Cluster expansion of the wavefunction. Pseudo-orbital theory based on the SAC expansion and its application to the spin density of open-shell systems[a]

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We have studied the pseudo-orbital theory, which is based on the symmetry-adapted-cluster (SAC) expansion of an exact wavefunction proposed previously, in comparison with the conventional open-shell orbital theories, and applied it to the calculations of the spin densities of the first-row atoms, $Li(^2S)$, $Li(^2P)$, $Be^+(^2S)$, $B^{2+}(^2S)$, $B(^2P)$, $C(^3P)$, $N(^4S)$, $O(^3P)$, and $F(^2P)$. We have started from the RHF reference wavefunction and considered mainly the spin-polarization excitation operator and its self-consistency effect. This pseudo-orbital theory corresponds to an extension of the UHF and spin-extended HF (SEHF) theories, and yet it is free from the theoretical defects found previously for these theories. The relative magnitudes of the calculated spin densities are predicted to be in the order of the UHF or SEHF, present, and first-order (FO) CI in the decreasing order. This sequence has been confirmed in the calculated spin densities for the first-row atoms. For the three-electron atoms the present theory gives an excellent agreement with experiment, and for boron through fluorine the present results are fairly better than those of the UHF and SEHF theories and reasonable within the orbital theoretic approach. The calculated energies are also satisfactory when the angular correlation is included within the pseudo-orbital theory.

I. INTRODUCTION

Spin density distributions in atoms and molecules are observed in various fields of magnetic resonance experiments (e.g., ESR, NMR, Mössbauer, etc.) as hyperfine splitting constants.[1] They offer important informations concerning electronic structures, molecular geometries, the nature of molecular motions and interactions, etc.[1] However, on the theoretical side, the convenient orbital theories such as the unrestricted Hartree–Fock (UHF) theory,[2] the spin-projected[3] (or spin-annihilated)[4] UHF theory, and the spin-extended HF (SEHF) theory[5] (or the GF theory after Goddard)[6] are poor for the descriptions of spin density.[7–11] The UHF wavefunction does not represent a pure spin symmetry,[3] and the spin-projected UHF wavefunction does not correspond to a variational energy minimum. Although the SEHF theory satisfies both of these requirements,[5] the calculated spin densities were usually too large to compare with the experimental values[7,9] (for boron through fluorine the calculated values are almost twice as large as the experimental values),[7] and the calculated correlation energies were also very poor.[7,9] On the other hand, the first-order (FO) CI theory including spin-polarization function gives spin densities which are smaller than the experimental values.[10,12] We hope to develop a convenient theory which is easy enough for routine calculations in experimental laboratories and yet gives reliable spin densities.

Previously,[10,11] we have analyzed the UHF, spin-projected UHF, and SEHF theories expanding their wavefunctions in the limited CI forms starting from the restricted HF (RHF)[13] reference wavefunction. The analysis has clarified the reason why these orbital theories are inadequate for *both* spin density and correlation energy of open-shell systems. Though these theories

were intended to include both of the spin-correlation and "alternant" (or "DODS—different orbitals for different spins"-type) electron-correlation effects, it was done within a *limited* freedom of the theories, so that these two effects *interfere* each other through variational processes and poor answers result for *both* properties.[10] As remarked previously,[14] such interference arises from the unphysical nature of the self-consistency terms included in these theories.[10]

Goddard[15] has reported that the correlation energies calculated by the SEHF theory for $He(^1S)$, $Li(^2S)$, and $Be(^1S)$ were 39%, 0.2%, and 15% of the total correlation energies. Similar trends were also found for the other two-, three-, and four-electron atoms.[15] The correlation energies calculated for boron through fluorine (which are open-shell atoms) were also very poor.[7] In these examples, the remarkably poor results for the open-shell atoms would be attributed to the above interference between the spin-correlation and alternant electron-correlation effects. For closed-shell systems, the spin correlation does not exist and then the above interference does not occur, so that the SEHF theory can reasonably accommodate the alternant correlation effect within an orbital theoretic framework.[5] This is not true, however, for open-shell systems.

On the basis of the above analysis, we have suggested some ways to eliminate such difficulties of these open-shell orbital theories.[10] The best way is of course to adopt a theory which includes sufficient freedom for the description of *both* spin correlation and electron correlation. Within an orbital theoretic framework, the spin-optimized HF (SOHF) theory[16] is promising in reference to the spin densities calculated for simpler atoms.[16b] Previously, we adopted multiconfiguration (MC) SCF theory as such an approach and obtained satisfactory results for $Li(^2S, ^2P)$ and $N(^4S)$.[17] So far, the Brueckner–Goldstone-type many-body perturbation theory reported by Kelly,[18] Das and co-workers,[19] and Hata,[20] and the

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[a] This paper also corresponds to Paper III of the series "On the orbital theories in the spin-correlation problems." Papers I and II are given in Refs. 11(a) and 10, respectively.

Bethe–Goldstone-type theory reported by Nesbet[21] have given the best agreement with the experimental spin densities. These authors have discussed the (important) effect of electron correlation on the calculated spin densities. On the other hand, Platas and Schaefer[22] have shown for $N(^4S)$ that the pair correlations have large canceling effects on the spin density and the net effect is quite small. From a practical point of view, these theories are much more difficult for applications than the theories mentioned above and are not suitable for routine calculations of spin densities in experimental laboratories.

Another, simpler way of eliminating the above-mentioned difficulty of the conventional orbital theory is to consider an extension of orbital theory in such a way that it includes effectively *only one* of the spin-correlation and alternant electron-correlation effects so that the theory is free from the interference.[10] In the present paper we consider such an extension of orbital theory that includes effectively only the spin-correlation effect. We will adopt the symmetry-adapted-cluster (SAC) expansion formalism given in the previous paper.[14] The SAC expansion is suitable for open-shell systems and represents a pure symmetry under consideration. It includes the self-consistency effect of the symmetry-adapted excitation operators in a correct way in contrast to the conventional cluster expansion theories and the conventional open-shell orbital theories (e.g., the UHF and SEHF theories).[14] We have referred to the extension of open-shell orbital theory in the SAC expansion formula as the pseudo-orbital theory,[14,23] and some preliminary results have been published recently.[23] Although the influence of electron correlation on spin density might not be small,[18–21] we will neglect it in the present calculations. We will, rather, include angular correlation effect *within* an orbital theoretic framework. We want to see in this study what extent we can get within a simple orbital–theoretic approach.

Lastly, we note that when we want to calculate only the correlation energy of open-shell systems *within* a simple orbital–theoretic framework, it is suggested that the term representing the spin-correlation effect be eliminated from the conventional theory (e.g., the SEHF theory). Such a procedure would eliminate the above-mentioned interference and then would give reasonable correlation energy *even* for open-shell systems. There the situation would be similar to the SEHF theory for closed-shell systems.[15] This procedure is analogous to the elimination of the "stability dilemma" reported separately for closed-shell orbital theories.[24] Of course, from such a wavefunction we cannot expect any reasonable spin-dependent properties.

In the next section we outline the pseudo-orbital theory based on the SAC expansion.[14] In Sec. III we first summarize the present method of calculation of spin density, and then analyze the spin correlation included in the pseudo-orbital theory in comparison with the previous analysis[10] for the FOCI, UHF, and SEHF theories. In Sec. IV we give the results of the calculations for the energies and spin densities of the first-row atoms and

compare them with the previous results. The conclusion of the present study is given in Sec. V.

II. PSEUDO-ORBITAL THEORY BASED ON THE SAC EXPANSION

In the previous paper[14] we proposed the symmetry-adapted-cluster (SAC) expansion of an exact wavefunction. It is constructed from the generators of the symmetry-adapted excited configurations having the symmetry under consideration and includes their higher-order and self-consistency effects. It is different from the conventional cluster expansions in several important points and is suitable for applications to open-shell systems. Further, it has been shown that the open-shell orbital theories can be extended in several ways in the SAC expansion formulas (the pseudo-orbital theory). It is based on the fact that the cluster expansion formalism *completely* includes the self-consistency effect of orbitals.[14,25] As such examples, we have shown that the open-shell UHF and SEHF theories can be expressed equivalently in the *conventional* cluster expansion formulas.

In the pseudo-orbital theory, we consider only the single excitation operators in the SAC expansion formula, i.e.,

$$\Phi_{PO} = \mathcal{O} \exp(\hat{S}_{(1)})\Phi_0$$

$$= \left[1 + \hat{S}_{(1)} + \mathcal{O}\left(\tfrac{1}{2}\hat{S}_{(1)}^2 + \frac{1}{3!}\hat{S}_{(1)}^3 + \cdots \right) \right] \Phi_0 , \qquad (1)$$

where the operators $\hat{S}_{(1)}$ is expanded by the symmetry-adapted single excitation operators $S_{\sigma_1, i}^+$ as

$$\hat{S}_{(1)} = \sum_{\sigma_1}^{f_1} \sum_i C_{\sigma_1, i} S_{\sigma_1, i}^+$$

$$= \sum_I C_I S_I^+ . \qquad (2)$$

Here we have used the same notation as in the previous paper.[14] As a reference wavefunction Φ_0, we choose here the RHF wavefunction[13]

$$\Phi_0 = \| \varphi_1 \alpha \varphi_1 \beta \cdots \varphi_k \alpha \varphi_k \beta \cdots \varphi_q \alpha \varphi_q \beta \varphi_{q+1}\alpha \cdots \varphi_m \alpha \cdots \varphi_p \alpha \| .$$
$$\qquad (3)$$

We use the indices k, k' for doubly occupied orbitals; m, m' for singly occupied orbitals; and t, t' for unoccupied orbitals. Our system has s unpaired α spins, i.e.,

$$s = p - q . \qquad (4)$$

The variational equation for the pseudo-orbital wavefunction is given by the following Brillouin-like equation,

$$\langle \Phi_{PO} | (H - E)S_I^+ | \Phi_{PO}' \rangle = 0 , \qquad (5)$$

for all the excitation operators S_I^+ included in the wavefunction (1). Here Φ_{PO}' is given by

$$\Phi_{PO}' = \exp(\hat{S}_{(1)})\Phi_0 \qquad (6)$$

which do not have the projection operator $\mathcal{O}$ in front of the unlinked terms.

For the present system, we have the following *spin-symmetry-adapted single-excitation operators*. For the excitations from the orbital k to t, we have $s + 1$ excitation operators

$$S_{0,tk}^+ = (a_{t\alpha}^+ a_{k\alpha} + a_{t\beta}^+ a_{k\beta})/\sqrt{2} , \tag{7}$$

$$S_{1,tk}^+ = S_{P,tk}^+$$

$$= (s+2)^{-1/2}\left[\left(\frac{s}{2}\right)^{1/2} (a_{t\alpha}^+ a_{k\alpha} - a_{t\beta}^+ a_{k\beta}) \right.$$

$$\left. + \left(\frac{2}{s}\right)^{1/2} a_{t\alpha}^+ a_{k\beta} \sum_{m=q+1}^{p} a_{m\beta}^+ a_{m\alpha} \right] , \tag{8}$$

$$S_{r,tk}^+ = [r(r-1)]^{-1/2} a_{t\alpha}^+ a_{k\beta}$$

$$\times \left[\sum_{m=p-r+2}^{p} a_{m\beta}^+ a_{m\alpha} - (r+1)a_{(p-r+1)\beta}^+ a_{(p-r+1)\alpha} \right] \quad 2 \leq r \leq s . \tag{9}$$

For the excitations from the orbital m to t, we have

$$S_{0,tm}^+ = a_{t\alpha}^+ a_{m\alpha} , \tag{10}$$

and for the excitations from k to m, we have

$$S_{0,mk}^+ = a_{m\beta}^+ a_{k\beta} . \tag{11}$$

The operators given by Eqs. (7), (10), and (11) are referred to as the singlet-type excitation operators, and that given by Eq. (8) as the spin-polarization excitation operator. When the system has an additional space symmetry, we have to take such space symmetry into account for some types of excitation operators. For atoms, for instance, we can include the angular correlation effect by considering such symmetry-adapted excitation operators (e.g., $s \to d$ excitations given below). These excitation operators generate the singly excited configurations having the symmetry under consideration on applying to the reference wavefunction Φ_0. The symmetry projection operator $\mathcal{O}$ in Eq. (1) then affects only the unlinked terms and projects from them the symmetry-adapted higher-excited configurations. Therefore, the pseudo-orbital wavefunction belongs to the pure symmetry under consideration. For the spin symmetry, the spin-projection operator $\mathcal{O}_s$ is given by[5]

$$\mathcal{O}_s = \prod_{s'(\neq s)} \left[\mathbf{S}^2 - \frac{s'}{2}\left(\frac{s'}{2}+1\right) \right] , \tag{12}$$

where $\mathbf{S}^2$ is the spin-squared operator. All of the excitation operators given above satisfy the following commutation relations (quasiboson relations):

$$[S_I^+, S_J^+] = 0 , \quad [S_I, S_J] = 0 , \tag{13a}$$

$$[S_I, S_J^+]|\Phi_0\rangle = \delta_{IJ}|\Phi_0\rangle . \tag{13b}$$

Thus the configurations $|\Phi_0\rangle$ and $S_I^+|\Phi_0\rangle$ in the expansion (1) are mutually orthonormal. The exponentials of the excitation operators given by Eqs. (7)–(11) terminate at lower orders in the sense that

$$\exp\left(\sum_{tk} C_{0,tk} S_{0,tk}^+\right) = \prod_{tk} (1 + C_{0,tk} S_{0,tk}^+$$

$$- \tfrac{1}{2} C_{0,tk}^2 a_{t\alpha}^+ a_{t\beta}^+ a_{k\alpha} a_{k\beta}) , \tag{14a}$$

$$\exp\left(\sum_{tk} C_{P,tk} S_{P,tk}^+\right)$$

$$= \prod_{tk} \left(1 + C_{P,tk} S_{P,tk}^+ + \frac{1}{2}\frac{s}{s+2} C_{P,tk}^2 a_{t\alpha}^+ a_{t\beta}^+ a_{k\alpha} a_{k\beta}\right) , \tag{14b}$$

$$\exp\left(\sum_{tk} C_{r,tk} S_{r,tk}^+\right) = \prod_{tk} (1 + C_{r,tk} S_{r,tk}^+) , \tag{14c}$$

$$\exp\left(\sum_{tm} C_{0,tm} S_{0,tm}^+\right) = \prod_{tm} (1 + C_{0,tm} S_{0,tm}^+) , \tag{14d}$$

$$\exp\left(\sum_{mk} C_{0,mk} S_{0,mk}^+\right) = \prod_{mk} (1 + C_{0,mk} S_{0,mk}^+) . \tag{14e}$$

In Eqs. (14a) and (14b) the operator $a_{t\alpha}^+ a_{t\beta}^+ a_{k\alpha} a_{k\beta}$ generates the pair excitation from the orbital k to t. It represents an important part of the self-consistency effect.

The most general pseudo-orbital wavefunction within the framework of this section is obtained by including all of the excitation operators given by Eqs. (7)–(11) in the expansion (1), i.e.,

$$\Phi_{PO1} = \mathcal{O} \exp\left(\sum_{\sigma=0}^{s} \sum_{tk} C_{\sigma,tk} S_{\sigma,tk}^+ \right.$$

$$\left. + \sum_{tm} C_{0,tm} S_{0,tm}^+ + \sum_{mk} C_{0,mk} S_{0,mk}^+ \right)\Phi_0 . \tag{15}$$

For the calculations of spin-dependent properties, an interesting pseudo-orbital wavefunction is given by[14]

$$\Phi_{PO2} = \mathcal{O} \exp\left(\sum_{tk} C_{0,tk} S_{0,tk}^+ + \sum_{tk} C_{P,tk} S_{P,tk}^+ \right.$$

$$\left. + \sum_{tm} C_{0,tm} S_{0,tm}^+ + \sum_{mk} C_{0,mk} S_{0,mk}^+ \right)\Phi_0 . \tag{16}$$

This wavefunction corresponds to an extension of the UHF and SEHF theories, which are written equivalently in the conventional cluster expansion forms as[14]

$$\Phi_{UHF} = \mathfrak{N} \exp\left(\sum_{tk} C'_{0,tk} S_{0,tk}^+ + \sum_{tk} C'_{T,tk} S_{T,tk}^+ \right.$$

$$\left. + \sum_{tm} C'_{0,tm} S_{0,tm}^+ + \sum_{mk} C'_{0,mk} S_{0,mk}^+ \right)\Phi_0 \tag{17}$$

and

$$\Phi_{SEHF} = \mathfrak{N}\mathcal{O}_s \exp\left(\sum_{tk} C''_{0,tk} S_{0,tk}^+ + \sum_{tk} C''_{T,tk} S_{T,tk}^+ \right.$$

$$\left. + \sum_{tm} C''_{0,tm} S_{0,tm}^+ + \sum_{mk} C''_{0,mk} S_{0,mk}^+ \right)\Phi_0 , \tag{18}$$

respectively. The expansions (17) and (18) belong to the conventional expansions [Eqs. (2) and (24) of Ref. 14] and are different from the SAC expansion since the operator $S_{T,tk}^+$ (triplet-type excitation operator) given by

$$S_{T,tk}^+ = (a_{t\alpha}^+ a_{k\alpha} - a_{t\beta}^+ a_{k\beta})/\sqrt{2} \tag{19}$$

does not satisfy the spin-symmetry requirement for the present system. This is the origin of the theoretical defects of the UHF and SEHF theories[10,14] mentioned in the Introduction. In the pseudo-orbital wavefunction (16) this point is improved by replacing $S_{T,tk}^+$ with the spin-adapted spin-polarization operator $S_{P,tk}^+$. Because of this improvement the present theory is free from such defect, as shown later in Sec. III. The pseudo-orbital wavefunction (16) satisfies, after variation, the Brillouin-like relation (5) for the four types of operators $S_{P,tk}^+$, $S_{0,tk}^+$, $S_{0,tm}^+$, $S_{0,mk}^+$. However, among these operators, the contributions of the singlet-type operators $S_{0,tk}^+$, $S_{0,tm}^+$, and $S_{0,mk}^+$ would be small since the RHF

wavefunction Φ_0 satisfies the Brillouin theorem for these excitations. Then, we may neglect these excitation operators and obtain a simpler pseudo-orbital wavefunction

$$\Phi_{PO3} = \mathcal{O} \exp\left(\sum_{tk} C_{P,tk} S^+_{P,tk} \right) \Phi_0 . \tag{20}$$

In comparison with the wavefunction Φ_{PO2} given by Eq. (16), this wavefunction neglects the coupling effect between the spin-polarization and singlet-type operators. Since the RHF wavefunction Φ_0 does not satisfy the Brillouin theorem for the spin-polarization excitations $S^+_{P,tk}$, which is of primary importance for the spin-dependent properties, it would be important for spin-density calculations to include the effect of this excitation operators self-consistently with the use of the SAC expansion formalism. (The CI formalism cannot include the self-consistency effect.) The pseudo-orbital wavefunction Φ_{PO3} given by Eq. (20) constitutes the first approximation to such approach. Since spin density is a one-electron property, we may expect a reasonable result within such an orbital theoretic approach. In the present calculations we have mostly used the wavefunction Φ_{PO3} given by Eq. (20). We have also examined the coupling effect between the spin-polarization and singlet-type excitation operators with the use of the wavefunction Φ_{PO2} given by Eq. (16). Such coupling effect has been confirmed to be small, as shown in Sec. IV.

In going from the pseudo-orbital wavefunction Φ_{PO1} given by Eq. (15) to the Φ_{PO2} given by Eq. (16), we have neglected the effect of the excitation operators $S^+_{r,tk}$ (2 $\leqslant r \leqslant s$) which appear for the higher spin–multiplet states. For these excitations the integrals appearing in the Brillouin theorem become

$$\langle \Phi_0 | H S^+_{r,tk} | \Phi_0 \rangle$$

$$= [r(r-1)]^{-1/2}[(r-1)\langle (p-r+1)k | t(p-r+1) \rangle$$

$$- \sum_{m=p-r+2}^{p} \langle mk | tm \rangle], \tag{21}$$

where the electron repulsion integral $\langle mk | tm \rangle$ is defined by $\langle \varphi_m(1)\varphi_k(2) | 1/r_{12} | \varphi_t(1)\varphi_m(2) \rangle$. For the systems in which all of the unpaired electrons lie in degenerate orbitals, the integrals $\langle mk | tm \rangle$ are the same independent of m, so that the integral given by Eq. (21) vanishes identically. Namely, for such systems the reference wavefunction Φ_0 apparently satisfies the Brillouin theorem for the excitations $S^+_{r,tk}$, so that the effects of these excitation operators are expected to be small. The first-row atoms studied in this paper are just such systems. Moreover, the first-order corrections to the orbitals due to these excitations are zero because these excitations are composed of the two simultaneous elementary excitations (real excitation and spin flip). Therefore, we have neglected the effects of these excitations in the present calculations.

Lastly we want to give a remark on the pseudo-orbital theory in comparison with the conventional orbital theory. For closed-shell systems all of the pseudo-orbital wavefunctions given above reduce to

$$\Phi_{RHF} = \mathcal{R} \exp\left(\sum_{tk} C_{0,tk} S^+_{0,tk} \right) \Phi_0 , \tag{22}$$

which can be retransformed into the closed-shell RHF wavefunction

$$\Phi_{RHF} = \| \psi_1 \bar{\psi}_1 \cdots \psi_k \bar{\psi}_k \cdots \psi_q \bar{\psi}_q \| \tag{23}$$

as shown by Thouless.[25] For open-shell systems, however, the pseudo-orbital wavefunctions can not necessarily be retransformed into a compact single determinantal forms,[26] although the UHF and SEHF wavefunctions given by Eqs. (17) and (18) can of course be retransformed into the more familiar single determinantal forms[14]

$$\Phi_{UHF} = \| \varphi_1^\alpha \bar{\varphi}_1^\beta \cdots \varphi_k^\alpha \bar{\varphi}_k^\beta \cdots \varphi_q^\alpha \bar{\varphi}_q^\beta \varphi_{q+1}^\alpha \cdots \psi_m^\alpha \cdots \varphi_p^\alpha \| , \tag{24}$$

$$\Phi_{SEHF} = \mathcal{R} \mathcal{O}_s \| \psi_1^\alpha \bar{\psi}_1^\beta \cdots \psi_k^\alpha \bar{\psi}_k^\beta \cdots \psi_q^\alpha \bar{\psi}_q^\beta \psi_{q+1}^\alpha \cdots \psi_m^\alpha \cdots \psi_p^\alpha \| . \tag{25}$$

This is why we have referred to the present theory as *pseudo*-orbital theory.

III. SPIN CORRELATION INCLUDED IN THE PSEUDO-ORBITAL THEORY

In this section, we first summarize the method of calculations of the pseudo-orbital wavefunction and the associated spin density. We adopt the linear approximation to the variational equation (5).[14] Then, we analyze the spin correlation included in the pseudo-orbital theory in comparison with the previous analysis for the first-order CI (FOCI), UHF, and SEHF theories.[10] The analysis will show the relative order of magnitudes of the spin densities calculated by these various theories and that the present theory is free from the theoretical defect found previously[10] for the UHF and SEHF theories.

A. Calculations of spin density

For the present orbital–theoretic approach, the RHF wavefunction can be considered to be a reasonably good starting wavefunction. Then we adopt the linear approximation[14] to the variational equation (5) for the determination of the pseudo-orbital wavefunctions given by Eqs. (16) and (20). In this approximation only a single diagonalization is required and the effect of the projection operator does not appear.[14] In the present calculation we have started from Eq. (38) of the previous paper (Ref. 14),[27] i.e.,

$$\langle 0 | H S^+_I | 0 \rangle + \sum_J C_J (\langle 0 | S_J H S^+_I | 0 \rangle$$

$$+ \langle 0 | H S^+_I S^+_J | 0 \rangle - E_0 \delta_{IJ}) = 0 , \tag{26}$$

where $| 0 \rangle$ denotes $| \Phi_0 \rangle$ and $E_0 = \langle 0 | H | 0 \rangle$. Then the required diagonalization is given by[14]

$$\mathbf{U}^T (\mathbf{A} + \mathbf{B}) \mathbf{U} = \mathbf{D} , \tag{27}$$

where the matrices $\mathbf{A}$ and $\mathbf{B}$ are given by

$$\mathbf{A} = \langle 0 | \mathbf{S} H \mathbf{S}^+ | 0 \rangle , \quad \mathbf{B} = \langle 0 | H (\mathbf{S}^+)^T \mathbf{S}^+ | 0 \rangle , \tag{28}$$

where $\mathbf{S}^+ = (S^+_1, \ldots, S^+_I, \ldots)$ and S^+_I represent the excitation operators included in Eqs. (16) and (20). Using the diagonal transformation $\mathbf{U}$, we define new sets of excitation operators and coefficients by

$$\mathbf{R}^+ = \mathbf{S}^+ \mathbf{U} , \quad \mathbf{C}' = \mathbf{U}^T \mathbf{C} . \tag{29}$$

Then, the pseudo-orbital wavefunction is solved at once as

$$\Phi_{PO} = \mathfrak{N}\left(1 + \sum_I C_I' R_I^+\right)|0\rangle , \qquad (30a)$$

$$C_I' = \langle 0|HR_I^+|0\rangle/(E_0 - D_I) , \qquad (30b)$$

where $\mathfrak{N}$ is the normalization factor given by

$$\mathfrak{N} = \left(1 + \sum_I C_I'^2\right)^{-1/2} . \qquad (30c)$$

In this approximation the energy of the system is given by[14]

$$E = E_0 + \sum_I \langle 0|HR_I^+|0\rangle\langle 0|R_I H|0\rangle/(E_0 - D_I) , \qquad (31)$$

which has a sum-over-state form familiar in the perturbation theory.[28]

In the linear approximation given above, the self-consistency effect of the excitation operator is included through the B matrix defined by Eq. (28). The A matrix represents the Hamiltonian matrix between the excited configurations, which also appears in the conventional CI theory. For the analysis given later it is convenient to divide the elements of the diagonal matrix D into these two contributions, i.e.,

$$D_I = F_I + K_I' , \qquad (32a)$$

where

$$F_I = \langle 0|R_I HR_I^+|0\rangle = (\mathbf{U}^T\mathbf{AU})_{II} , \qquad (32b)$$

$$K_I' = \langle 0|HR_I^+R_I^+|0\rangle = (\mathbf{U}^T\mathbf{BU})_{II} . \qquad (32c)$$

F_I represents the energy of the state $R_I^+|0\rangle$ and the integral K_I' was referred to previously[28] as the generalized exchange integral since it is of the order of magnitude of the usual exchange repulsion integral, except for the sign which depends on the nature of the excitation. With the use of these quantities, the coefficient C_I' given by Eq. (30b) is written as

$$C_I' = \langle 0|HR_I^+|0\rangle/(E_0 - F_I - K_I') . \qquad (33)$$

In comparison with the conventional perturbation formula, this expression includes the additional generalized exchange integral.[28]

From the above wavefunction, we calculate the spin density correct to the second order in the coefficients. Up to this order the effect of the projection operator does not appear.[14,23] From Eq. (30) we obtain the spin density ρ as

$$\rho = \rho_{SD} + \rho_{SP} , \qquad (34a)$$

$$\rho_{SD} = \mathfrak{N}^2\langle 0|\rho(r)|0\rangle \qquad (34b)$$

$$\rho_{SP} = 2\sum_I C_I'\langle 0|R_I\rho(r)|0\rangle$$
$$+ \sum_{IJ} C_I'C_J'\langle 0|R_I\rho(r)R_J^+|0\rangle , \qquad (34c)$$

where the subscripts SD and SP mean the spin-delocalization and spin-polarization contributions, respectively,[11,29] and $\rho(r)$ is the spin density operator given by

$$\rho(r) = 2\sum_\nu S_{z\nu}\delta(r - r_\nu) . \qquad (35)$$

B. Analysis of spin correlation included in the pseudo-orbital theory

We now analyze the spin correlation included in the pseudo-orbital theory and prepare some prospects before entering into the calculations.

For this purpose, we consider here the spin density correct only to the first order in the coefficients and adopt an approximation to replace the transformed excitation operators R_I^+ with the primitive ones $S_{P,tk}^+$. Though this approximation is not necessarily a good one and we do *not* adopt it in the actual calculations, it is convenient for relating various theories.[10,28,30] In this approximation the integral F_I given by Eq. (32b) becomes the energy of the singly excited spin-polarization configuration, i.e.,

$$E_{P,tk} = \langle 0|S_{P,tk}HS_{P,tk}^+|0\rangle , \qquad (36a)$$

and the generalized exchange integral K_I' becomes

$$\langle 0|HS_{P,tk}^+S_{P,tk}^+|0\rangle = -\frac{s}{s+2}K_{tk} , \qquad (36b)$$

where K_{tk} is the ordinary exchange integral between the orbitals k and t. In Eq. (36b) the unlinked operator $S_{P,tk}^{+2}$ is written as

$$S_{P,tk}^+S_{P,tk}^+ = \frac{s}{s+2}a_{t\alpha}^+a_{t\beta}^+a_{k\alpha}a_{k\beta} , \qquad (37)$$

where $a_{t\alpha}^+a_{t\beta}^+a_{k\alpha}a_{k\beta}$ is the pair excitation operator from k to t. This unlinked operator is the one which has appeared in the last term of Eq. (14b) and constitutes an important term in the self-consistency effect of the spin-polarization excitation operator. Thus, using the formulas summarized in the preceding section, we obtain from the pseudo-orbital wavefunction (20) the spin-polarization (SP) contribution to spin density, ρ_{SP}, as

$$\rho_{SP} \simeq 2\sum_{tk}\frac{\sum_m\langle mt|km\rangle}{E_{P,tk} - E_0 - [s/(s+2)]K_{tk}}\varphi_t(r)\varphi_k(r) , \qquad (38)$$

where we have used the following relations,

$$\langle 0|HS_{P,tk}^+|0\rangle = -\left(\frac{s+2}{2s}\right)^{1/2}\sum_m\langle mt|km\rangle , \qquad (39a)$$

$$\langle 0|S_{P,tk}\rho(r)|0\rangle = \left(\frac{2s}{s+2}\right)^{1/2}\varphi_t(r)\varphi_k(r) . \qquad (39b)$$

In Table I, we have compared the SP contribution to spin density, ρ_{SP}, of the present theory [Eq. (38)] with those obtained previously[10] for the FOCI, UHF, and SEHF theories in the same approximation. For the spin-delocalization (SD) contribution ρ_{SD}, all of these theories are assumed to give the same value in the present approximation.

As shown later, Table I gives a basis for clarifying the relations among the spin densities of the various theories. However, before entering into such discussions, it would be important to show how the differences in Table I among the various theories have arisen. In the following we first discuss the origins of such differences, comparing the pseudo-orbital theory and the

TABLE I. Approximate formulas for the spin-polarization contribution to spin density, ρ_{SP}, for various theories.[a]

Theories	ρ_{SP}
FOCI[b]	$2\sum_{tk} \dfrac{\sum_m \langle mt \mid km \rangle}{E_{P,tk} - E_0} \varphi_t(r)\, \varphi_k(r)$
UHF[b,c]	$2\sum_{tk} \dfrac{\sum_m \langle mt \mid km \rangle}{E_{P,tk} - E_0 - (1/s)\sum_m (K_{tm} + K_{mk}) - K_{tk}} \varphi_t(r)\, \varphi_k(r)$
SEHF[b]	$2\sum_{tk} \dfrac{\sum_m \langle mt \mid km \rangle}{E_{P,tk} - E_0 - [(s+2)/s]K_{tk}} \varphi_t(r)\, \varphi_k(r)$
Present	$2\sum_{tk} \dfrac{\sum_m \langle mt \mid km \rangle}{E_{P,tk} - E_0 - [s/(s+2)]K_{tk}} \varphi_t(r)\, \varphi_k(r)$

[a]For the projected UHF (PUHF) theory, see Eq. (52) of the text.

[b]Previous results (Ref. 10).

[c]The term $-(1/s)\sum_m (K_{tm} + K_{mk})$ in the denominator has arisen from the spin contamination included in the UHF theory [see Eq. (49)].

SEHF theory, and then we discuss what Table I implies about the relations in the spin densities of the various theories.

As seen in Table I, the SP contribution of the SEHF theory is different from that of the present theory only in the prefactor of the exchange integral K_{tk} in the denominator. Previously,[10] this expression for the SEHF theory has been obtained from the CI expansion analysis of the SEHF wavefunction. In the present analysis it is convenient to start from the cluster expansion formula for the SEHF theory given by Eq. (18). Since the reference wavefunction Φ_0 in Eq. (18) satisfies the Brillouin theorem for the singlet-type excitation operators, $S_{0,tk}^+$, $S_{0,tm}^+$, and $S_{0,mk}^+$, we may neglect their contributions and approximate the SEHF wavefunction as

$$\Phi_{SEHF} \simeq \Re\mathcal{O}_s \exp\left(\sum_{tk} C_{T,tk}'' S_{T,tk}^+ \right) \Phi_0 , \qquad (40)$$

which has a form similar to the pseudo-orbital wavefunction (20). We note that the exponential of the triplet-type operator $S_{T,tk}^+$ is written as

$$\exp\left(\sum_{tk} C_{T,tk}'' S_{T,tk}^+ \right)$$

$$= \prod_{tk} \left(1 + C_{T,tk}'' S_{T,tk}^+ + \tfrac{1}{2} C_{T,tk}''^2 a_{t\alpha}^+ a_{t\beta}^+ a_{k\alpha} a_{k\beta} \right) . \qquad (41)$$

Here we have used the following relation for the unlinked operator $S_{T,tk}^{+2}$:

$$S_{T,tk}^+ S_{T,tk}^+ = a_{t\alpha}^+ a_{t\beta}^+ a_{k\alpha} a_{k\beta} . \qquad (42)$$

In comparison with Eq. (14b) for the spin-polarization operator $S_{P,tk}^+$, Eq. (41) is different in the contribution of the pair excitation operator. [Compare also Eq. (42) with Eq. (37).] Further, the approximation adopted in preparing Table I corresponds to approximating the wavefunction (40) as

$$\Phi_{SEHF} \approx \Re\mathcal{O}_s \left(1 + \sum_{tk} C_{T,tk}'' S_{T,tk}^+ \right.$$

$$\left. + \tfrac{1}{2} \sum_{tk} C_{T,tk}''^2 a_{t\alpha}^+ a_{t\beta}^+ a_{k\alpha} a_{k\beta} \right) \Phi_0 \qquad (43a)$$

and applying the variational principle to this expression. In Eq. (43a) only the diagonal terms are kept in the second-order self-consistency terms. Operating the spin-projection operator to the rhs, we rewrite Eq. (43a) as

$$\Phi_{SEHF} \approx \Re\left(1 + \sum_{tk} C_{P,tk}' S_{P,tk}^+ \right.$$

$$\left. + \tfrac{1}{2}\frac{s+2}{s} \sum_{tk} C_{P,tk}'^2 a_{t\alpha}^+ a_{t\beta}^+ a_{k\alpha} a_{k\beta} \right) \Phi_0 , \qquad (43b)$$

where we have used

$$\mathcal{O}_s S_{T,tk}^+ \Phi_0 = \left(\frac{s}{s+2} \right)^{1/2} S_{P,tk}^+ \Phi_0 , \qquad (44a)$$

$$C_{P,tk}' \equiv \left(\frac{s}{s+2} \right)^{1/2} C_{T,tk}'' , \qquad (44b)$$

and the fact that the pair excited configuration $a_{t\alpha}^+ a_{t\beta}^+ a_{k\alpha} a_{k\beta} \mid \Phi_0 \rangle$ belongs to the symmetry under consideration. In the same approximation the pseudo-orbital wavefunction (20) is written as

$$\Phi_{PO3} \approx \left(1 + \sum_{tk} C_{P,tk} S_{P,tk}^+ \right.$$

$$\left. + \tfrac{1}{2}\frac{s}{s+2} \sum_{tk} C_{P,tk}^2 a_{t\alpha}^+ a_{t\beta}^+ a_{k\alpha} a_{k\beta} \right) \Phi_0 , \qquad (45)$$

where we have referred to Eqs. (14b) and (37). Thus, in this approximation, the SEHF theory [Eq. (43b)] and the pseudo-orbital theory [Eq. (45)] differ only in the prefactors of their self-consistency terms. In Table I, the terms including the exchange integral K_{tk} in the denominators arise from the Hamiltonian matrices between the Φ_0 and these second-order self-consistency terms (i.e., the **B** matrices). This is understood with reference to Eqs. (36b) and (37). The prefactors of the integral K_{tk} [$(s+2)/s$ for SEHF and $s/(s+2)$ for the present theory] are just the prefactors in the self-consistency terms of Eqs. (43b) and (45).

Thus, the difference between the pseudo-orbital theory and the SEHF theory is attributed to the difference in the self-consistency terms (unlinked terms) included in these theories. Actually, this is valid *without* the approximations adopted in the above analysis.[14] Although the self-consistency term of the present theory directly represents the higher-order terms of the symmetry-adapted spin-polarization operator $S_{P,tk}^+$, that of the SEHF theory is the higher-order terms of the symmetry-*non*-adapted (then unphysical) operator $S_{T,tk}^+$ and does not correspond correctly to the spin-polarization operator $S_{P,tk}^+$ in the linked term $\mathcal{O}_s S_{T,tk}^+ \Phi_0$ [see Eq. (44a)]. In other words, although the spin-projection operator $\mathcal{O}_s$ in the SEHF theory corrects the linked term, it cannot correct the unlinked self-consistency terms.

In order to see this from a different aspect, we next investigate how the different self-consistency terms in the present and SEHF theories work in the variational process. This analysis shows that the present pseudo-orbital theory is free from the interference between the spin-correlation and alternant electron-correlation effects found previously for the SEHF theory.[10] In Table II, we have compared the energy expressions obtained

TABLE II. Approximate energy expressions obtained before variation for the present and SEHF theories

	$s \rightarrow 0$ (No spin correlation)
Present theory	
$\tilde{E}_{\text{present}} \simeq E_0 + 2 \sum_{tk} C_{P,tk} \langle 0 \mid H S^+_{P,tk} \mid 0 \rangle$	Zero
$+ 2 \sum_{tk} (C_{P,tk})^2 (E_{P,tk} - E_0)$	Zero
$- \dfrac{s}{s+2} \sum_{tk} (C_{P,tk})^2 K_{tk}$	Zero
SEHF theory	
$\tilde{E}_{\text{SEHF}} \simeq E_0 + 2 \left(\dfrac{s}{s+2}\right)^{1/2} \sum_{tk} C''_{T,tk} \langle 0 \mid H S^+_{P,tk} \mid 0 \rangle$	Zero
$+ \dfrac{2s}{s+2} \sum_{tk} (C''_{T,tk})^2 (E_{P,tk} - E_0)$	Zero
$- 2 \sum_{tk} (C''_{T,tk})^2 K_{tk}$	Nonzero

before variation for the present and SEHF theories. They are calculated from Eq. (45) for the present theory and from Eq. (43a) for the SEHF theory. We have kept up to second-order terms and neglected all the off-diagonal terms in the second-order contributions. This approximation is consistent with the approximation adopted in preparing Table I.

First we note that in Table II the last terms including the exchange integral K_{tk} have arisen from the unlinked terms and represent the self-consistency effects included in these theories. Bearing this in mind, let us consider the limit in which the number of unpaired spins, s approaches zero, i.e., the singlet state or the closed-shell limit. Then, there should be no spin correlation in the system. Accordingly, in the present theory, all of the three correction terms vanish identically since the spin-polarization operator does not occur at this limit. On the other hand, in the SEHF theory, the last term remains nonzero even at this limit [i.e., the coefficients $(C''_{T,tk})^2$ remain as *independent* variables][14] and represents the so-called "alternant" or "DODS" (different orbitals for different spins)-type electron-correlation effects. Thus, *for* closed-shell systems the SEHF theory includes the electron-correlation effect[5] in a *limited* way through the unlinked terms.[14,24] However, in *open-shell* systems, a problem arises for the SEHF theory. It arises because the first correction term including $\sum C''_{T,tk} \langle 0 \mid H S^+_{P,tk} \mid 0 \rangle$, which represents solely the spin-polarization correction, and the last term, which represents partially the (pure) self-consistency effect of the spin-polarization correction *and* partially the alternant correlation effect as shown above, have the *common* coefficients $C''_{T,tk}$. Therefore, through the variational process, these two correlation effects will interfere with each other through the unlinked terms so that poor answers will result for *both* corrections. If we want to calculate these two corrections simultaneously *without* such interference, we have to give more freedom in the theory giving the *independent* coefficients

for both corrections (e.g., by considering both of the single and double excitation operators, $\hat{S}_{(1)}$ and $\hat{S}_{(2)}$ in the SAC expansion formula).[14] Thus, in the SEHF theory, the unphysical nature of its unlinked self-consistency term causes the interference between the spin correlation and the alternant correlation effects. Because of this interference, the SEHF theory gives larger spin densities than the experimental values [as seen later in the sequence (51)] and poor correlation energy as found by Goddard[7,15] for the first-row atoms. In the present pseudo-orbital theory, however, such interference does not occur. The last term in Table II correctly represents the self-consistency effect of the spin-polarization excitation operator, so that it vanishes identically at the limit $s = 0$.

As discussed in the previous paper,[14] a similar analysis holds in general and shows a superiority of the SAC expansion [Eq. (14) of Ref. 14]

$$\Psi = \mho \exp(\hat{S})\Phi_0$$

$$= \left[1 + \hat{S} + \mho \left(\tfrac{1}{2}\hat{S}^2 + \frac{1}{3!}\hat{S}^3 + \cdots \right) \right] \Phi_0 \qquad (46)$$

over the projection of the conventional expansion [Eq. (24) of Ref. 14]

$$\Psi = \mho \exp(\hat{T})\Phi_0 . \qquad (47)$$

The SEHF wavefunction given by Eq. (18) belongs to this class of wavefunction.[14] A similar analysis is also possible for the conventional cluster expansion [Eq. (2) of Ref. 14]

$$\Psi = \exp(\hat{T})\Phi_0 . \qquad (48)$$

The UHF wavefunction given by Eq. (17) belongs to this class of wavefunction. In general, for open-shell systems, only the SAC expansion (46) includes in a correct way the higher-order and self-consistency effects of the symmetry-adapted excitation operators, in contrast to the conventional cluster expansions (47) and (48).[14] The expansion (48), further, has a defect in that it does not represent in general a pure symmetry state.[14]

Bearing the above analyses in mind, we now discuss what Table I implies about the relations among the spin densities of the various theories. Table I shows that among the various theories the approximate formulas for the SP contribution to spin density, ρ_{SP}, differ only in the energy denominator. In comparison with the FOCI theory, the theories belonging to the orbital theory (the UHF, SEHF, and present theories) have additional terms including exchange integrals. For the SEHF and present theories these additional terms have arisen from the self-consistency terms as shown above. For the UHF theory the term $-(1/s)\sum_m (K_{tm} + K_{mk})$ has arisen from the spin contamination included in the theory, i.e.,

$$E_{T,tk} = \langle 0 \mid S_{T,tk} H S^+_{T,tk} \mid 0 \rangle$$

$$= E_{P,tk} - (1/s) \sum_m (K_{tm} + K_{mk}), \qquad (49)$$

and the term $-K_{tk}$ has arisen from the self-consistency term.[10] Since these exchange integrals are positive, we may expect the following sequence for the calculated spin densities of simpler atoms and molecules,[31]

$$|\rho_{SP}^{FOCI}| < |\rho_{SP}^{Present}| < |\rho_{SP}^{SEHF}|, \ |\rho_{SP}^{UHF}|, \qquad (50)$$

namely, the spin density calculated by the present theory would lie between the FOCI value and the SEHF and UHF values. The difference between the SEHF and UHF values has been discussed in Ref. 10. On the other hand, many previous calculations for simpler atoms[7,12] and molecules[8,9] have given the following sequence of spin densities relative to the experimental (or full CI) values, i.e.,

$$|\rho_{SP}^{FOCI}| < |\rho_{SP}^{exptl}| < |\rho_{SP}^{SEHF}|, \ |\rho_{SP}^{UHF}|, \qquad (51)$$

where ρ_{SP}^{exptl} is defined by $\rho_{SP}^{exptl} = \rho^{exptl} - \rho_{SD}^{RHF}$. In the previous paper[10] we have also investigated the origin for this sequence.[31] For the SEHF and UHF theories, it is due to the interference between the spin-correlation and alternant electron-correlation effects as analyzed above. For the UHF theory, it is also due to the spin contamination included in the theory. For the FOCI theory, it is due to the neglect of the self-consistency effect. Comparing the sequence (50) with the sequence (51), we may expect that the present pseudo-orbital theory would give better agreement with the experimental value than the conventional FOCI, SEHF, and UHF theories. This is confirmed in the next section for the calculated spin densities of the first-row atoms.

Thus, it is concluded from the above analyses that the proper inclusion of the self-consistency effect (represented by the higher-order unlinked terms) is quite important, since as seen in the next section the above difference in the self-consistency term causes a large difference in the calculated spin density.[31] The pseudo-orbital theory realizes this requirement in a simple orbital-theoretic framework.

Lastly, we remark that the spin density of the spin-projected[3] (or spin-annihilated)[4,11] UHF (PUHF) theory is related to that of the UHF theory by[11]

$$\rho_{SP}^{PUHF} \simeq \frac{s}{s+2} \, \rho_{SP}^{UHF}. \qquad (52)$$

Again, we have the factor $s/(s+2)$. This relation has been confirmed to hold to a good approximation for various doublet and triplet radicals.[11,32] It has also given a convenient method for separating the UHF (or PUHF) spin density into the SD and SP contributions.[11,32]

IV. SPIN DENSITIES CALCULATED FOR FIRST-ROW ATOMS

We have applied the pseudo-orbital theory to the calculations of spin densities of the first-row atoms. Most of the calculations were performed based on the simpler wavefunction given by Eq. (20). The results are given in Tables III–VII. We then examine the coupling effect between the spin-polarization and singlet-type excitation operators as represented by the wavefunction given by Eq. (16). The results are given in Table VIII.

The first-row atoms calculated in the present paper are the three-electron atoms $Li(^2S)$, $Li(^2P)$, $Be^+(^2S)$, and $B^{2+}(^2S)$, and the atoms $B(^2P)$, $C(^3P)$, $N(^4S)$, $O(^3P)$, and $F(^2P)$. From the computational standpoint it is con-

TABLE III. Energies for three-electron atoms.[a]

Method	$Li(^2S)$	$Li(^2P)$	$Be^+(2S)$	$B^{2+}(^2S)$
RHF[b]	−7.432726	−7.365068	−14.27605	−23.37599
UHF[c]	−7.432749	−7.365076	⋯	⋯
PUHF[c]	−7.432767	−7.365080	⋯	⋯
SEHF (GF)	−7.432813[c]	−7.365091[c]	−14.27762[d]	−23.37632[d]
SOHF	−7.447565[b]	−7.380087[b]	−14.29162[d]	−23.38992[d]
Present[a]	−7.432780	−7.365071	−14.27627	−23.37631
exptl[c]	−7.47807	−7.41016	−14.3208[e]	−23.4206[e]

[a]The basis sets used in the present calculations are those determined by Kaldor and Harris (Footnote b below).

[b]U. Kaldor and F. E. Harris, Phys. Rev. 183, 1 (1969).

[c]W. A. Goddard, Phys. Rev. 176, 106 (1968).

[d]R. C. Ladner and W. A. Goddard, J. Chem. Phys. 51, 1073 (1969).

[e]C. E. Moore, Natl. Bur. Stand. Circ. 467 (1949).

venient to classify these atoms into two groups, the first one being the three-electron atoms and the second one being B through F. For the calculations of spin density, the three-electron atoms are much easier than B through F. For B–F, the unpaired electrons are all in the p orbitals so that the RHF wavefunction does not give spin density. Their spin densities are all due to the SP mechanism. Since these atoms have two inner cores, 1s and 2s orbitals, and their first-order contributions are rather canceling, as is well known,[12] the calculations become more difficult for B–F than for the three-electron atoms. The secondary effects such as the effect of d orbitals,[12] the effect of electron correlation,[17–22] etc., can become more important for B–F than for the three-electron atoms. (The effect of f orbitals is known to be very small.)[12,22] For this reason we have included in the present calculations the d orbitals (i.e., the angular correlation effect) for B–F, but for the three-electron atoms we have used only the sp basis. Within the sp basis the spin-polarization operator given by Eq. (8) is symmetry adapted, but when we include d orbitals, the operator has to be modified for the $s \to d$ excitations; namely, we have added to these operators the terms which rearrange the assignments of the unpaired electrons among three p orbitals so that the $s \to d$ excitation becomes symmetry adapted. Owing to the inclusion of d orbitals, the present calculations for B–F include angular correlation effect within the orbital theoretic framework. It is accommodated through the spin-polarization excitation operators.

In Tables III and IV we have compared the energies obtained by the present theory with the previous ones, and in Tables V and VI we have given such comparisons for the spin density. The results for the three-electron atoms are given in Tables III and V and the results for B through F are given in Tables IV and VI. The basis set used in the present calculations are summarized in the footnotes of Tables III and IV. All of the sp basis sets used are of near Hartree–Fock limit quality.

Table III summarizes the energies calculated for the three-electron atoms. Since the pseudo-orbital theory is based on the orbital theoretic idea, its energy is essentially the same as those of the RHF, UHF, and SEHF

TABLE IV. Energies for the atoms B through F.[a-c]

Method	Inclusion of d orbitals	B(^2P)	C(^3P)	N(^4S)	O(^3P)	F(^2P)
RHF[d]	No	−24.52905	−37.68861	−54.40092	−74.80935	−99.40932
UHF	No[d]	−24.52930	−37.68998	−54.40453	−74.81394	−99.41129
	Yes[e]	−24.53313	−37.69371		−74.81738	−99.41478
SEHF(GF)[d]	No	−24.52980	−37.69114	−54.40642	−74.81684	−99.41415
SOHF	No	−24.54605[f]	−37.70680[f]	−54.42129[g]	···	···
CI-POL[h]	Yes	−24.55129	−37.72814	−54.45176	−74.85571	−99.43811
CI-FO[i]	Yes	−24.58742	−37.75068	−54.45663	−74.85898	−99.43976
Present (A)	No[a,b]	−24.53014	−37.69281	−54.41041	−74.81378	−99.41073[b]
(B)	Yes[a,b]	−24.55285	−37.75408	−54.52555	−74.87408	−99.43311[b]
(C)	Yes[a]	−24.55287	−37.75410	−54.52557	−74.87415	−99.43336
exptl[d]		−24.6579	−37.8558	−54.6122	−75.1099	−99.8059

[a]Basis sets used in the present calculations: Calculation A, sp basis given by Goddard[7] except for fluorine; Calculation B, sp basis given by Goddard[7] plus d basis given by Schaefer et al.[12] except for fluorine; Calculation C, the accurate sp basis given by Bagus and Gilbert[34] plus d basis given by Schaefer et al.[12]

[b]For fluorine we have used the following sp basis for Calculations A and B; 9.016(1s), 10.32(3s), 6.80(3s), 4.136(3s), 2.433(3s), 1.11(3s), 1.44(4s), 1.601(2p), 3.124(2p), 6.00(2p), 9.435(2p). (See Ref. 33.)

[c]The difference in the uses of Eqs. (37) and (38) of Ref. 14 is small. The energies calculated with the former are −37.75144 for C(^3P) and −54.51882 for N(^4S) for Calculation B.

[d]W. A. Goddard, Phys. Rev. **182**, 48 (1969).

[e]P. J. Hay and W. A. Goddard, Chem. Phys. Lett. **9**, 356 (1971).

[f]U. Kaldor, Phys. Rev. A **2**, 1267 (1970).

[g]U. Kaldor, Phys. Rev. A **1**, 1586 (1970).

[h]H. F. Schaefer, R. A. Klemm, and F. E. Harris, Phys. Rev. **176**, 49 (1968).

[i]H. F. Schaefer, R. A. Klemm, and F. E. Harris, Phys. Rev. **181**, 137 (1969).

theories. As expected, the effect of the spin-polarization operator is small for the energy. The SEHF theory does not improve the energy for these open-shell atoms despite that the theory is supposed to include the alternant correlation effect. This is due to the interference with the spin-correlation effect as analyzed previously. The spin-optimized (SO) HF theory,[16] which is a type of the MC−SCF theory among independent spin functions,[17] gives lower energy since it includes both spin correlation and electron correlation in a more refined way than the SEHF theory. However, since this theory does not include the angular correlation effect, its energy approaches at best the radial limit.

The energies given in Table IV for B through F are due to the two types of calculations. One is based on the sp basis, and the other is based on the spd basis and includes the angular correlation effect. The present calculations have been performed with both types of basis sets.[33] The relations among the energies calculated without d orbitals are similar to those seen in Table III for the three-electron atoms. The present results are close to the results of the RHF, UHF, and SEHF theories. The SEHF theory does not improve the energy of these atoms because of the interference analyzed previously. The SOHF theory gives the best results within the calculations without d orbitals. On the other hand, we see that the effects of d orbitals are very important for these atoms. This is most clearly seen by comparing the present calculations A and B. In the former we have included only the sp basis[7] and in the latter we have further added the d basis.[12] In Calculation C, we have used a sp basis[34] different from the calculations A and B but the same d basis as the calculation

TABLE V. Spin densities for three-electron atoms.[a]

Atoms	RHF[b]	UHF[c]	PUHF[c]	SEHF (GF)	SOHF[b]	CI	Present[a]	exptl
Li(^2S)	0.1666	0.2248	0.1866	0.2406[c]	0.2265	0.2065[e]	0.2243	0.2313[c]
Li(^2P)	0.0	−0.01747	−0.00582	−0.02304[c]	−0.0169	−0.01402[f]	−0.01678	−0.01693[g]
Be$^+$(^2S)	0.7942	···	···	1.008[d]	0.9938	···	0.9694	···
B^{2+}(^2S)	2.1554	···	···	2.521[d]	2.5166	···	2.4838	···

[a]For the basis set used in the present calculations, see Footnote a of Table III.

[b]U. Kaldor and F. E. Harris, Phys. Rev. **183**, 1 (1969).

[c]W. A. Goddard, Phys. Rev. **176**, 106 (1968).

[d]R. C. Ladner and W. A. Goddard, J. Chem. Phys. **51**, 1073 (1969).

[e]A. W. Weiss, Phys. Rev. **122**, 1826 (1961).

[f]K. Ishida and H. Nakatsuji, Chem. Phys. Lett. **19**, 268 (1973).

[g]J. D. Lyons and T. P. Das, Phys. Rev. A **2**, 2250 (1970).

TABLE VI. Spin densities for boron through fluorine.[a]

Atoms	UHF Without d[b]	UHF With d[c]	SEHF(GF)[b] Without d	SOHF Without d	CI (with d) CI-POL[f]	CI (with d) CI-FO[g]	Present (with d) Calculation B	Present (with d) Calculation C	exptl[b]
B(^2P)	0.0192	0.0218	0.0362	0.0022[d]	0.0073	0.0041	0.0147	0.0132	0.0081
C(^3P)	0.0753	0.0784	0.0733	0.0423[d]	0.0277	0.0288	0.0487	0.0506	...
N(^4S)	0.1853	0.1853	0.1579	0.120[e]	0.0730	0.0714	0.1176	0.1206	0.09705
O(^3P)	0.1944	0.194	0.2137	...	0.0610	0.0628	0.0712	0.0717	0.11398
F(^2P)	0.1298	0.122	0.2454	...	0.0470	0.0496	0.0305	0.0345	0.07184

[a]For the basis set used in the present calculations, see Table IV footnotes.
[b]W. A. Goddard, Phys. Rev. 182, 48 (1969).
[c]P. J. Hay and W. A. Goddard, Chem. Phys. Lett. 9, 356 (1971).
[d]U. Kaldor, Phys. Rev. A 2, 1267 (1970).
[e]U. Kaldor, Phys. Rev. A 1, 1586 (1970).
[f]H. F. Schaefer, R. A. Klemm, and F. E. Harris, Phys. Rev. 176, 49 (1968).
[g]H. F. Schaefer, R. A. Klemm, and F. E. Harris, Phys. Rev. 181, 137 (1969).

B. (The calculations B and C show that the sp basis dependence is negligibly small for the energy.) We note that the present results including angular correlations are *even lower* than the SOHF results which include radial correlation effect within the sp basis. Hay and Goddard have reported the UHF calculations including d orbitals.[35] In their calculations the effect of d orbitals are relatively small. For nitrogen they have found that the orbitals are stable for the mixing of d orbitals. In contrast to the present results, these results are probably due to the fact that their UHF wavefunctions are the mixed states for both spin and space symmetries. Their wavefunctions are the mixtures of the higher-multiplet *excited* states into the pure ground states.[11]

Between the two types of the limited CI calculations including d orbitals, the "polarization" CI (CI-POL) and the "first-order" CI (CI-FO)[36] calculations reported by Schaefer, Klemm, and Harris,[12] the CI-POL wavefunction is closer to the FOCI wavefunction[36] denoted in the present paper. Their CI-FO wavefunction[12] includes the limited types of electron correlation[37] within up to the valence shells (internal and semi-internal correlations in the Sinanoğlu's "charge" wavefunction[38]). However, neither of these wavefunctions includes the self-consistency effect. In Table I, we see that the present pseudo-orbital theory including d orbitals gives lower energy than the CI-POL theory except for fluorine.[33] The present results are comparable to the CI-FO results. Further, we note that the present results were obtained with a much smaller number of independent variables than those included in the CI-POL and CI-FO wavefunctions. In the CI-POL wavefunction, the numbers of the configurations were 53, 65, 41, 77, and 65 for B, C, N, O, and F, respectively, and in the CI-FO wavefunctions they were 153, 181, 73, 113, and 95, respectively.[12] In the present wavefunctions, the number of the variables $C_{P,tk}$ in Eq. (20) were only 22 (Calculation B) and 18 (Calculation C) for all of the atoms B-F. This clearly shows an effectiveness of the self-consistency effect of the spin-polarization excitations included in the present theory through the SAC expansion formalism. Since the diagonal element of the **B** matrix, which is given by Eq. (36b), increases with the increase in the number of the unpaired spins s, the self-consistency ef-

fect is expected to increase with the increase in s. Accordingly, the lowering is largest for N ($s = 3$) and then for C and O ($s = 2$), and smallest for B ($s = 1$). Thus, from Table IV, we may conclude that the inclusion of the angular correlation effects and the proper inclusion of the self-consistency effects are important for the energy lowering of these atoms.

We next compare the spin densities calculated by the present theory with the previous results. We first discuss the results for the three-electron atoms shown in Table V. Although the energies of the RHF, UHF, SEHF, and present theories within the sp basis are very close, as seen in Table III, their spin densities are quite different from each other. The RHF values give the amounts of the SD contributions. For these atoms the sequences given by (50) and (51) hold for the total spin density since both of the SD and SP contributions have the same sign (positive) for the ^2S states and the SD contribution is zero for the ^2P state. In agreement with these predicted sequences, the present results are smaller than the UHF and SEHF values and larger than the CI results. The present results are very close to the experimental values: the error is 3% for Li(^2S) and 0.9% for Li(^2P). For these atoms, it is known that the effect of electron correlation is small.[19-21] The Brueckner–Goldstone-type many-body theory has given 0.2297[19a] and 0.232[20] for Li(^2S) and −0.01652[19c] for Li(^2P), and the Bethe–Goldstone-type theory has given −0.01708[21b] for Li(^2P). The present results are also very close to the results of the SOHF theory[16b] despite the fact that the SOHF theory is much more difficult in applications than the present theory but includes the electron correlation effect.

In Table VI, we have summarized the spin densities for B through F. In these atoms the unpaired spins are in the p orbitals so that the RHF theory does not give spin density. Their spin densities are due only to the SP mechanism. The effects of the d orbitals are known to be very important for the spin densities of these atoms.[12,22] Then, we have given in Table VI the present results calculated with the d orbitals. The two sets of calculations are different only in the sp basis. Further, in Table VII we have partitioned the present results into different contributions in order to see why the d orbitals

TABLE VII. Approximate partitioning of the spin density into different contributions.[a-c]

Contributions	Li(^2P)	B(^2P)	C(^3P)	N(^4S)	O(^3P)	F(^2P)
First order						
$1s \to ns$	−0.01681	−0.0654	−0.2296	−0.5223	−0.4734	−0.3107
$2s \to ns$	•••	0.0592	0.2245	0.5416	0.4698	0.2990
Sum of above	−0.01681	−0.0062	−0.0051	0.0192	−0.0036	−0.0118
Second order						
$1s, 2s \to ns, ms$	0.00004	0.0027	0.0034	0.0124	0.0055	0.0034
$1s, 2s \to nd$	•••	0.0192	0.0535	0.0866	0.0688	0.0386
Mixed term	•••	−0.0009	−0.0031	−0.0007	0.0005	0.0003
Sum of above	0.00004	0.0209	0.0538	0.0984	0.0748	0.0423
Total sum	−0.01678	0.0147	0.0487	0.1176	0.0712	0.0305

[a]Calculation B for boron through fluorine (see Table IV).
[b]The partitioning is approximate since the excitation operators $R^+_{p,tk}$ in Eq. (34c) are linear combinations of the primitive operators $S^+_{p,tk}$ as given by Eq. (29).
[c]The spin densities obtained without d orbitals (Calculation A) are B(−0.0065), C(0.0027), N(0.0443), O(0.0139), and F(−0.0018).

are so important for these atoms. Although the first-order contribution is dominant for Li(^2P), it is very small for B−F because of the large cancelation between the $1s$ and $2s$ contributions. (The $s \to d$ excitations do not directly contribute to the first-order spin density.) Then, for B through F, the relatively small secondary effects can become very important. Within the second-order terms the contributions of the $s \to d$ excitations are much more important than those of the $s \to s$ excitations. This partitioning reconfirms the importance of the d orbitals for the spin densities of B−F. The trend shown in Table VII is similar to that reported by Platas and Schaefer for N(^4S).[22] However, we note that the effects of d orbitals on the UHF spin densities are relatively small,[35] as seen in Table VI. Such a trend of the UHF theory was also seen for the energies of these atoms (Table IV).

Now we return to Table VI and compare the present results with the previous ones including the effects of d orbitals. In agreement with the predicted sequence (50), the present results are always smaller than the UHF results including d orbitals, but they are larger than the results of the CI-POL and the CI-FO calculations, except for fluorine. Although the sequence (50) has been given for the first-order spin density, it has actually originated from the same sequence for the coefficients [C'_i of Eq. (30b) for the present theory].[10] Then the same sequence as that of (50) would also hold for the second-order spin density. The difference between the present and the CI-POL results is attributed to the self-consistency effect included in the present theory. Comparing the CI-POL values with the CI-FO values, we see that the electron correlation of the type included additionally in the CI-FO wavefunction is relatively unimportant for the spin density. The self-consistency effect is much more important for the spin density than this type of electron correlation effect. Although the spin densities calculated by the SEHF theory do not include the effect of d orbitals, we may estimate the order of the effect from the UHF results calculated with and without d orbitals. We then believe that even if d orbitals are included in the SEHF calculations, the resultant spin densities would still be larger than the present values as predicted by the sequence (50). It is interesting to note that the present results are very close to the results of the SOHF theory, despite the fact that the latter does not include the effect of d orbitals but includes the electron-correlation effect. Such a trend has also been seen in Table V for the three-electron atoms.

In comparison with the experimental values, the present theory gives much better agreement than the UHF and the SEHF theories within a simple orbital-theoretic framework. This is due to the elimination of the interference between the spin-correlation and electron-correlation effects. In comparison with the CI-POL and CI-FO results, the present results may also be said to become closer to the experimental values except for fluorine, although the numbers of the variational parameters are much smaller in the present calculations than those in the CI-POL and CI-FO calculations. For more definite conclusions, however, we need more examples of the present and FOCI calculations. Although the present results still deviate to some extent from the experimental values, the deviations are not systematic as the UHF, SEHF, CI-POL, and CI-FO results are. This may suggest that the present theory does not include a serious theoretical defect which may cause a systematic error. We believe that the present pseudo-orbital theory based on the wavefunction (20) is more suitable than the conventional theories for the routine calculations of the spin density in experimental laboratories. The present theory is simple enough in application as required for such theory.

Lastly, we give additional data which shows that the coupling effect between the spin-polarization operator and the singlet-type excitation operator as included in the pseudo-orbital wavefunction (16) is small. Among the singlet-type excitation operators included in Eq. (16), the operators $S^+_{0,tm}$ and $S^+_{0,mk}$ do not give any direct contributions to the spin densities of B−F up to the second order in the coefficients (i.e., within the present accuracy). Then, we have examined the coupling effect between the operators $S^+_{p,tk}$ and $S^+_{0,tk}$ with the use of the

TABLE VIII. Coupling effect of the spin-polarization and singlet-type excitation operators on the energies and spin densities of the first-row atoms.[a]

Atoms	Without coupling		With coupling		exptl	
	Energy	Spin density	Energy	Spin density	Energy	Spin density
$B(^2P)$	−24.55285	0.0147	−24.55290	0.0149	−24.6579	0.0081
$C(^3P)$	−37.75408	0.0487	−37.75419	0.0555	−37.8558	···
$N(^4S)$	−54.52555	0.1176	−54.52575	0.1204	−54.6122	0.09705
$O(^3P)$	−74.87408	0.0712	−74.87414	0.0792	−75.1099	0.11398
$F(^2P)$	−99.43311	0.0305	−99.43321	0.0295	−99.8059	0.07184

[a]The basis sets are for Calculation B (see Table IV).

pseudo-orbital wavefunction

$$\Phi_{PO4} = \mathcal{O}\left(\sum_{tk} C_{P,tk} S_{P,tk}^{+} + \sum_{tk} C_{0,tk} S_{0,tk}^{+}\right)\Phi_0. \qquad (53)$$

We have also considered the symmetry adapted $s \rightarrow d$ excitations for the additional singlet-type excitation operators.

In Table VIII we have compared the energies and spin densities of B–F obtained from the wavefunction (53) with those obtained from the wavefunction (20). We see that the coupling effect is negligibly small for the energy and also very small for the spin density. The effect does not account for the deviations between the calculated and experimental values. For further improvement, the inclusion of the electron-correlation effect would be necessary. It is interesting to study such an effect in the SAC expansion formalism[14] by considering the double excitation operator $\hat{S}_{(2)}$ in addition to the pseudo-orbital wavefunction given by Eq. (1).

V. CONCLUSION

In this paper, we have considered an application of the symmetry-adapted-cluster (SAC) expansion proposed previously[14] to open-shell systems, limiting ourselves to only the single excitation operator $\hat{S}_{(1)}$. The pseudo-orbital theory thus obtained gives a natural extension of the open-shell orbital theory. Here, we have started from the RHF reference wavefunction and considered mainly the spin-polarization excitation operator and its self-consistency effect. This theory corresponds to an extension of the UHF and SEHF theories (which are equivalent to the conventional cluster expansions including $\hat{T}_1$ alone) and yet it is free from the theoretical defects found previously for these theories. It is concluded that a proper inclusion of the (unlinked) self-consistency effect is quite important and that the pseudo-orbital theory realizes this requirement in a simple orbital theoretic framework, in contrast to the FOCI, UHF, and SEHF theories. The analysis of these wavefunctions has shown the existence of the following relation for simpler atoms and molecules, i.e.,

$$|\rho_{SP}^{FOCI}| < |\rho_{SP}^{present}| < |\rho_{SP}^{SEHF}|, \quad |\rho_{SP}^{UHF}|,$$

where ρ_{SP} means the spin-polarization contribution to spin density. This sequence has been confirmed in the calculated spin densities for the first-row atoms.

From the applications of the pseudo-orbital theory to the first-row atoms, it is shown that within the sp basis

the present theory gives the energy close to the conventional orbital theories. However, when the angular correlation effect is included with the use of the d orbitals (this is relatively easy in the present theory than in the conventional orbital theories), the present theory gives considerably lower energy than the conventional theories because of the proper inclusion of the angular correlation effect through the SAC expansion formalism. For the spin density, the present results for the three-electron atoms are excellent in comparison with the experimental values, and for B through F the present results are fairly better than those of the UHF and SEHF theories and reasonable within a simple orbital–theoretic approach. Because of the simplicity of calculations and the absence of theoretical defects, we think that the present pseudo-orbital theory is more suitable than conventional theories for the routine calculations of the spin density in experimental laboratories.

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