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Spin-Optimized Self-Consistent-Field Function. III. Ground States of Boron and Carbon Atoms

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The spin-optimized self-consistent-field (SOSCF) function, a product of one-electron spatial orbitals multiplied by a spin function optimized in the relevant (S, M_S) space, is calculated for $B(^2P)$ and $C(^3P)$. The energy reduction relative to restricted Hartree-Fock values is considerable and includes most of the "radial correlation energy." The hfs constants are calculated and found to be in very good agreement with experiment, where experimental values are known. The use of partial spaces for the spin-function variation is considered. The spatial orbitals are described, and as observed previously for other atoms, they possess no radial nodes.

INTRODUCTION

The spin-optimized self-consistent-field (SOSCF) function described in the first paper of this series[1] is of the form

$$\Psi = \mathcal{A}\, \Xi \Theta \quad , \tag{1}$$

where Ξ is a product of one-electron spatial orbitals,

$$\Xi = \chi_1(1)\chi_2(2) \cdots \chi_n(n) \quad , \tag{2}$$

and Θ is a linear combination of all independent spin functions θ_k spanning the space of appropriate S and M_s,

$$\Theta = \sum_k t_k \theta_k \quad . \tag{3}$$

The orbitals χ_i and the coefficients t_k are optimized simultaneously.[1]

In Paper I,[1] we investigated three- and four-electron atoms. Ladner and Goddard[2] obtained the spin-coupling-optimized GI (SOGI) functions (equivalent to our SOSCF, though calculated by different methods) for several other three- and four-electron systems, and Hameed *et al.*[3] applied their best radial N-orbital (BRNO) method, without simultaneous optimization of spin and spatial parts in Ψ of Eq. (1) to the lithium atom. The spin-function space for all these systems is two dimensional (except for the triplet states of H_4, for which three independent spin functions exist[2]; however, considerations of spatial symmetry reduce the number of applicable functions to two or even one[2]), so that Θ of Eq. (3) contains only one free parameter t_1/t_2. Larger systems may have many more such parameters,[4] leading to more complicated calculations and possibly showing features not observed in previous investigations of the small systems. Atomic nitrogen was the first larger system studied by the SOSCF method, with special emphasis on the spin density at the nucleus, responsible for the hfs of the atomic spectrum.[5] It was found that the SOSCF function gave considerably better results than other orbital-product self-consistent-field (SCF) methods. Another interesting inference was that not all possible spin functions had to be taken into account.[5] Further studies by the SOSCF method, applied to the boron and carbon atoms, are reported in this paper.

SPIN FUNCTIONS

The construction of the θ_k's [Eq. (3)] for atomic nitrogen was described in detail in II.[5] The same method is applied here, first building spin functions for four nonequivalent s electrons, then coupling them with one or two equivalent p electrons to get all possible functions of $B(^2P)$ and $C(^3P)$, respectively. All five possible functions[4] spanning the five-electron doublet space are employed for boron. They are

$$\begin{aligned}
\theta_1 &= \tfrac{1}{2}(\alpha\beta\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta + \beta\alpha\beta\alpha)\alpha \quad , \\
\theta_2 &= (2\alpha\alpha\beta\beta + 2\beta\beta\alpha\alpha - \alpha\beta\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta \\
&\quad - \beta\alpha\beta\alpha)\alpha/\sqrt{12} \quad , \\
\theta_3 &= [(2\alpha\alpha\alpha\beta - 2\alpha\alpha\beta\alpha)\beta - (\alpha\beta\alpha\beta - \alpha\beta\beta\alpha + \beta\alpha\alpha\beta \\
&\quad - \beta\alpha\beta\alpha)\alpha]/\sqrt{12} \quad , \\
\theta_4 &= [(2\alpha\beta\alpha\alpha - 2\beta\alpha\alpha\alpha)\beta - (\alpha\beta\alpha\beta - \beta\alpha\alpha\beta \\
&\quad + \alpha\beta\beta\alpha - \beta\alpha\beta\alpha)\alpha]/\sqrt{12} \quad , \\
\theta_5 &= [(\beta\beta\alpha\alpha - \alpha\alpha\beta\beta)\alpha + (\alpha\alpha\alpha\beta + \alpha\alpha\beta\alpha - \alpha\beta\alpha\alpha \\
&\quad - \beta\alpha\alpha\alpha)\beta]/\sqrt{6} \quad .
\end{aligned} \tag{4}$$

The requirement that the two p orbitals of $C(^3P)$ have the same radial dependence (l-equivalence restriction) eliminates three of the nine functions[4] that describe a six-electron triplet, leaving a six-dimensional spin-function space:

$$\begin{aligned}
\theta_1 &= \tfrac{1}{2}(\alpha\beta\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta + \beta\alpha\beta\alpha)\alpha\alpha \ , \\
\theta_2 &= (2\alpha\alpha\beta\beta + 2\beta\beta\alpha\alpha - \alpha\beta\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta \\
&\quad - \beta\alpha\beta\alpha)\alpha\alpha/\sqrt{12} \ , \\
\theta_3 &= [(\alpha\alpha\alpha\beta - \alpha\alpha\beta\alpha)(\alpha\beta + \beta\alpha) - (\alpha\beta\alpha\beta - \alpha\beta\beta\alpha \\
&\quad + \beta\alpha\alpha\beta - \beta\alpha\beta\alpha)\alpha\alpha]/\sqrt{8} \ , \\
\theta_4 &= [(\alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha)(\alpha\beta + \beta\alpha) - (\alpha\beta\alpha\beta - \beta\alpha\alpha\beta \\
&\quad + \alpha\beta\beta\alpha - \beta\alpha\beta\alpha)\alpha\alpha]/\sqrt{8} \ , \qquad (5) \\
\theta_5 &= \tfrac{1}{4}[(\alpha\alpha\alpha\beta + \alpha\alpha\beta\alpha - \alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha)(\alpha\beta + \beta\alpha) \\
&\quad - 2(\alpha\alpha\beta\beta - \beta\beta\alpha\alpha)\alpha\alpha] \ , \\
\theta_6 &= [6\alpha\alpha\alpha\alpha\beta\beta - 1.5(\alpha\alpha\alpha\beta + \alpha\alpha\beta\alpha + \alpha\beta\alpha\alpha \\
&\quad + \beta\alpha\alpha\alpha)(\alpha\beta + \beta\alpha) + (\alpha\alpha\beta\beta + \alpha\beta\alpha\beta + \beta\alpha\alpha\beta \\
&\quad + \alpha\beta\beta\alpha + \beta\alpha\beta\alpha + \beta\beta\alpha\alpha)\alpha\alpha]/\sqrt{60} \ .
\end{aligned}$$

The reduction in the number of applicable spin functions may be traced to the nonexistence of a ^1P state for the p^2 configuration. This state exists for two nonequivalent p electrons, and may then combine with the ^3S state (with three spin functions) of the four nonequivalent s electrons to yield the "missing" three functions. A similar situation occurs in the case of atomic nitrogen.[5]

The maximally paired Hartree-Fock function (MPHF, equivalent to Goddard's G1[6]) for the atoms studied here is obtained when Θ of (3) is made equal to θ_1 of (4) or (5), which has singlet factors $\alpha\beta - \beta\alpha$ coupling both 1s and 2s electron pairs. The same factor is connected with the 1s pair in θ_4, and functions of the form (1) having only t_1 and t_4 [Eq. (3)] different from zero will therefore be called "1s paired." Similarly, a "2s-paired" function will have all $t_k = 0$ except t_1 and t_3. In addition, we employ functions in which θ_1, θ_3, and θ_4 contribute to Θ; these will be called "partly paired" functions. It should be noted that the spatial orbitals χ_i are separately optimized for each of these functions. For a description of the optimization procedure see I.[1]

SPATIAL BASIS FUNCTIONS

The spatial orbitals χ_i [Eq. (2)] are expanded in Slater-type basis functions. The basis sets, listed in Tables I and II, fall into two classes. Type-I sets are those satisfying (approximately) the cusp condition[7] for the s orbitals. This is achieved by having only one 1s orbital in the set, with an exponent (approximately) equal to the nuclear charge and no 2s orbitals. One basis set (set 11 for carbon) satisfies the p orbital cusp condition too. Other sets are denoted type II. Sets 1 and 2 for both atoms are taken from Bagus and Gilbert,[8] set 3 from Clementi, Roothaan, and Yoshimine,[9] and sets 4–11 are from Goddard's extensive investigations.[10] All these sets were obtained by the respective authors with the restricted Hartree-Fock (RHF) energy as optimization criterion. In addition, we employ the set 1a for boron, optimized for the spin-extended Hartree-Fock (SEHF) calculation.[11]

hfs CONSTANTS

The hyperfine splitting of atomic energy levels has been analyzed by Trees.[12] The contributions of the different terms in the hfs operator are

TABLE I. Basis sets for boron.

	Not satisfying cusp condition (type II)
(1)	1s −7.732, 4.413; 3s −2.431; 2s −1.152; 2p −4.558, 1.753, 0.931
(1a)	1s −7.7317, 4.4106; 3s −2.4269; 2s −1.1421; 2p −4.5582, 1.7498, 0.9340
(2)	1s −7.338, 3.996; 3s −4.796; 2s −1.724, 1.110; 2p −5.509, 2.155, 1.243, 0.845
(3)	1s −4.4661, 7.8500; 2s −0.8320, 1.1565, 1.9120, 3.5213; 2p −0.8783, 1.3543, 2.2296, 5.3665
	Approximately satisfying cusp condition for s orbitals (type I)
(4)	1s −4.9986; 3s −5.431, 2.537, 1.398; 2p −1.0029, 2.210
(5)	1s −5.0145; 3s −5.794, 4.08, 2.4173, 1.3776; 2p −1.003, 2.2082
(6)	1s −5.016; 3s −5.79, 4.08, 2.405, 1.374; 2p −0.934, 1.754, 4.54
(7)	1s −5.015; 3s −5.79, 4.06, 2.424, 1.393, 0.69; 2p −0.931, 1.752, 4.54
(8)	1s −5.015; 3s −5.79, 4.06, 2.424, 1.393, 0.69; 2p −5.509, 2.155, 1.243, 0.845
(9)	1s −5.0172; 3s −5.83, 3.98, 2.392, 1.403, 0.65; 4s −0.88; 2p −0.931, 1.752, 4.54
(10)	1s −5.0172; 3s −5.83, 3.98, 2.392, 1.403, 0.65; 4s −0.88; 2p −5.509, 2.155, 1.243, 0.845

TABLE II. Basis sets for carbon.

	Not satisfying cusp condition (type II)
(1)	1s −9.153, 5.382; 3s −3.076; 2s −1.428; 2p −5.152, 2.177, 1.150
(2)	1s −9.055, 5.025; 3s −6.081; 2s −2.141, 1.354; 2p −6.827, 2.779, 1.625, 1.054
(3)	1s −5.4125, 9.2863; 2s −1.011, 1.502, 2.5897, 4.2595; 2p −0.9554, 1.4209, 2.5873, 6.3438
	Approximately satisfying cusp condition for s orbitals (type I)
(4)	1s −5.989; 3s −6.464, 3.08, 1.691; 2p −1.2547, 2.725
(5)	1s −6.012; 3s −6.93, 4.84, 2.872, 1.648; 2p −1.255, 2.725
(6)	1s −6.0129; 3s −6.93, 4.77, 2.877, 1.6553; 2p −1.1502, 2.178, 5.159
(7)	1s −6.013; 3s −6.93, 4.75, 2.877, 1.673, 0.85; 2p −1.1502, 2.178, 5.159
(8)	1s −6.016; 3s −6.95, 4.74, 2.859, 1.675, 0.89; 2p −1.054, 1.625, 2.781, 6.824
(9)	1s −6.018; 3s −6.98, 4.58, 2.894, 1.667, 0.87; 4s −0.996; 2p −1.1505, 2.179, 5.17
(10)	1s −6.018; 3s −6.98, 4.58, 2.894, 1.667, 0.87; 4s −0.996; 2p −1.054, 1.625, 2.781, 6.824
	Approximately satisfying cusp condition for all orbitals
(11)	1s −6.016; 3s −6.95, 4.74, 2.859, 1.675, 0.89; 2p −3.088; 4p −1.163, 1.847, 2.998, 4.85

described in detail by Schaefer *et al.*[13] and by Goddard,[10] who also gives explicit formulas for the states of interest to us. The magnetic hfs terms for the ground state of boron are given by

$$a_{3/2}=\tfrac{1}{3}[2(2/g_s)a_l+a_d+a_c]=\tfrac{2}{3}[(2/g_s)\langle r_l^{-3}\rangle - \tfrac{1}{5}\langle r_d^{-3}\rangle]+(8\pi/9)\,Q(0)\ ,$$

$$a_{1/2}=\tfrac{1}{3}[4(2/g_s)a_l-10a_d-a_c]=\tfrac{4}{3}[(2/g_s)\langle r_l^{-3}\rangle + \langle r_d^{-3}\rangle]-(8\pi/9)\,Q(0)\ , \tag{6}$$

$$a_{3/2,1/2}=\tfrac{1}{3}[(2/g_s)a_l+\tfrac{5}{4}a_d-a_c]=\tfrac{1}{3}[(2/g_s)\langle r_l^{-3}\rangle - \tfrac{1}{2}\langle r_d^{-3}\rangle]-(8\pi/9)\,Q(0)\ ;$$

and for $C(^3P)$

$$a_2=\tfrac{1}{2}[(2/g_s)a_l+a_d+a_c]=\tfrac{1}{2}[(2/g_s)\langle r_l^{-3}\rangle + \tfrac{1}{5}\langle r_d^{-3}\rangle]+\tfrac{2}{3}\pi\,Q(0)\ ,$$

$$a_1=\tfrac{1}{2}[(2/g_s)a_l-5a_d+a_c]=\tfrac{1}{2}[(2/g_s)\langle r_l^{-3}\rangle - \langle r_d^{-3}\rangle]+\tfrac{2}{3}\pi\,Q(0)\ , \tag{7}$$

$$a_{2,1}=(1/2\sqrt{3})\,(2/g_s)a_l+2a_d-a_c]=(1/2\sqrt{3})\,[(2/g_s)\times\langle r_l^{-3}\rangle + \tfrac{2}{5}\langle r_d^{-3}\rangle - \tfrac{4}{3}\pi\,Q(0)\ ,$$

$$a_{1,0}=\sqrt{\tfrac{2}{3}}[(2/g_s)a_l-\tfrac{5}{2}a_d-a_c]=\sqrt{\tfrac{2}{3}}\,[(2/g_s)\langle r_l^{-3}\rangle - \tfrac{1}{2}\langle r_d^{-3}\rangle - \tfrac{4}{3}\pi\,Q(0)]\ .$$

a_l, a_d, and a_c are the expectation values, taken with a function with highest eigenvalues of $\hat{L}_z$ and $\hat{S}_z$ ($M_L=L$, $M_s=S$), of the following operators, contributing to the magnetic hfs operator:

$$a_l=\frac{1}{L}\left\langle \sum_i \frac{\hat{l}_{zi}}{r_i^3}\right\rangle\ ,$$

$$a_d=\frac{1}{SL(2L-1)}\left\langle \sum_i \frac{(3\cos^2\theta_i-1)\hat{s}_{zi}}{r_i^3}\right\rangle\ , \tag{8}$$

$$a_c=\frac{1}{S}\,\langle \textstyle\sum_i \delta(r_i)\hat{s}_{zi}\rangle \equiv \frac{1}{2S}\,Q(0)\ .$$

$Q(0)$ is the spin density at the nucleus and g_s is the electron g factor. The parameters $\langle r_l^{-3}\rangle$ and $\langle r_d^{-3}\rangle$, equal in the RHF approximation, are not equal in general, because of the different operators involved.[10, 13]

The electric quadrupole coupling constant b_J is given by[10]

$$b_J=-q_J Q\ , \tag{9}$$

where Q is the nuclear quadrupole moment, and the electric field gradient q_J is the expectation value of the operator $\sum_i[(3\cos^2\theta_i-1)/r_i^3]$. With the wave functions used here we get[10]

$$q_J=-\tfrac{2}{5}\langle r_l^{-3}\rangle \quad \text{for } B(^2P_{3/2})$$

and (10)

$$q_J=\tfrac{2}{5}\langle r_l^{-3}\rangle \quad \text{for } C(^3P_2)\ .$$

RESULTS AND DISCUSSION

Energies, spin densities, and expectation values of $\langle r_l^{-3}\rangle$ calculated with the different basis sets are presented in Tables III and IV. It has been observed by Goddard in his GF calculations for first-row atoms[10] (the GF function[6] is equivalent to our SEHF[14, 15]) that spin-independent properties such as E and $\langle r_l^{-3}\rangle$ are not sensitive to orbital cusps, while a reasonable prediction of spin density at atomic nuclei requires that the s orbitals satisfy the cusp condition. This observation ap-

TABLE III. Calculated properties for B (a.u.).[a]

Basis set[b]		Energy				Spin density at the nucleus			$\langle r_l^{-3}\rangle$	
	RHF	UHF	SEHF	MPHF	SOSCF	UHF	SEHF	SOSCF	UHF	MPHF	SOSCF
1 (4/3)	−24.529 02	−24.529 18	−24.529 52	−24.544 25	−24.544 64	0.0057	0.0256	−0.0085	0.7787	0.7757	0.7858
1a			−24.529 53	−24.544 25	−24.544 66		0.0283	−0.0072		0.7769	0.7873
2 (5/4)	−24.529 06	−24.529 25	−24.529 66	−24.545 16	−24.545 60	0.0110	0.0486	−0.0240	0.7806	0.7773	0.7897
3 (6/4)	−24.529 05	−24.529 30	−24.529 80	−24.545 04	−24.545 45	0.0258	0.0439	−0.0241	0.7814	0.7770	0.7894
4 (4/2)		−24.528 73		−24.543 27	−24.543 62	−0.0153		−0.0235	0.7540	0.7511	0.7605
5 (5/2)		−24.528 85		−24.545 18	−24.545 55	0.0115		−0.0049	0.7544	0.7513	0.7617
6 (5/3)		−24.529 20	−24.529 59	−24.545 51	−24.545 91	0.0145	0.0285	−0.0012	0.7789	0.7759	0.7864
7 (6/3)		−24.529 28	−24.529 75	−24.545 60	−24.546 01	0.0192	0.0350	0.0016	0.7797	0.7762	0.7874
8 (6/4)		−24.529 28		−24.545 60	−24.546 02	0.0195		0.0019	0.7816	0.7774	0.7897
9 (7/3)		−24.529 29		−24.545 62	−24.546 05	0.0189		0.0018	0.7798	0.7762	0.7876
10 (7/4)		−24.529 30	−24.529 80	−24.545 63	−24.546 05	0.0192	0.0361	0.0022	0.7817	0.7774	0.7900

[a] RHF results are from Refs. 8 and 9, UHF from Ref. 10, and SEHF from Refs. 10 and 11.
[b] (n/m) denotes a set with ns and mp basis orbitals.

TABLE IV. Calculated properties for C (a. u.).[a]

Basis set		Energy				Spin density at the nucleus			$\langle r_l^{-3}\rangle$	
	RHF	UHF	SEHF	MPHF	SOSCF	UHF	SEHF	SOSCF	UHF	MPHF	SOSCF
1 (4/3)	−37.688 54	−37.689 42	−37.690 21	−37.703 83	−37.705 31	0.0194	0.0244	−0.0218	1.6996	1.6896	1.7084
2 (5/4)	−37.688 62	−37.689 70	−37.690 68	−37.704 61	−37.706 37	0.1334	0.1298	−0.0482	1.7060	1.6939	1.7181
3 (6/4)	−37.688 81	−37.689 98		−37.704 54	−37.706 27	0.1011		−0.0305	1.7080	1.6928	1.7192
4 (4/2)		−37.688 24		−37.701 62	−37.703 12	−0.0219		−0.0468	1.6547	1.6436	1.6652
5 (5/2)		−37.688 64		−37.703 79	−37.705 43	0.0650		0.0178	1.6565	1.6438	1.6684
6 (5/3)		−37.689 67	−37.690 66	−37.704 76	−37.706 46	0.0709	0.0675	0.0265	1.7012	1.6902	1.7122
7 (6/3)		−37.689 90	−37.691 01	−37.704 84	−37.706 63	0.0819	0.0786	0.0393	1.7036	1.6906	1.7148
8 (6/4)		−37.689 94		−37.704 88	−37.706 68	0.0824		0.0408	1.7088	1.6940	1.7207
9 (7/3)		−37.689 95		−37.704 98	−37.706 77	0.0743		0.0409	1.7039	1.6906	1.7155
10 (7/4)		−37.689 98	−37.691 14	−37.705 00	−37.706 80	0.0753	0.0733	0.0423	1.7091	1.6939	1.7212
11 (6/5)		−37.689 95		−37.704 87	−37.706 67	0.0811		0.0411	1.7094	1.6944	1.7212

[a] RHF results are from Refs. 8 and 9, UHF from Ref. 10, and SEHF from Refs. 10 and 15.

TABLE V. Energy and hfs constants of B (^2P).

	Energy	$\langle r_l^{-3}\rangle$	$\langle r_d^{-3}\rangle$	$Q(0)$	$a_{3/2}$	$a_{1/2}$	$a_{\frac{3}{2},\frac{1}{2}}$	$q_{3/2}$
RHF (Ref. 9)	−24.52905	0.7755	0.7755	0	0.413	2.067	0.129	−0.310
UHF (Ref. 10)	−24.52930	0.7817	0.7817	0.0192	0.470	2.030	0.076	−0.313
SEHF (Ref. 11)	−24.52980	0.7943	0.7924	0.0362	0.524	2.013	0.031	−0.318
MPHF	−24.54563	0.7774	0.7774	0	0.415	2.073	0.130	−0.311
SOSCF	−24.54605	0.7900	0.7894	0.0022	0.427	2.098	0.125	−0.316
Limited CI:								
Polarization (Ref. 13)	−24.55129	0.7572	0.8167	0.0073	0.407	2.085		−0.297
First order (Ref. 16)	−24.58742	0.7674	0.8301	0.0041	0.421	2.107		−0.273
Experimental	−24.6579 [a]	···	···	···	0.4284[b]	2.1382[b]	···	$-0.01147/Q$[b]

[a] C. W. Scherr, J. M. Silverman, and F. A. Matsen, Phys. Rev. 127, 830 (1962).

[b] G. Wessel, Phys. Rev. 92, 1581 (1953); H. Lew and R. S. Title, Can. J. Phys. 38, 868 (1960). Q is the quadrupole moment of ^{11}B.

plies to SOSCF functions too, as indicated by our work on nitrogen[5] and by the present results. Type-II basis sets yield erratic spin densities, while results with type-I sets converge quite well.

Our MPHF and SOSCF results are compared in Tables V and VI with Goddard's unrestricted Hartree-Fock (UHF) and GF calculations,[10] with two limited configuration-interaction (CI) functions of Schaefer, Klemm, and Harris,[13, 16] and with experimental values. The comparison with experiment is difficult for several reasons. The nuclear quadrupole moments of both atoms considered, as well as the dipole moment of carbon isotopes, have not been determined experimentally. The reduced hfs constants of carbon and the electric field gradient at the boron nucleus cannot therefore be extracted from experimental data. Even when the reduced constants are known, as is the case for the magnetic terms of boron, the information available does not suffice to analyze them in terms of the primary integrals $\langle r_l^{-3}\rangle$, $\langle r_d^{-3}\rangle$, and $Q(0)$, since only two parameters $a_{3/2}$ and $a_{1/2}$ have been measured. Previous estimates[11, 17] were based on the assumption that the two $\langle r^{-3}\rangle$ integrals were equal. This assumption was checked for atoms with sufficient experimental evidence available, and proved invalid.[18] This is especially important for the spin density at the boron nucleus which is very sensitive to the values of other parameters,[11, 13] and no reliable estimate of it can be made until more experimental data, in particular $a_{3/2,1/2}$, become available.

Comparing the different methods we see that the SOSCF function yields appreciably better values of $a_{3/2}$ and $a_{1/2}$ for boron than other Hartree-Fock methods. The energy reduction with respect to the RHF value is considerable and includes most of the "radial correlation energy" of atomic boron, which is 0.024 hartree,[19] though it is only 13% of the total correlation energy.

TABLE VI. Energy and hfs constants of C (^3P).

	Energy	$\langle r_l^{-3}\rangle$	$\langle r_d^{-3}\rangle$	$Q(0)$	a_2	a_1	$a_{2,1}$	$a_{1,0}$	q_2
RHF (Ref. 9)	−37.68861	1.6922	1.6922	0	1.014	−0.001	0.683	0.689	0.677
UHF (Ref. 10)	−37.68998	1.7091	1.7091	0.0753	1.182	0.157	0.599	0.439	0.684
SEHF (Ref. 10)	−37.69114	1.7233	1.7202	0.0733	1.186	0.154	0.607	0.453	0.689
MPHF	−37.70500	1.6939	1.6939	0	1.016	−0.001	0.684	0.691	0.678
SOSCF	−37.70680	1.7212	1.7195	0.0423	1.120	0.088	0.644	0.557	0.688
Limited CI:									
Polarization (Ref. 13)	−37.72814	1.6633	1.7686	0.0277	1.055	−0.005			0.655
First order (Ref. 16)	−37.75068	1.6785	1.7824	0.0228	1.074	0.006			0.615
Experiment	−37.8558 [a]	···	···	···	$1.0710/\lvert\mu\rvert$[b]	$0.0192/\lvert\mu\rvert$[b]	···	···	$0.02106/Q$[b]

[a] C. W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev. 127, 830 (1962).

[b] R. A. Haberstroh, W. J. Kossler, O. Ames, and D. R. Hamilton, Phys. Rev. 136, B932 (1964). μ is the magnetic dipole moment of the ^{11}C nucleus and Q is its electric quadrupole moment.

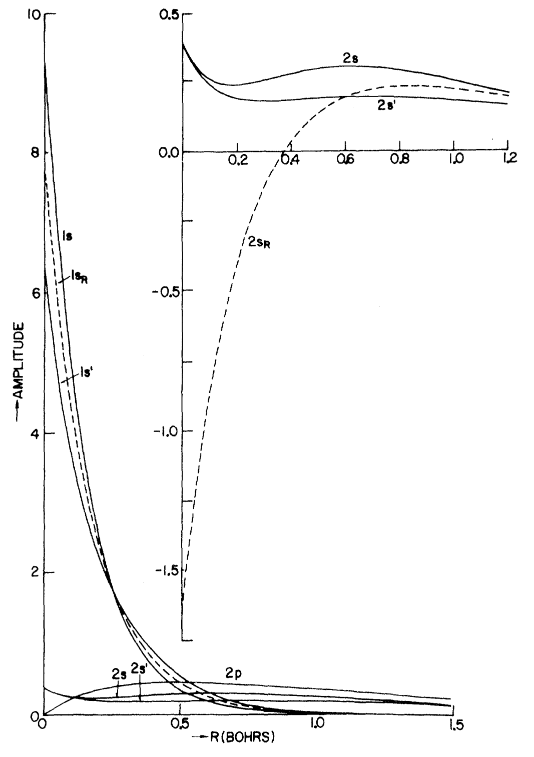

FIG. 1. SOSCF orbitals for carbon (basis set 10). Dashed lines are RHF orbitals. The RHF $2p$ orbital is not shown, as it falls on the SOSCF $2p$.

Partial Spin-Function Spaces

In the previous paper of this series,[5] we tried using subspaces of the six-dimensional spin-function space of N(^{4}S). We found that the total SOSCF energies and, more important, spin densities could be closely approximated by summing up the contributions of the 1s and 2s shells, calculated individually with the help of the two-dimensional "2s-paired" and "1s-paired" functions, respectively.[5] A similar investigation of the boron and carbon atoms gave disappointing results (Table VII), with the sums of individual contributions to the spin density considerably higher than the SOSCF value. Close agreement with SOSCF results was, however, achieved by using the "partly paired" function, to which spin functions with a singlet coupling of either of the s electron pairs (or both) were allowed to contribute. The various spin functions are listed in Table VIII. It appears that the problem of working with partial spin-function spaces requires further investigations.

Spatial Orbitals

The orbitals obtained in the present work display much the same behavior as the nitrogen orbitals.[5] Their main departure from other Hartree-Fock type functions is the absence of radial nodes, first observed in Goddard's G1 (equivalent to our MPHF) calculations for Li,[20] and later in our SOSCF work on Li,[1] Be,[1] and N.[5] This absence results from the lack of orthogonality relations between SOSCF orbitals, which are not eigenfunctions of the same operators. The carbon SOSCF orbitals are shown in Fig. 1 together with their RHF counterparts. The value of the orbitals in the vicinity of the nucleus depends quite strongly on the spin function and basis set (see Table IX and Fig. 2). This dependence disappears rapidly away from the origin (Fig. 2), and the variation in orbital overlaps (Table X) is much smaller. It should be mentioned that the 2p orbital is virtually independent of these factors, and remains almost invariant (the maximum amplitude does not change by more than 1%) for all spin functions and basis sets used (except for the very small sets).

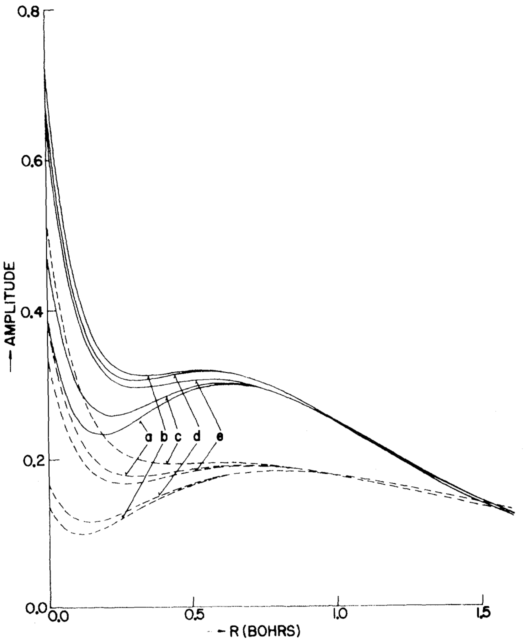

FIG. 2. Carbon 2s orbitals for different spin functions (basis set 10). Solid lines are 2s and dashed lines are 2s' orbitals. Spin functions (see Table VIII) are (a) SOSCF, (b) MPHF, (c) 1s paired, (d) 2s paired, and (e) partly paired.

TABLE VII. Results with paired functions

Basis set	Energy relative to MPHF value					Spin density at nucleus				
	1*s* paired	2*s* paired	Sum	Partly paired	SOSCF	1*s* paired	2*s* paired	Sum	Partly paired	SOSCF
B5	−0.000 33	−0.000 01	−0.000 34	−0.000 35	−0.000 37	0.0819	−0.0714	0.0105	−0.0059	−0.0049
B7	−0.000 38	−0.000 01	−0.000 39	−0.000 40	−0.000 42	0.0884	−0.0708	0.0176	0.0005	0.0015
B10	−0.000 38	−0.000 01	−0.000 39	−0.000 40	−0.000 42	0.0892	−0.0709	0.0183	0.0010	0.0022
C5	−0.001 55	−0.000 04	−0.001 59	−0.001 61	−0.001 64	0.2813	−0.2392	0.0421	0.0141	0.0178
C7	−0.001 70	−0.000 04	−0.001 74	−0.001 75	−0.001 79	0.2994	−0.2373	0.0621	0.0353	0.0393
C10	−0.001 72	−0.000 04	−0.001 76	−0.001 77	−0.001 80	0.3021	−0.2370	0.0651	0.0382	0.0423

TABLE VIII. Coefficients of spin functions.

	θ_1[a]	θ_2	θ_3	θ_4	θ_5	θ_6
			Boron atom[b]			
1*s* paired	0.5736	0	0	−0.0440	0	· · ·
2*s* paired	0.5777	0	0.0024	0	0	· · ·
Partly paired	0.5753	0	0.0031	−0.0444	0	· · ·
SOSCF	0.5664	−0.0129	0.0027	−0.0441	−0.0018	· · ·
			Carbon atom[b]			
1*s* paired	0.5649	0	0	−0.0886	0	0
2*s* paired	0.5752	0	0.0041	0	0	0
Partly paired	0.5681	0	0.0049	−0.0890	0	0
SOSCF	0.5608	−0.0138	0.0044	−0.0881	−0.0021	−0.0004

[a] See Eqs. (4) and (5).

[b] Basis set 10.

TABLE IX. Orbital densities at nucleus.

	Set	1*s*	1*s*′	2*s*	2*s*′
		Boron			
MPHF	3	7.5465	4.0899	0.4034	0.1341
	10	7.0327	4.5844	0.4995	0.0978
SOSCF	3	7.5440	4.1245	0.2060	0.2411
	10	7.0254	4.6295	0.2447	0.2456
1*s* paired	10	7.0340	4.6111	0.4279	0.2064
2*s* paired	10	7.0321	4.5849	0.4915	0.1050
Partly paired	10	7.0399	4.6020	0.4840	0.1459
		Carbon			
MPHF	3	9.8099	5.6532	0.5654	0.1872
	10	9.2024	6.2445	0.7083	0.1342
SOSCF	3	9.8345	5.7370	0.3255	0.3734
	10	9.2154	6.3388	0.3900	0.3821
1*s* paired	10	9.2078	6.3431	0.4721	0.5144
2*s* paired	10	9.1974	6.2493	0.6667	0.1684
Partly paired	10	9.2262	6.3153	0.6431	0.3362

TABLE X. Orbital overlaps.

	Set	$(1s\,\vert\,1s')$	$(2s\,\vert\,2s')$	$(1s\,\vert\,2s)$	$(1s'\,\vert\,2s')$	$(1s\,\vert\,2s')$	$(1s'\,\vert\,2s)$
				Boron			
MPHF	3	0.9620	0.9063	0.2761	0.2146	0.1458	0.3849
	10	0.9566	0.9028	0.2768	0.2165	0.1276	0.4060
SOSCF	3	0.9642	0.9095	0.2417	0.2025	0.1641	0.3208
	10	0.9605	0.9088	0.2395	0.2049	0.1592	0.3272
1*s* paired	10	0.9584	0.9046	0.2622	0.2145	0.1450	0.3729
2*s* paired	10	0.9566	0.9033	0.2758	0.2173	0.1291	0.4045
Partly paired	10	0.9571	0.9017	0.2661	0.2122	0.1294	0.3893
				Carbon			
MPHF	3	0.9685	0.9237	0.2930	0.2334	0.1635	0.3956
	10	0.9635	0.9198	0.2929	0.2360	0.1429	0.4184
SOSCF	3	0.9701	0.9234	0.2392	0.2115	0.1691	0.3134
	10	0.9673	0.9228	0.2399	0.2162	0.1681	0.3206
1*s* paired	10	0.9677	0.9236	0.2544	0.2296	0.1895	0.3280
2*s* paired	10	0.9640	0.9213	0.2904	0.2377	0.1497	0.4114
Partly paired	10	0.9653	0.9189	0.2636	0.2263	0.1546	0.3673

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Alkali-Rare-Gas van der Waals Molecules and Ground-State Relaxation Processes in Optical Pumping

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Relaxation experiments performed on alkali atoms polarized in their ground state by optical pumping in the presence of a rare gas have been previously reported and interpreted. It was shown that the relaxation governed by the spin-orbit interaction is strongly affected by the formation of chemically unstable Rb-Kr molecules bound by van der Waals forces. The previous theoretical analysis, restricted to the longitudinal relaxation, is extended here to relaxation processes involving the transverse components of the electronic polarization and hyperfine "coherences" (elements of the density matrix between different hyperfine states). The effects resulting from the action of a rf field are also examined. The main results of this work, among others, are (a) the prediction of a Zeeman transition-line pressure shift, in some circumstances larger by several orders of magnitude than the one calculated by Herman, and having a very peculiar variation with the rare-gas pressure; (b) a quantitative explanation of the anomalous pressure dependence of the hyperfine transition linewidth discovered by Bender and Cohen; (c) a proposal of a method of detection of rf transitions between states of the alkali–rare-gas molecules by their effect on the relaxation process.

INTRODUCTION

It has been shown recently[1,2] that the relaxation of the longitudinal polarization of ground-state alkali atoms in a rare-gas medium is strongly affected by the presence of alkali–rare-gas molecules bound by van der Waals forces. An alkali atom has a certain probability to be captured by a rare-gas atom into a molecular state during a three-body collision. During the lifetime of the molecule likely to be destroyed at the next collision, the electronic spin $\vec{S}$ is subjected to the molecular spin-orbit interaction $\gamma \vec{S}\cdot\vec{N}$ ($\vec{N}$ is the relative orbital momentum of the two bound atoms). This type of collision, called "sticking" collision in Ref. 1, is a very efficient relaxation mechanism, especially when the polarization $\langle\vec{S}\rangle$ has enough time to perform a complete precession around $\vec{N}$. Up to now, the experimental and theoretical analysis of the "sticking" collisions has