground term is experimentally an almost pure ^4S term, to whose hyperfine structure only the core polarization contributes appreciably.

As a compromise between accuracy and simplicity, we aim to introduce in every computation, together with the ground-state term T_0 of $1s^2 2s^2 2p^N$, only the excited configurations which, when looked upon in the central-field perturbation method, contribute to the crossed second order of the Coulomb and hfs operators. In other words, we introduce those excited configurations which give rise to nonzero off-diagonal matrix elements of $H_{\rm hfs}$ with the ground configuration. Because the three hfs operators of interest are of the double tensor type $T^{(\kappa k)}$ with $k = 1$ or 2, we see that the relevant excitations are the following:

$$1s \to nd, \quad 2s \to n'd,$$
$$2p \to nf, \quad 2p \to np.$$

If we had introduced only one of these types of excitations with only one type of coupling at a time in a series of MCHF calculations, then it would have been necessary to use only one configuration (and one new orbital) for each of the excitations. This is easily seen by noting, for example, that

$$\begin{aligned}\psi &= c_1 \,|1s^2 2s^2 2p^2\,{}^3P) + \sum_n \alpha_n \,|[(1snd)\,{}^3D\,2s^2 2p^2\,{}^1D]\,{}^3P)\\ &= c_1\,|1s^2 2s^2 2p^2\,{}^3P) + \alpha'\,|[(1sd')\,{}^3D 2s^2 2p^2\,{}^1D]\,{}^3P),\end{aligned} \tag{3}$$

where

$$\begin{aligned}\alpha' &= \Big[\sum_n \alpha_n^2\Big]^{1/2},\\ d' &= \sum_n \alpha_n nd/\alpha'.\end{aligned} \tag{4}$$

Since we introduce all these excitations and certain others, as well, at one time, we should, in principle, use several orbitals for each type of excitation. For simplicity and because the interactions among the excitations will not, in general, greatly change the MCHF equations for the added orbitals, we will use only one orbital for each of these excitations. We will, however, construct configurations (terms) for all allowed angular momentum couplings using that orbital. (In the following, we shall use the words configuration and term interchangeably to refer to definite eigenfunctions of L^2 and S^2. The word configuration may also be used to refer only to the distribution of electrons into orbitals. The meaning of these words will be clear from their content.) For example, for the $1s \to d_I$ excitation for C, we introduce the following three configurations:

$$|[(1sd_{\rm I})\,{}^3D 2s^2 2p^2\,{}^1D]\,{}^3P),$$
$$|[(1sd_{\rm I})\,{}^3D 2s^2 2p^2\,{}^3P]\,{}^3P),$$
$$|[(1sd_{\rm I})\,{}^1D 2s^2 2p^2\,{}^3P]\,{}^3P).$$

We will show, in Sec. IV, that for O the second-order contributions for these excitations using just one MCHF orbital for each excitation are usually close to the second-order contributions obtained by Kelly[3(a)] using many-body perturbation theory. We denote the orbital used for each type of excitation as follows:

$$\begin{aligned}&d_{\rm I};\; 1s \to d_{\rm I},\\ &d_{\rm II}:,\; 2s \to d_{\rm II},\\ &f_{\rm II};\; 2p \to f_{\rm II},\\ &p_{\rm II};\; 2p \to p_{\rm II}.\end{aligned} \tag{5}$$

It has been shown for carbon[13] and for other first-row atoms,[13,14] that the "quasidegenerate" excitation $2s^2 2p^N \to 2p^{N+2}$ is extremely important for the calculation of the total electronic energy. Thus, although the $1s^2 2p^{N+2}$ configuration brings no second-order contribution to the hfs, we add it to the list of singly excited configurations retained above. In a sense, if the Coulomb interaction is neglected entirely, this configuration represents a "zero-order" correction for $H_{\rm elec}$.

The $1s \to d_{\rm I}$ excitation makes only a very small contribution to the energy, ~0.000 04 a.u. for O. Because of this small contribution we had difficulty solving the $d_{\rm I}$ MCHF orbital equation. To overcome this difficulty, we introduced the double-excited configuration $d_{\rm I}{}^2({}^1S)2s^2 2p^N$ which makes a much larger contribution to the energy ~0.003 a.u. for O.

The $2p \to p_{\rm II}$ excitation presented a different problem. In general, the off-diagonal matrix elements $(2p^{N-1}p_{\rm II}\,|H_{\rm elec}|\,2p^N)$ will include integrals involving the kinetic energy and central-field operators. Because of limitations in the computer program,[11] we were not able to introduce terms with off-diagonal matrix elements of this form into the calculation. If, however, the term $(2p)^N\alpha SL$ has several parents, there correspond several terms SL in the configuration $2p^{N-1}p_{II}$. Following Bauche and Klapisch,[15] we note that one of these terms (or the only term if there is only one) may be written as

$$\psi_x = \sum (p^{N-1}\overline{\psi}, p\,|\}\,p^N\alpha SL)\,|[(2p)^{N-1}\overline{\psi}, p_{II}]SLM_LM_s\rangle, \tag{6}$$

where $(p^{N-1}\overline{\psi}, p\,|\}\,p^N\alpha SL)$ is a fractional parentage coefficient.[16] It can be shown that while $(\psi_x\,|H_{\text{elec}}|\,2p^N)$ does include one-electron terms, the matrix elements for terms orthogonal to ψ_x do not. Thus, although we cannot include terms of the form ψ_x, we can and do include the terms orthogonal to ψ_x. There are two such terms for O and F, respectively.

Bauche and Klapisch[15] have shown that, as an extension of Brillouin's theorem, $(\psi_x\,|H_{\text{elec}}|\,2p^N)$ has a numerical value of zero for the Hartree-Fock solution for the configuration $2p^N$ provided only that p_{II} in ψ_x is orthogonal to the Hartree-Fock $2p$ orbital. Although this matrix element will not be zero for the $2p^N$ configuration constructed from the MCHF orbitals, we expect that it will have a small value. Thus, the term ψ_x will probably not make a significant contribution to the electronic wave function or to the hfs constants and its inclusion would not significantly change our results.

As we noted above, our configurations are related to those which contribute to the hfs constants in crossed second-order perturbation theory. They are also related to those used by Schaefer *et al.*[5] in constructing wave functions which they described as polarization and "first-order" wave functions. We discuss briefly, below, the relationship between our work and these two approaches.

In addition to the excitations of Eq. (5), we have included $2s^22p^N \to 2p^{N+2}$ and $1s^2 \to d_I^2$, which do not contribute to the hfs constants in second order. (We shall discuss in Sec. IV the effect of including the latter excitation on the second-order contributions from $1s$ excitations.) However, we note that we compute the hfs constants as expectation values of H_{hfs} for our MCHF wave functions. Moreover, we solve orbital equations for the $1s$, $2s$, and $2p$ orbitals and do not leave them fixed as HF orbitals. We shall, in Sec. IV, compare for O both the second-order hfs constants obtained using our MCHF orbitals and our results for $\langle\psi_{\text{MCHF}}\,|H_{\text{hfs}}|\,\psi_{\text{MCHF}}\rangle$ with Kelly's second- and higher-order perturbation-theory results.

The polarization wave function of Schaefer *et al.*[5(a)] includes the excitations described by Eq. (5) and also $1s \to s$ and $2s \to s$ excitations. The first-order wave function[5(b)] includes the polarization excitations plus double excitations provided that at least one excitation is into the $2p$ shell. Except for $2s^22p^N \to 2p^{N+2}$ and $1s^2 \to d_I^2$, our excitations are a subset of those used for the polarization functions; and except for $1s^2 \to d_I^2$, they are a subset of those used for the first-order functions. Both polarization and first-order functions were determined by traditional configuration-interaction (CI) methods using a fairly large set of orbitals. Thus, the polarization functions contained 53, 65, 77, and 65 configurations, respectively, for B, C, O, and F, and the first-order functions contained 153, 181, 113, and 95 configurations, respectively; our MCHF wave functions contained only 7, 9, 11, and 9.

III. RESULTS

A. Configurations Used for the MCHF Wave Functions

Table I lists the excited Russell-Saunders terms T_i introduced in the four MCHF computations for B, C, O, and F. The terms noted T_9 and T_{10} (for O) and T_7 and T_8 (for F) cannot be written in concise form, as they are selected linear combinations of terms of the type $(1s^22s^22p^{N-1}S_1L_1, p_{II})SL$ (see above). They are for O

$$\begin{aligned} T_9 &\propto \sqrt{3}\,|[1s^22s^22p^3\,{}^2D, p_{II}]\,{}^3P\rangle \\ &\quad + \sqrt{5}\,|[1s^22s^22p^3\,{}^2P, p_{II}]\,{}^3P\rangle, \\ T_{10} &\propto 4\,|[\cdots 2p^3\,{}^4S, p_{II}]\,{}^3P + \sqrt{5}\,|[\cdots 2p^3\,{}^2D, p_{II}]\,{}^3P\rangle \\ &\quad - \sqrt{3}\,|[\cdots 2p^3\,{}^2P, p_{II}]\,{}^3P\rangle, \end{aligned} \tag{7}$$

and for F

$$\begin{aligned} T_7 &\propto |[1s^22s^22p^4\,{}^1D, p_{II}]\,{}^2P\rangle \\ &\quad - \sqrt{5}\,|[1s^22s^22p^4\,{}^1S, p_{II}]\,{}^2P\rangle, \\ T_8 &\propto 2\,|[\cdots 2p^4\,{}^3P, p_{II}]\,{}^2P\rangle \\ &\quad - \sqrt{5}\,|[\cdots 2p^4\,{}^1D, p_{II}]\,{}^2P\rangle \\ &\quad - |[\cdots 2p^4\,{}^1S, p_{II}]\,{}^2P\rangle. \end{aligned} \tag{8}$$

To eliminate any ambiguity as to the phases of the various states, we present in the last column of the table the expressions for the off-diagonal matrix elements of H_{elec} between the excited terms and the corresponding ground terms T_0. In the relevant Slater integrals, the symbols nl have been omitted for brevity.

TABLE I. Configurations used in the MCHF calculations on boron, carbon, oxygen, and fluorine. The matrix elements of H_{elec} between the excited configurations and the reference configuration $(1s^2 2s^2 2p^n)$ are given in terms of Slater integrals. The orbital indices of the Slater G^ν and R^ν integrals are suppressed.

Excitation	i	Configuration (T_i)	$\langle T_0 \vert H_{\text{elec}} \vert T_i \rangle$	i	Configuration (T_i)	$\langle T_0 \vert H_{\text{elec}} \vert T_i \rangle$
		Boron			Carbon	
None	0	$[1s^2 2s^2 2p]\,^2P$	$\cdots$	0	$[1s^2 2s^2 2p^2]\,^3P$	$\cdots$
$2s^2 \rightarrow 2p^2$	1	$[1s^2 2p^3]\,^2P$	$-\sqrt{2}G^1/3$	1	$[1s^2 2p^4]\,^3P$	$G^1/3$
$1s \rightarrow d_{\text{I}}$	2	$[(1sd_{\text{I}})^3D 2s^2 2p]\,^2P$	$R^1/\sqrt{3}$	2	$[(1sd_{\text{I}})^3D 2s^2 (2p^2)^3P]\,^3P$	$-\sqrt{2}R^1/3$
	3	$[(1sd_{\text{I}})^1D 2s^2 2p]\,^2P$	$-2R^2/5+R^1/3$	3	$[(1sd_{\text{I}})^3D 2s^2 (2p^2)^1D]\,^3P$	$-R^1/\sqrt{3}$
				4	$[(1sd_{\text{I}})^1D 2s^2 (2p^2)^3P]\,^3P$	$2R^2/5-R^1/3$
$1s^2 \rightarrow d_{\text{I}}^2$	4	$[(d_{\text{I}}^2)^1S 2s^2 2p]\,^2P$	$G^2/5$	5	$[(d_{\text{I}}^2)^1S 2s^2 (2p^2)^3P]\,^3P$	$G^2/\sqrt{5}$
$2s \rightarrow d_{\text{II}}$	5	$[1s^2 (2sd_{\text{II}})^3D 2p]\,^2P$	$R^1/\sqrt{3}$	6	$[1s^2 (2sd_{\text{II}})^3D (2p^2)^3P]\,^3P$	$-\sqrt{2}R^1/3$
	6	$[1s^2 (2sd_{\text{II}})^1D 2p]\,^2P$	$-2R^2/5+R^1/3$	7	$[1s^2 (2sd_{\text{II}})^3D (2p^2)^1D]\,^3P$	$-R^1/\sqrt{3}$
				8	$[1s^2 (2sd_{\text{II}})^1D (2p^2)^3P]\,^3P$	$2R^2/5-R^1/3$
		Oxygen			Fluorine	
None	0	$[1s^2 2s^2 2p^4]\,^3P$	$\cdots$	0	$[1s^2 2s^2 2p^5]\,^2P$	$\cdots$
$1s \rightarrow d_{\text{I}}$	1	$[(1sd_{\text{I}})^3D 2s^2 (2p^4)^3P]\,^3P$	$-\sqrt{2}R^1/3$	1	$[(1sd_{\text{I}})^3D 2s^2 2p^5]\,^2P$	$R^1/\sqrt{3}$
	2	$[(1sd_{\text{I}})^3D 2s^2 (2p^4)^1D]\,^3P$	$-R^1/\sqrt{3}$	2	$[(1sd_{\text{I}})^1D 2s^2 2p^5]\,^2P$	$2R^2/5-R^1/3$
	3	$[(1sd_{\text{I}})^1D 2s^2 (2p^4)^3P]\,^3P$	$-2R^2/5+R^1/3$			
$1s^2 \rightarrow d_{\text{I}}^2$	4	$[(d_{\text{I}})^{2\,1}S 2s^2 (2p^4)^3P]\,^3P$	$G^2/\sqrt{5}$	3	$[(d_{\text{I}})^{2\,1}S 2s^2 2p^5]\,^2P$	$G^2/\sqrt{5}$
$2s \rightarrow d_{\text{II}}$	5	$[1s^2 (2sd_{\text{II}})^3D (2p^4)^3P]\,^3P$	$-\sqrt{2}R^1/3$	4	$[1s^2 (2sd_{\text{II}})^3D 2p^5]\,^2P$	$R^1/\sqrt{3}$
	6	$[1s^2 (2sd_{\text{II}})^3D (2p^4)^1D]\,^3P$	$-R^1/\sqrt{3}$	5	$[1s^2 (2sd_{\text{II}})^1D 2p^5]\,^2P$	$2R^2/5-R^1/3$
	7	$[1s^2 (2sd_{\text{II}})^1D (2p^4)^3P]\,^3P$	$-2R^2/5+R^1/3$			
$2p \rightarrow f_{\text{II}}$	8	$[1s^2 2s^2 (2p^3)^2D f_{\text{II}}]\,^3P$	$-3\sqrt{2}R^2/5\sqrt{5}$	6	$[1s^2 2s^2 (2p^4)^1D f_{\text{II}}]\,^2P$	$3\sqrt{2}R^2/5\sqrt{5}$
$2p \rightarrow P_{\text{II}}$	9	T_9	$3R^2/5\sqrt{16}$	7	T_7	$3R^2/5\sqrt{10}$
(See text)	10	T_{10}	$-3R^2/5\sqrt{2}$	8	T_8	$3\sqrt{3}R^2/5\sqrt{10}$

TABLE II. Orbital properties (in a.u.) of the MCHF orbitals.

	Boron			Carbon			Oxygen			Fluorine		
	ϵ	A_0	$\langle r \rangle$	ϵ	A_0	$\langle r \rangle$	ϵ	A_0	$\langle r \rangle$	ϵ	A_0	$\langle r \rangle$
$1s$	7.6743	20.8919	0.3239	11.3100	27.7754	0.2663	20.6480	43.4382	0.1960	26.3552	52.0800	0.1733
$2s$	0.5277	3.9254	1.9669	0.7374	5.4233	1.5856	1.2789	8.4495	1.1435	1.6098	10.2271	1.0031
$2p$	0.3852	3.3444	2.0830	0.4756	6.0988	1.6820	0.6515	14.6432	1.2276	0.7401	20.6062	1.0831
d_{I}	50.9400	562.6949	0.3603	73.9037	1087.7641	0.3001	133.9072	3090.7272	0.2233	172.8751	4785.8900	0.1963
d_{II}	0.6071	1.3788	2.3900	0.8105	3.0945	1.9530	1.4030	10.5219	1.4184	1.7985	16.5900	1.2433
f_{II}							0.6984	16.5552	1.6273	0.8059	30.6688	1.4390
p_{II}							0.6606	8.8918	2.7316	0.8388	12.6487	2.4093

TABLE III. MCHF energies and weights of the terms. The list of terms is in the same order as in Table I.

	B	C	O	F
Excitation		Weights		
None	0.963 68	0.977 19	0.991 27	0.995 67
$2s^2 \rightarrow 2p^2$	0.227 42	−0.146 04		
$1s \rightarrow d_{\mathrm{I}}$	−0.000 49	0.000 41	0.000 37	−0.000 43
	0.000 32	0.000 50	0.000 46	−0.000 21
		−0.000 29	0.000 23	
$1s^2 \rightarrow d_{\mathrm{I}}^2$	−0.005 57	−0.004 70	−0.003 55	−0.003 15
$2s \rightarrow d_{\mathrm{II}}$	0.137 89	−0.097 36	−0.067 68	0.074 45
	−0.023 35	−0.117 47	−0.087 56	−0.002 78
		0.021 60	0.005 19	
$2p \rightarrow f_{\mathrm{II}}$			0.033 86	−0.030 02
$2p \rightarrow p_{\mathrm{II}}$			−0.021 32	−0.020 38
			0.059 14	−0.042 08
Wave function		Energies (a.u.)		
Hartree-Fock	−24.529 07	−37.688 63	−74.809 41	−99.409 36
MCHF (this work)	−24.584 36	−37.746 25	−74.856 02	−99.439 86
Polarization[a]	−24.551 29	−37.728 14	−74.855 71	−99.438 11
First-order[a]	−24.587 42	−37.750 68	−74.858 98	−99.439 76

[a] See Ref. 5.

B. MCHF Results: Properties of Wave Functions

We first built the complete matrices of the Coulomb operator for the chosen terms. The orders of the matrices are equal to 7, 9, 11, and 9 for B, C, O, and F, respectively. Then the four MCHF computations were performed.

The main features of the radial functions obtained are listed in Table II. They are, for each orbital: ϵ_{nl}, the orbital energy; $A_0(nl) = [R_{nl}(r)/r^l]_{r=0}$, where $R_{nl}(r)$ is the radial wave function; and $\langle r\rangle_{nl}$, the mean value of r for the nl orbital.

The mixing coefficients of the terms and total electronic energies are given in Table III. For each atom, the terms appear in the same order as in Table I. We compare our electronic energies with the Hartree-Fock values and those obtained by Schaefer *et al.*[5] for their polarization and first-order wave functions. To obtain the Hartree-Fock values given in this and the following table, we have computed the Hartree-Fock wave functions using the MCHF program.[11] It is interesting to note that our MCHF energies are very close to the energies obtained by Schaefer *et al.*[5] for their first-order wave functions.

C. MCHF Results: Hyperfine Structure Constants

We constructed the matrices of the $l^{(1)}$, $\{s^{(1)}C^{(2)}\}^{(1)}$, and $C^{(2)}$ parts of H_{hfs} for the chosen terms. Using the MCHF radial functions we obtained by numerical integration the values of all necessary integrals

$$\int_0^\infty R_{nl}(r)\frac{1}{r^3}R_{n'l}(r)r^2dr.$$

These integrals were used to evaluate $\langle \Psi_{\mathrm{MCHF}}|H_{\mathrm{hfs}}|\Psi_{\mathrm{MCHF}}\rangle$. Table IV presents, under the heading MCHF (nonrelativistic), our results for the hyperfine structures of the $1s^22s^22p^N$ Hund terms, in terms of effective values of $\langle r_l^{-3}\rangle_{2p}$, $\langle r_{sC}^{-3}\rangle_{2p}$, and $\langle r_Q^{-3}\rangle_{2p}$. We also present in this table, Kelly's[3(a)] many-body perturbation-theory results (MBPT) for O, and the polarization and first-order wave-function results of Schaefer *et al.*[5] Values of $\langle r^{-3}\rangle$ derived from experiment[6] are presented for O and F. For comparison with these experimental values we have included relativistic corrections to our MCHF results. These corrections are taken from Judd.[8,17]

IV. DISCUSSION

A. Comparison with Experiment

Through his experiments,[6] Harvey determined the quantities $\langle r_l^{-3}\rangle_{2p}$ and $\langle r_{sC}^{-3}\rangle_{2p}$ for O and F ground terms. From Table IV, we note that our MCHF values including relativistic corrections are within 2% of the experimental values for O and within 1% for F. Our values are not as accurate as those of Kelly,[3(a)] which are the best yet computed. But, in view of the simplicity of the model used, they are very satisfactory.

Our values are close to and always larger than the values obtained by Schaefer *et al.*[5] using polarization and first-order wave functions. For O, their results appear to be in slightly better agreement with experiment than ours; for F, this situation is reversed. This agreement with their results is impressive indeed when we consider the simplicity of our wave functions.

B. Reduction of Number of Excited Terms

Limited as it is, the set of excited terms which we used can be further reduced if we content ourselves with including only configurations which can make contributions to the hfs in true second-order perturbation theory. We recall, following Kelly,[5] that the first-order perturbation contribution to the hfs involves only the matrix element $\langle T_0 | H_{\text{hfs}} | T_0 \rangle$; that second-order perturbation contributions involve products $\langle T_0 | H_{\text{hfs}} | T_i \rangle \times \langle T_i | H_{\text{elec}} | T_0 \rangle$; and that higher- ($n$th) order contributions involve products of one matrix element of H_{hfs} and several ($n-1$) of H_{elec}.

TABLE IV. Values of $\langle r^{-3} \rangle_{2p}$ in a.u. The MCHF values are compared to other calculated values and to those obtained from experiment.

			B	C	O	F
$\langle r_l^{-3} \rangle_{2p}$	MCHF	nonrel.	0.801	1.682	4.647	7.313
	(this work)	rel.[a]	0.802	1.685	4.663	7.345
	MBPT[b]	nonrel.	...	...	4.547	...
		rel.	...	...	4.563	...
	Polarization wave function[c]		0.767	1.679	4.613	7.276
	First-order wave function[c]		0.757	1.663	4.570	7.234
	Experiment[d]		...	...	4.58	7.35
$\langle r_{sC}^{-3} \rangle_{2p}$	MCHF	nonrel.	0.884	1.829	5.240	8.121
	(this work)	rel.[a]	0.887	1.838	5.285	8.209
	MBPT[b]	nonrel.	...	...	5.126	...
		rel.	...	...	5.170	...
	Polarization wave function[c]		0.830	1.782	5.125	7.963
	First-order wave function[c]		0.817	1.769	5.100	7.950
	Experiment[d]		...	...	5.19	8.14
$\langle r_Q^{-3} \rangle_{2p}$	MCHF	nonrel.	0.695	1.504	4.241	6.745
	(this work)	rel.[a]	0.696	1.507	4.257	6.777
	MBPT[b]	nonrel.	...	...	4.205	...
		rel.	...	...	4.216	...
	Polarization wave function[c]		0.744	1.637	4.334	6.880
	First-order wave function[c]		0.683	1.537	4.307	6.852
$\langle r^{-3} \rangle$	Hartree-Fock[e]		0.776	1.692	4.974	7.545

[a] Relativistic corrections are taken from Judd, Refs. 8 and 17.
[b] Many-body perturbation-theory results of Kelly, Ref. 3(a).
[c] Schaefer, Klemm, and Harris, Ref. 5. Relativistic corrections are not included.
[d] Harvey, Ref. 6.
[e] The restricted Hartree-Fock values have been recomputed for numerical wave functions.

TABLE V. Second-order contributions to the hfs in oxygen.

	$\langle r_l^{-3} \rangle$		$\langle r_{sC}^{-3} \rangle$		$\langle r_Q^{-3} \rangle$	
	This work	Kelly[a] MBPT	This work	Kelly[a] MBPT	This work	Kelly[a] MBPT
$1s \to d$	0	0	0.226	0.141	−0.193	−0.115
$2s \to d$	0	0	0.086	0.077	0.009	−0.007
$2p \to f$	0	0	0.072	0.065	−0.072	−0.065
$2p \to p$	−0.246	−0.229	−0.049	−0.046	−0.442	−0.412

[a] Reference 3(a).

As an example, we show how this reduction of configurations may be made for O. For the $2p \to p_{\text{II}}$ excitation, we form the orthogonal linear combinations [cf Eq. (7)]:

$$\begin{aligned} |T_9'\rangle &= \sqrt{5}\,|T_9\rangle/\sqrt{6} + |T_{10}\rangle/\sqrt{6}\,, \\ |T_{10}'\rangle &= |T_9\rangle/\sqrt{6} - \sqrt{5}\,|T_{10}\rangle/\sqrt{6}\,. \end{aligned} \tag{9}$$

From Table I, we note that $\langle T_0 | H_{\text{elec}} | T_9' \rangle = 0$. Thus only T_{10}' will make a second-order perturbation contribution to the hfs. In an analogous way, the terms T_1 and T_2 of Table I can be transformed into

$$\begin{aligned} |T_1'\rangle &= \sqrt{3}\,|T_1\rangle/\sqrt{5} - \sqrt{2}\,|T_2\rangle/\sqrt{5}\,, \\ |T_2'\rangle &= \sqrt{2}\,|T_1\rangle/\sqrt{5} + \sqrt{3}\,|T_2\rangle/\sqrt{5}\,; \end{aligned} \tag{10}$$

and the term T_1' can be deleted for the purpose of second-order computations. The same applies to T_5 and T_6. Thus, if we wish to include in our MCHF calculation only configurations which can contribute in true second-order perturbation theory to $\langle r^{-3} \rangle$, we require only 7, 7, 8, and 8 terms for B, C, O, and F, respectively.

We can now examine whether the contributions to the hfs from configurations which contribute first to the third and higher orders are important. For example, for our 11-configuration MCHF wave function for O, we have calculated the contributions to the hfs parameters from T_9' and T_{10}' [cf. Eq. (9)] as

$$C_0 C_i' \langle T_0 | H_{\text{hfs}} | T_i' \rangle\,,$$

where $i = 9$ or 10 and C_0 and C_i' are the MCHF mixing coefficients of $|T_0\rangle$ and $|T_i'\rangle$, respectively. We find that the contribution to $\langle r_l^{-3} \rangle_{2p}$ from T_{10}' is -0.246 a.u., whereas that from T_9' is -0.033.

This indicates that these configurations can contribute to the hfs well over 10% of the second-order effects.

C. Oxygen: Comparison with Kelly's Results

For oxygen, we can test the quality of our results in more detail. In his paper,[3(a)] Kelly lists the second-order contributions to the $\langle r^{-3}\rangle$ quantities, obtained by MBPT. Table V presents his results and ours for the four relevant excitations and the three interesting parts of the hfs. Our second-order values are computed after transforming T_1, T_2, T_5, T_6, T_9, and T_{10}, as explained above, and deleting the contributions coming from T_1', T_5', and T_9'. The second-order values are obtained, as described above, from

$$C_0 \sum_i C_i \langle T_0 | H_{\text{hfs}} | T_i \rangle ,$$

where the sum over i is not taken for 1, 5, and 9 and the primed quantities are used for $i = 2$, 6, and 10.

Considering the figures for $\langle r_{sC}^{-3}\rangle$, we see that, for the $2s$ and $2p$ excitations, our values differ from Kelly's by approximately 10%. In contrast, for the $1s \rightarrow d_{\text{I}}$ excitation, our value is in excess by about 60% with respect to Kelly's figure. This difference in behavior is confirmed by the figures for $\langle r_l^{-3}\rangle$ and $\langle r_Q^{-3}\rangle$. To try and interpret this we looked at the contribution of the $1s \rightarrow d_{\text{II}}$ excitation to $\langle r_{sC}^{-3}\rangle$; this contribution can be computed from the radial functions obtained for O, but the corresponding RS terms cannot be introduced in the MCHF procedure because they have the same angular form as the $1s \rightarrow d_{\text{I}}$ terms. We obtain a value around 5% of the second-order $1s \rightarrow d_{\text{I}}$ effect. Consequently, the difference between Kelly's figures and ours for the $1s \rightarrow d_{\text{I}}$ excitation must be attributed to the fact that our d_{I} function is essentially stabilized, in the MCHF procedure, by the $1s^2 \rightarrow d_{\text{I}}{}^2$ excitation (see above), which is of no interest for the second-order hfs values.

We conclude that to get correct second-order results through the MCHF method, we must whenever possible, content ourselves with the introduction of those excited terms which are primarily useful for the studied atomic property (the hfs, here).

To be more precise, this means that we should avoid including in an MCHF wave function the terms which have zero matrix elements with the reference configuration for *either* H_{elec} or H_{hfs}. For O, for example, this means that T_1', T_5', and T_9' should not be included since the matrix element of H_{elec} with T_0 is zero. Of course, $T_4(1s^2 \rightarrow d_{\text{I}}^2)$ should not be included, but also $T_3(1s \rightarrow d_{\text{I}})$ and $T_7(2s \rightarrow d_{\text{II}})$ since for both the matrix element of H_{hfs} with T_0 is zero.

D. Contact Contributions to hfs

As a by-product of our work on the orbit-dependent parts of the hfs, we can get some information about the quantity $|\psi(0)|^2$. We take once more O as an example.

Owing to the occurrence of the excited configurations $1sd_{\text{I}}2s^2 2p^4$ and $1s^2 2sd_{\text{II}}2p^4$ in the expansion for the ground-state term, the mean value of the Fermi hfs contact term is not zero. Following Abragam and Pryce,[18] let us compute the quantity

$$\chi = \frac{4\pi}{S} \langle \sum \delta_i(\vec{r}_i) s_{iz} \rangle_\psi ,$$

where ψ is the state ${}^3P_2$, $M_J = 2$, and the spin S is 1. We get, using the $A_0(1s)$ and $A_0(2s)$ values in Table II,

$$\chi_{s \rightarrow d} = 0.373 \text{ a.u.}$$

Bagus *et al.*[19] have published theoretical values of the Fermi contact term obtained from the spin unrestricted Hartree-Fock method (SUHF). This method can be called a second-order method, since it takes into account implicitly the $1s \rightarrow ns$ and $2s \rightarrow ns$ excitations.[3(b),20] It yields

$$\chi_{\text{SUHF}} = 1.228 \text{ a.u.}$$

We conclude that, to compute the Fermi contact term, the third-order contributions (as are those from the $s \rightarrow d$ excitations) are of *essential* importance. This result is also clear from the work of Kelly[3(b)] on the contact term in oxygen. [We note that the third-order diagrams of Figs. 3(a) and 3(b) of Ref. 3(b) involve configurations of the form that we have included in our MCHF wave function.] However, the importance is demonstrated here in terms of a CI wave function. In terms of the CI wave function, the large contribution of these $s \rightarrow d$ excitations is clear. The diagonal contribution to χ of, say, T_5 and T_6 for O is proportional to $C_5^2 |\varphi_{2s}(0)|^2$ and $C_6^2 |\varphi_{2s}(0)|^2$, where C_5^2 and C_6^2 (the MCHF mixing coefficients) are ~0.005 and $|\varphi_{2s}(0)|^2$ is quite large; $A_0^2(2s)$ is ~70 a.u. (cf. Table II).

V. CONCLUSION

The MCHF method yields, without too much labor, relatively accurate *ab initio* values for the orbit-dependent part of the hyperfine structure. Agreement with experimental results for O and F is satisfactory. The MCHF results are also quite close to the polarization and "first-order" wave function results of Schaefer *et al.*[5] In comparison with their wave functions, we note, however, that we have (1) used fewer types of excitations (especially, in comparison with the first-order wave function), and (2) used only one "optimized" orbital for each type of excitation. Thus our MCHF wave functions are very compact. Further, (3) the MCHF method, since it involves numerical integration of Hartree-Fock-like equations for the orbitals, avoids the problem of determining optimum (or near optimum) nonlinear parameters for the basis functions used by Schaefer *et al.*[5]

Two numerical difficulties with the MCHF method should, however, be noted. First, we were not able to obtain convergence for excited orbitals which have a very small effect on the total energy. Second, the fact that the computer program which we used[11] does not allow for the occurrence of interconfigurational off-diagonal elements involving the kinetic energy and the electron-nucleus interaction also limits its possibilities.

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