CLUSTER EXPANSION OF THE WAVEFUNCTION. PSEUDO-ORBITAL THEORY APPLIED TO SPIN CORRELATION

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We have discussed the utility of the cluster expansion of the wavefunction and proposed a pseudo-orbital theory which constitutes a generalization of the orbital-theoretic idea. It has been applied to the calculation of spin densities of the first-row atoms. The results are encouraging in comparison with the experimental values.

The cluster expansion of the wavefunction gives a compact and precise way of constructing an exact wavefunction Ψ from the approximate one Φ_0 [1,2], that is

$$\Psi = \exp(T)\Phi_0 , \qquad (1)$$

where T is a generating operator for a linked cluster expansion [2]. We are developing a simple method for calculating the electronic structures of atoms and molecules on the basis of this expansion. We expand the operator T by means of the excitation operator S^+ as

$$T = \sum_i C_i S_i^+ + \sum_{i>j} C_{ij} S_{ij}^+ + \dots , \qquad (2)$$

where S_i^+, S_{ij}^+, etc. are the symmetry-adapted one- and two-electron excitation operators and C_i, C_{ij}, etc. are the coefficients to be determined variationally. The main effects of the first and second terms of T are to improve basic orbitals and pair-correlations, respectively.

To approximate the operator T by the first term corresponds to take into account the effect of S_i self-consistently. It constitutes a generalization of the basic idea of the orbital theory. For instance, let Φ_0 be an arbitrary Slater determinant for closed-shell system and S_i^+ be a singlet excitation operator. Then, the resultant Ψ is easily shown to be identical with the Hartree–Fock (HF) wavefunction. Such formulation has been adopted previously for the derivation of the coupled perturbed HF theory [3]. A merit of this formulation of the orbital theoretic idea is that the freedom in the choice of S_i^+ is much wider than that permitted in the conventional orbital theory. It is especially so for the open-shell electronic system. We may call such presentation of orbital theoretic idea as pseudo-orbital theory.

Similarly, in the many-electron theory of Sinanoğlu [1] and in the self-consistent geminal theory, the operator T was approximated essentially by the second term of eq. (2). When we consider both S_i^+ and S_{ij}^+ in eq. (2), we can take into account the coupled effects of orbital correction and pair-correlation correction simultaneously in a self-consistent fashion. There, the basic standpoint would be close to that of the multi-configuration (MC) SCF theory.

We have applied the pseudo-orbital theory to the calculation of spin density. The quantity gives a good criterion in examining the validity of spin-correlation included in various theories [4]. It has been shown that the present theory does not have the defects found for the conventional orbital theories such as the unrestricted (U) HF and the spin-extended (SE) HF theories [4]. We report here the preliminary results. As the reference wavefunction Φ_0, we have chosen the restricted (R) HF wavefunction [5],

$$\Phi_0 = \|\varphi_1\bar{\varphi}_1 \dots \varphi_k\bar{\varphi}_k \dots \varphi_q\bar{\varphi}_q\,\varphi_{q+1} \dots \varphi_m \dots \varphi_p\| , \qquad (3)$$

and as the excitation operator S_i^+, we have chosen the generator of the spin-polarization configuration, i.e.

$$S^+_{tk} = (s+2)^{1/2}\left[(s/2)^{1/2}(a^+_{t\alpha}a_{k\alpha} - a^+_{t\beta}a_{k\beta}) + (2/s)^{1/2}a^+_{t\alpha}a_{k\beta}\sum_m a^+_{m\beta}a_{m\alpha}\right], \quad (4)$$

where $s = p-q$ and the suffices k, m, and t denote doubly occupied, singly occupied, and unoccupied orbitals in the RHF wavefunction. Since the spin-density is a one-electron property, we expect that the quantity could be calculated to good approximation within the orbital theoretic approach considering S^+_{tk} self-consistently. Although the pseudo-orbital theory realizes such an idea in a simple compact form, i.e.

$$\Psi = \exp\left[\sum_{tk} C_{tk}S^+_{tk}\right]\Phi_0 , \quad (5)$$

it would be difficult to express such an idea within a conventional orbital theory. In this calculation, we have applied the variational principle to the energy correct to second order for the coefficients C_{tk}. Then, the resultant wavefunction is correct up to first order *. The variationally determined wavefunction is written in a sum-over-state form as

$$\Psi = N\left[1 + \sum_{tk}\frac{\langle\Phi_0|R_{tk}H|\Phi_0\rangle}{E_0 - D_{tk}}R^+_{tk}\right]\Phi_0 , \quad (6)$$

* In the second-order term, the term including $S^+_{tk}S^+_{ul}\Phi_0$ ($t \neq u, k \neq l$) destroys spin-symmetry. However, its contribution to spin density is quite small since it begins to contribute from the fourth order in the coefficient. (The values in table 1 do not include such a contribution.)

where R^+_{tk} is connected with S^+_{tk} by an orthogonal transformation

$$\boldsymbol{R}^+ = \boldsymbol{S}^+\mathbf{U}, \quad (7)$$

in which the matrix $\mathbf{U}$ is defined by

$$\mathbf{U}^+(\mathbf{A}+\mathbf{B})\mathbf{U} = \mathbf{D}, \quad (8)$$

$$\mathbf{A} = \langle\Phi_0|SHS^+|\Phi_0\rangle, \quad \mathbf{B} = \langle\Phi_0|H(S^+)^{\mathrm{T}}S^+|\Phi_0\rangle , \quad (9)$$

where $\mathbf{D}$ is a diagonal matrix with diagonal element D_{tk}. $\boldsymbol{S}^+$ and $\boldsymbol{R}^+$ are the row vectors composed of the excitation operators S^+_{tk} and R^+_{tk}. The calculation requires only a single diagonalization in eq. (8). In comparison with the singly-excited CI (or Tamm–Dancoff) formulation, the present theory includes the contribution of the $\mathbf{B}$ matrix in the energy denominator of eq. (6). It arises from the self-consistency and is of the order of magnitude of the exchange integral [3].

Table 1 summarizes the preliminary results for the first-row atoms. They are correct up to the second-order in the coefficients. For boron through fluorine, we have added the d-orbital bases. As has been shown by Schaefer et al. [6], we have also confirmed the importance of the d-orbitals. In the present pseudo-orbital theory, the inclusion of the d-orbitals is easily done by slightly modifying the excitation operators S^+_{tk} given by eq. (4). In the conventional orbital theory, its inclusion could be done only after the remove of the symmetry constraint and the subsequent projection. As seen in table 1, the general agreement of the present results with the experimental values is satisfactory. Our results are also close to the results of the spin-optimized

Table 1
Spin densities for first-row atoms

	UHF	SEHF	SOHF	FOCI	Present	Experiment
Li ^2S	0.2248 a)	0.2406 a)	0.2265 d)	0.2065 g)	0.2243	0.2313
^2P	−0.01747 a)	−0.02304 a)	−0.0169 d)	−0.02222 h)	−0.0168	−0.01693
Be^+ ^2S		1.008 c)	0.9938 d)		0.9694	
B^{2+} ^2S		2.521 c)	2.516 d)		2.484	
B ^2P	0.0192 b)	0.0361 b)	0.0022 e)	0.0041 i)	0.0147	0.0081
C ^3P	0.0753 b)	0.0733 b)	0.0423 e)	0.0288 i)	0.0487	
N ^4S	0.1853 b)	0.1579 b)	0.1200 f)	0.0714 i)	0.1176	0.09705
O ^3P	0.1944 b)	0.2137 b)		0.0628 i)	0.0712	0.11398
F ^2P	0.1298 b)	0.2455 b)		0.0496 i)	0.0305	0.071835

a) Ref. [7]. b) Ref. [8]. c) Ref. [9]. d) Ref. [10]. e) Ref. [11]. f) Ref. [12]. g) Ref. [13]. h) Ref. [14]. i) Ref. [15].

(SO) HF theory which is much more difficult to perform than the present theory. We further note that the present results lie between the UHF or the SEHF results and the first-order (FO) CI results, i.e.,

$$|\rho_{\mathrm{FOCI}}| < |\rho_{\mathrm{present}}| < |\rho_{\mathrm{UHF}}|, |\rho_{\mathrm{SEHF}}| , \qquad (10)$$

except for fluorine. This relation can also be derived theoretically from an approximate analysis of the present theory as has been done previously for the UHF, SEHF, and FOCI theories [4]. Such an analysis has shown that the present theory is free from the defects existing in the UHF and SEHF theories. We believe that the present theory is simple enough for routine calculations of spin density in experimental laboratories and yet produces reliable results. More details of this preliminary report will be published elsewhere in the near future.

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