

## On the orbital theories in the spin-correlation problems. II. Unrestricted and spin-extended Hartree-Fock theories\*

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(Received 1 May 1972)

A perturbation-variation treatment is applied to interconnect the unrestricted, projected unrestricted, and spin-extended Hartree-Fock wavefunctions with the first order sum-over-state perturbation wavefunction. The restricted Hartree-Fock wavefunction is chosen as a starting point. From these, the interrelations among these theories are clarified not only for the first order correction to the wavefunctions but also for their spin densities. Moreover, the natures of the unrestricted and spin-extended Hartree-Fock theories in the spin-correlation problems are examined in the light of the physical reality of the correlation phenomena in open-shell electronic systems. These results are ascertained numerically by referring the spin densities calculated by these various methods and obtained from experiments.

### I. INTRODUCTION

Since quantum chemistry deals with essentially insoluble many-body problems, the approximate "concept" which extracts an essence of the physical reality becomes very important. Among these approximate concepts, the orbital model (Hartree-Fock theory) has worked very well in the elucidation of the electronic structures of atoms, molecules and solids. It is distinguished from other theories by its physical simplicity and visuality.<sup>1</sup> However, there are still many things when we go beyond the Hartree-Fock theory. These phenomena, which are called collectively electron correlation phenomena, are topics of current interest in quantum chemistry.<sup>2</sup> Among these, spin-correlation is the main interest of this series of papers.

There are several methods which are based essentially on the orbital model and which also include spin-correlation effects in open-shell electronic systems. Among these, we focus our present interest on the unrestricted,<sup>3</sup> the projected<sup>4</sup> (or annihilated<sup>5</sup>) unrestricted and spin-extended<sup>1,6</sup> Hartree-Fock theories. The unrestricted Hartree-Fock (UHF) wavefunction is a single determinant in which different orbitals are allowed for different spins. However, objections can be raised to spin-density calculations with this method, since its wavefunction is not an eigenfunction of  $S^2$ . The projected (or annihilated) unrestricted Hartree-Fock (PUHF) wavefunction is the spin-projected (or spin-annihilated) function of the UHF wavefunction after energy minimization. Then this wavefunction does not satisfy the variation condition. The spin-extended Hartree-Fock (SEHF) wavefunction is the function which minimizes the energy after spin-projection of a single determinant and accords with the GF method of Goddard.<sup>7</sup> An extension of these methods was recently made

by varying the orbitals within all the spin functions of the same multiplicity.<sup>8</sup>

In the previous paper of this series,<sup>9</sup> we analyzed the UHF wavefunction in configuration-interaction language to first order and showed a simple relation existing between the UHF and PUHF wavefunctions. From this, we found a simple method to separate the spin density calculated by the UHF method into contributions due to the spin-polarization (SP) and spin-delocalization (SD) mechanisms.<sup>9,10a</sup> Because of the physical simplicity and visuality of each mechanism, a more profound understanding than before on the nature of spin density has become possible.<sup>10</sup>

In the present study, our purposes are twofold; one is to interconnect these theories in relation to the first order sum-over-state perturbation (FO-SOSP) theory and the second is to clarify the natures of these orbital theories in spin-correlation problems. In the following two sections, we present perturbation-variation descriptions of the UHF and SEHF wavefunctions to first order, taking the restricted Hartree-Fock (RHF) wavefunction as a starting point. The results on these orbital theories are compared in Sec. IV with the FO-SOSP theory starting from the RHF wavefunction. The interrelations among these theories are clarified not only for their first order corrections to the wavefunctions but also for their spin densities. Then, in Sec. V, the natures of the UHF and SEHF theories in the spin-correlation problems are examined in the light of the physical reality of the correlation phenomena in open-shell electronic systems.<sup>11</sup> Lastly in Sec. VI, concluding remarks on the results are given.

### II. PERTURBATION-VARIATION DESCRIPTION OF THE UHF WAVEFUNCTION

The starting wavefunction of the present study is the RHF single determinant<sup>12</sup> built up from  $q$

closed orbitals and  $s (= p - q)$  open orbitals,

$${}^s\Psi_0 = \|\psi_1\bar{\psi}_1 \cdots \psi_k\bar{\psi}_k \cdots \psi_q\bar{\psi}_q \psi_{q+1} \cdots \psi_m \cdots \psi_p\|. \quad (1)$$

The superscript  $s$  means that the configuration is an eigenfunction of  $S^2$  with eigenvalue  $(s/2)(s/2 + 1)$ .  $\|\cdots\|$  denotes a normalized determinant.

In the following,  $k, l$  refer to closed orbitals,  $m, n$  to open orbitals,  $t, u$  to vacant orbitals and  $i, j$  to general orbitals. These orbitals constitute an orthonormal set. The important feature of the RHF wavefunction is the following Brillouin theorem. Consider the one-electron excited configurations of the forms,

$${}^s\Psi_k^t(1) = \|\psi_1\bar{\psi}_1 \cdots \psi_i\bar{\psi}_i(\alpha\beta - \beta\alpha)/\sqrt{2} \cdots \psi_q\bar{\psi}_q \psi_{q+1} \cdots \psi_p\|,$$

$${}^s\Psi_k^m = \|\psi_1\bar{\psi}_1 \cdots \psi_k\bar{\psi}_m \cdots \psi_q\bar{\psi}_q \psi_{q+1} \cdots \psi_p\|, \quad (2)$$

$${}^s\Psi_m^t = \|\psi_1\bar{\psi}_1 \cdots \psi_q\bar{\psi}_q \psi_{q+1} \cdots \psi_{m-1}\bar{\psi}_i \psi_{m+1} \cdots \psi_p\|;$$

then the Hamiltonian matrix elements between  ${}^s\Psi_0$  of Eq. (1) and the configurations given in Eq. (2) vanish:

$$\begin{aligned} \langle {}^s\Psi_0 | \mathcal{H} | {}^s\Psi_k^t(1) \rangle &= 0, \\ \langle {}^s\Psi_0 | \mathcal{H} | {}^s\Psi_k^m \rangle &= 0 \\ \langle {}^s\Psi_0 | \mathcal{H} | {}^s\Psi_m^t \rangle &= 0 \end{aligned} \quad (3)$$

The UHF single determinant built up from  $p$   $\alpha$ -spin and  $q$   $\beta$ -spin orbitals is written as

$$\Psi_{\text{UHF}} = \|\phi_1^\alpha \bar{\phi}_1^\beta \cdots \phi_k^\alpha \bar{\phi}_k^\beta \cdots \phi_q^\alpha \bar{\phi}_q^\beta \phi_{q+1}^\alpha \cdots \phi_m^\alpha \cdots \phi_p^\alpha\|, \quad (4)$$

which is an eigenfunction of  $S_z$  with eigenvalue  $s/2$ , but not an eigenfunction of  $S^2$ . Note that  $\Psi_{\text{UHF}}$  is independent of unitary transformations within the  $\alpha$ - and  $\beta$ -spin orbitals except for an unimportant constant factor. This holds also for the RHF wavefunction of Eq. (1) for unitary transformations within the closed and open orbitals. After relevant unitary transformations,<sup>13</sup> the differences between the UHF and RHF orbitals become very

small.<sup>14</sup> We set these differences as  $f_i^\alpha$  and  $f_i^\beta$ .

$$\begin{aligned} \phi_i^\alpha &= \psi_i + f_i^\alpha \quad i = 1, \cdots, p, \\ \phi_i^\beta &= \psi_i + f_i^\beta \quad i = 1, \cdots, q. \end{aligned} \quad (5)$$

In the treatment below, it is more convenient to substitute

$$\begin{aligned} \sigma_k &= (f_k^\alpha + f_k^\beta)/2, \\ \pi_k &= (f_k^\alpha - f_k^\beta)/2 \quad k = 1, \cdots, q. \end{aligned} \quad (6)$$

Then, Eq. (5) becomes

$$\begin{aligned} \phi_k^\alpha &= \psi_k + \pi_k + \sigma_k, \\ \phi_k^\beta &= \psi_k - \pi_k + \sigma_k, \\ \phi_m^\alpha &= \psi_m + f_m^\alpha. \end{aligned} \quad (7)$$

In Eq. (7),  $\pi_k$  represents the spin-polarization effect on the originally doubly-occupied RHF closed orbital  $\psi_k$ , and is called *orbital spin-polarization*.  $\sigma_k$  represents the shift of the mean value of the  $\phi_k^\alpha$  and  $\phi_k^\beta$  orbitals from the RHF orbital  $\psi_k$ , and is called *closed orbital shift*.  $f_m^\alpha$  is called *open orbital shift*.

In the UHF method, the total energy expressed by

$$E_{\text{UHF}} = \langle \Psi_{\text{UHF}} | \mathcal{H} | \Psi_{\text{UHF}} \rangle / \langle \Psi_{\text{UHF}} | \Psi_{\text{UHF}} \rangle, \quad (8)$$

is minimized to all orders of the independent orbital corrections  $f_i^\alpha$  and  $f_i^\beta$  and therefore, to all orders of the independent corrections  $\pi_k$ ,  $\sigma_k$ , and  $f_m^\alpha$ . However, since our main interest in the present study lies in the spin-correlation correction which comes chiefly from the first order correction to the RHF wavefunction, it may be sufficient to minimize the energy correct to second order in  $\pi_k$ ,  $\sigma_k$ , and  $f_m^\alpha$ .<sup>15,16</sup> Inserting Eq. (7) into Eq. (4) and expanding it up to second order, we obtain the following expression (except for a normalization factor):

$$\begin{aligned} \Psi_{\text{UHF}} &= {}^s\Psi_0 + \sqrt{2} \sum_k^c \|\psi_1\bar{\psi}_1 \cdots \pi_k \psi_k(\alpha\beta + \beta\alpha)/\sqrt{2} \cdots \psi_q\bar{\psi}_q \psi_{q+1} \cdots \psi_p\| \\ &+ \sqrt{2} \sum_k^c \|\psi_1\bar{\psi}_1 \cdots \sigma_k \psi_k(\alpha\beta - \beta\alpha)/\sqrt{2} \cdots \psi_q\bar{\psi}_q \psi_{q+1} \cdots \psi_p\| \\ &+ \sum_m^o \|\psi_1\bar{\psi}_1 \cdots \psi_q\bar{\psi}_q \psi_{q+1} \cdots f_m^\alpha \cdots \psi_p\| \\ &+ \sum_k^c \|\psi_1\bar{\psi}_1 \cdots \sigma_k \bar{\sigma}_k \cdots \psi_q\bar{\psi}_q \psi_{q+1} \cdots \psi_p\| \\ &- \sum_k^c \|\psi_1\bar{\psi}_1 \cdots \pi_k \bar{\pi}_k \cdots \psi_q\bar{\psi}_q \psi_{q+1} \cdots \psi_p\| \\ &+ \sqrt{2} \sum_k^c \|\psi_1\bar{\psi}_1 \cdots \pi_k \sigma_k(\alpha\beta + \beta\alpha)/\sqrt{2} \cdots \psi_q\bar{\psi}_q \psi_{q+1} \cdots \psi_p\| \\ &+ 2 \sum_k^c \sum_{l < i}^c \{ \|\psi_1\bar{\psi}_1 \cdots \pi_k \psi_k(\alpha\beta + \beta\alpha)/\sqrt{2} \cdots \pi_l \psi_l(\alpha\beta + \beta\alpha)/\sqrt{2} \cdots \psi_q\bar{\psi}_q \psi_{q+1} \cdots \psi_p\| \end{aligned}$$

$$\begin{aligned}
& + \|\psi_1 \bar{\psi}_1 \cdots \sigma_k \psi_k (\alpha\beta - \beta\alpha) / \sqrt{2} \cdots \sigma_l \psi_l (\alpha\beta - \beta\alpha) / \sqrt{2} \cdots \psi_q \bar{\psi}_q \psi_{q+1} \cdots \psi_p\| \} \\
& + 2 \sum_k^c \sum_{l \neq k}^c \|\psi_1 \bar{\psi}_1 \cdots \pi_k \psi_k (\alpha\beta + \beta\alpha) / \sqrt{2} \cdots \sigma_l \psi_l (\alpha\beta - \beta\alpha) / \sqrt{2} \cdots \psi_q \bar{\psi}_q \psi_{q+1} \cdots \psi_p\| \\
& + \sqrt{2} \sum_k^c \sum_m^o \{ \|\psi_1 \bar{\psi}_1 \cdots \pi_k \psi_k (\alpha\beta + \beta\alpha) / \sqrt{2} \cdots \psi_q \bar{\psi}_q \psi_{q+1} \cdots f_m^\alpha \cdots \psi_p\| \\
& \quad + \|\psi_1 \bar{\psi}_1 \cdots \sigma_k \psi_k (\alpha\beta - \beta\alpha) / \sqrt{2} \cdots \psi_q \bar{\psi}_q \psi_{q+1} \cdots f_m^\alpha \cdots \psi_p\| \} \\
& + \sum_{m < n}^o \sum_n^o \|\psi_1 \bar{\psi}_1 \cdots \psi_q \bar{\psi}_q \psi_{q+1} \cdots f_m^\alpha \cdots f_n^\alpha \cdots \psi_p\| + (\text{higher order terms}), \tag{9}
\end{aligned}$$

where  $\sum^c$  and  $\sum^o$  mean the sums within the closed and open orbitals, respectively.

Now, let us expand the orbital corrections  $\pi_k$ ,  $\sigma_k$ , and  $f_m^\alpha$  in terms of the complete set of the RHF orbitals  $\{\psi_t\}$ . From the antisymmetric property of determinants, the expansions become

$$\pi_k = \sum_t^v a_k^t \psi_t, \quad \sigma_k = \sum_t^v b_k^t \psi_t, \quad f_m^\alpha = \sum_t^v c_m^t \psi_t, \tag{10}$$

where  $t$  runs over the vacant orbitals. Insertion of Eq. (10) into Eq. (9) gives the UHF wavefunction written in configuration interaction language to second order. Among the first order one-electron excited configurations, the most important is the configuration  $\Psi_k^t$  arising from the second term of

Eq. (9).

$$\Psi_k^t = \|\psi_1 \bar{\psi}_1 \cdots \psi_i \psi_k (\alpha\beta + \beta\alpha) / \sqrt{2} \cdots \psi_q \bar{\psi}_q \psi_{q+1} \cdots \psi_p\|. \tag{11}$$

Note that this configuration is not an eigenfunction of  $S^2$  and can be expanded by the spin eigenfunctions as,<sup>9</sup>

$$\Psi_k^t = [s/(s+2)]^{1/2} {}^s\Psi_k^t(2) + [2/(s+2)]^{1/2} {}^{s+2}\Psi_k^t, \tag{12}$$

where the configurations,  ${}^s\Psi_k^t(2)$  and  ${}^{s+2}\Psi_k^t$  satisfy

$$S^2 {}^s\Psi_k^t(2) = (s/2)(s/2+1) {}^s\Psi_k^t(2), \tag{13}$$

$$S^2 {}^{s+2}\Psi_k^t = (s/2+1)(s/2+2) {}^{s+2}\Psi_k^t$$

and are given by

$${}^s\Psi_k^t(2) = (s+2)^{-1/2} \left\| \psi_i \psi_k \psi_{q+1} \cdots \psi_p \left\{ \left( \frac{s}{2} \right)^{1/2} (\alpha\beta + \beta\alpha) \alpha \cdots \alpha - \left( \frac{2}{s} \right)^{1/2} \alpha \alpha \sum_j^s \alpha \cdots \alpha \beta \alpha \cdots \alpha \right\} \right\|, \tag{14}$$

$${}^{s+2}\Psi_k^t = (s+2)^{-1/2} \|\psi_i \psi_k \psi_{q+1} \cdots \psi_p \{ (\alpha\beta + \beta\alpha) \alpha \cdots \alpha + \alpha \alpha \sum_j^s \alpha \cdots \alpha \beta \alpha \cdots \alpha \}\|, \tag{15}$$

where we use abbreviations such as

$$\begin{aligned}
& \|\psi_1 \bar{\psi}_1 \cdots \psi_i \psi_k (\alpha\beta + \beta\alpha) \cdots \psi_q \bar{\psi}_q \psi_{q+1} \cdots \psi_p\| \\
& = \|\psi_i \psi_k \psi_{q+1} \cdots \psi_p (\alpha\beta + \beta\alpha) \alpha \cdots \alpha\|. \tag{16}
\end{aligned}$$

Note that  ${}^{s+2}\Psi_k^t$  is the main spin-contaminating configuration of the UHF wavefunction.<sup>9</sup> The effects of spin-annihilation<sup>5</sup> and spin-projection<sup>4</sup> on the UHF spin density can be analyzed by using Eq. (12).<sup>9</sup> Among the second order two-electron excited configurations, the most important is the configuration,

$${}^s\Psi_{kk}^{tt} = \|\psi_1 \bar{\psi}_1 \cdots \psi_i \bar{\psi}_i \cdots \psi_q \bar{\psi}_q \psi_{q+1} \cdots \psi_p\|, \tag{17}$$

arising from the sixth term of Eq. (9). Note that the above two-electron excited configuration is usually one of the most important configurations in electron correlation corrections.<sup>17</sup> The matrix element between  ${}^s\Psi_0$  of Eq. (1) and  ${}^s\Psi_{kk}^{tt}$  of Eq. (17) becomes

$$\langle {}^s\Psi_0 | \mathcal{H} | {}^s\Psi_{kk}^{tt} \rangle = K_{kt}. \tag{18}$$

The UHF total energy correct to second order in

$\pi_k$ ,  $\sigma_k$  and  $f_m^\alpha$  is obtained from Eq. (8) by inserting the CI expression Eq. (9) and by using the Brillouin theorem shown in Eq. (3), but it is omitted for brevity. From the variation theorem, we can require the expansion coefficients  $a_k^t$ ,  $b_k^t$  and  $c_m^t$  which make this second order energy stationary. The results are summarized in Eqs. (A1)–(A3) of the Appendix. By using these coefficients, the UHF wavefunction correct to first order in the orbital corrections is written as,

$$\begin{aligned}
\Psi_{\text{UHF}} = & {}^s\Psi_0 + \sqrt{2} \sum_k^c \sum_t^v a_k^t \Psi_k^t + \sqrt{2} \sum_k^c \sum_t^v b_k^t {}^s\Psi_k^t(1) \\
& + \sum_m^o \sum_t^v c_m^t {}^s\Psi_m^t. \tag{19}
\end{aligned}$$

Equations (A1)–(A3) are coupled equations. In order to solve these equations, a SCF procedure becomes necessary. The situation is very similar to that which appears in the coupled Hartree–Fock perturbation theory.<sup>16</sup> As seen in this theory, the uncoupling of these equations makes the problems very simple. The uncoupled equations of Eqs. (A1)–(A3) are

$$a_k^t = \frac{\frac{1}{2} \sum_m^o (mt | km)}{[s/(s+2)]^s E_k^t(2) + [2/(s+2)]^{s+2} E_k^t - E_0 - K_{kt}}, \quad (20)$$

$$b_k^t = 0, \quad (21)$$

$$c_m^t = 0. \quad (22)$$

By using the relation

$${}^s E_k^t(2) - {}^{s+2} E_k^t = [(s+2)/2s] \sum_m^o (K_{mk} + K_{mt}), \quad (23)$$

Eq. (20) is also written as,

$$a_k^t = \frac{\frac{1}{2} \sum_m^o (mt | km)}{{}^s E_k^t(2) - E_0 - (1/s) \sum_m^o (K_{mk} + K_{mt}) - K_{kt}}. \quad (20')$$

As seen from Eqs. (21) and (22), the orbital shifts  $\sigma_k$  and  $f_m^\alpha$  are zero in the uncoupled approximation. This is expected from the Brillouin theorem, Eq. (3). However, in the coupled equations, they are not necessarily zero. Thus, the UHF wavefunction is written in the uncoupled approximation as,

$$\Psi_{\text{UHF}} = {}^s \Psi_0 + \sqrt{2} \sum_k^c \sum_t^v a_k^t \Psi_k^t. \quad (24)$$

Three remarks are necessary about Eq. (20).

First, the numerator comes from the matrix element  $\langle {}^s \Psi_0 | \mathcal{H} | \Psi_k^t \rangle = -(1/\sqrt{2}) \sum_m^o (mt | km)$  and second, the term  ${}^{s+2} E_k^t$  in the denominator comes from the spin-contaminating configuration  ${}^{s+2} \Psi_k^t$  appearing in Eq. (12) and third, the term  $K_{kt}$  in the denominator arises from the matrix element  $\langle {}^s \Psi_0 | \mathcal{H} | {}^s \Psi_{kk}^t \rangle$  as shown in Eq. (18).

### III. PERTURBATION-VARIATION DESCRIPTION OF THE SEHF WAVEFUNCTION

In this section, we consider the SEHF wavefunction along the similar line to the treatment of the previous section. In the SEHF method, the single determinant,

$$\Psi_{sp} = \|\phi_1^{\alpha'} \bar{\phi}_1^{\beta'} \dots \phi_k^{\alpha'} \bar{\phi}_k^{\beta'} \dots \phi_q^{\alpha'} \bar{\phi}_q^{\beta'} \phi_{q+1}^{\alpha'} \dots \times \phi_m^{\alpha'} \dots \phi_p^{\alpha'}\|,$$

having the same form as the UHF function of Eq. (4) is first spin-projected and then the component orbitals are varied to minimize the energy,

$$E_{\text{SEHF}} = \langle O_s \Psi_{sp} | \mathcal{H} | O_s \Psi_{sp} \rangle / \langle O_s \Psi_{sp} | O_s \Psi_{sp} \rangle, \quad (25)$$

where  $O_s$  is the projection operator<sup>1</sup> having the property,

$$S^2 O_s = (s/2)(s/2+1) O_s.$$

The differences between the SEHF orbitals and the RHF orbitals are defined similarly to Eqs. (5)–(7) and are expanded by the RHF orbital set as in Eq. (10):

$$\pi_k^t = \sum_t^v a_k^t \psi_t, \quad \sigma_k^t = \sum_t^v b_k^t \psi_t, \quad f_m^\alpha = \sum_t^v c_m^t \psi_t. \quad (26)$$

We assign primes for the SEHF case.

Since  $\Psi_{sp}$  has the same form as  $\Psi_{\text{UHF}}$ , the effect of the projection operator on  $\Psi_{sp}$  can be examined

up to second order by referring to Eq. (9). Among the terms of Eq. (9), only those terms which are not eigenfunctions of  $S^2$  suffer changes. Especially the following relation is obtained from Eq. (12).

$$O_s \Psi_k^t = [s/(s+2)]^{1/2} {}^s \Psi_k^t(2). \quad (27)$$

The expression of the SEHF energy correct to second order in the orbital corrections is easily derived by using Eq. (27) and the equality

$$\langle {}^s \Psi_0 | \mathcal{H} | O_s \Psi \rangle = \langle {}^s \Psi_0 | \mathcal{H} | \Psi \rangle,$$

but it is omitted for brevity. As before, the SEHF orbital corrections are obtained by varying this energy expression with respect to  $a_k^t$ ,  $b_k^t$ ,  $c_m^t$ . The results are the coupled equations given in the appendix. By using these coefficients, the SEHF wavefunction correct to first order in the orbital corrections is given by

$$\begin{aligned} {}^s \Psi_{\text{SEHF}} = & {}^s \Psi_0 + [2s/(s+2)]^{1/2} \sum_k^c \sum_t^v a_k^t {}^s \Psi_k^t(2) \\ & + \sqrt{2} \sum_k^c \sum_t^v b_k^t {}^s \Psi_k^t(1) + \sum_m^o \sum_t^v c_m^t {}^s \Psi_m^t. \end{aligned} \quad (28)$$

As seen in the previous section, the uncoupling of the coupled equations giving  $a_k^t$ ,  $b_k^t$  and  $c_m^t$  leads to the following simple equations:

$$a_k^t = \frac{\frac{1}{2} \sum_m^o (mt | km)}{[s/(s+2)] \{ {}^s E_k^t(2) - E_0 \} - K_{kt}}, \quad (29)$$

$$b_k^t = 0, \quad (30)$$

$$c_m^t = 0. \quad (31)$$

That is, in the uncoupled approximation, the orbital corrections  $\sigma_k^t$  and  $f_m^\alpha$  vanish as expected from the Brillouin theorem and the SEHF wavefunction becomes

$${}^s \Psi_{\text{SEHF}} = {}^s \Psi_0 + [2s/(s+2)]^{1/2} \sum_k^c \sum_t^v a_k^t {}^s \Psi_k^t(2). \quad (32)$$

In comparison with Eq. (20), note that in the denominator of Eq. (29) the term  $K_{kt}$  still appears, although the term due to the spin-contamination is, of course, projected out in Eq. (29).

### IV. COMPARISON WITH THE SUM-OVER-STATE PERTURBATION THEORY

In this section, we compare the results for the UHF and SEHF wavefunctions and the result for the PUHF wavefunction reported previously<sup>9</sup> to the first order sum-over-state perturbation (FO-SOSP) wavefunction based on the RHF wavefunction. Some relations among these theories will be clarified.

Considering the Brillouin theorem Eq. (3) for the RHF wavefunction,  $s$  spin-functions<sup>9</sup> arising from the one-electron excitation from the closed orbital  $k$  to the open orbital  $t$  interact with the RHF

TABLE I. First order coefficients in the uncoupled approximation.<sup>a</sup>

Method	$s a_k^t$	$s^{s+2} a_k^t$
FO-SOSP	$\frac{(1/2)^{1/2} \sum_m^o (mt   km)}{[s/(s+2)]^{1/2} \{ {}^s E_k^t(2) - E_0 \}}$	0
UHF <sup>b</sup>	$\frac{(1/2)^{1/2} \sum_m^o (mt   km)}{[(s+2)/s]^{1/2} \{ {}^s E_k^t(2) - E_0 - (1/s) \sum_m^o (K_{mk} + K_{mt}) - K_{kt} \}}$	$(2/s)^{1/2} s a_k^t$
PUHF <sup>b</sup>	$\frac{(1/2)^{1/2} \sum_m^o (mt   km)}{[(s+2)/s]^{1/2} \{ {}^s E_k^t(2) - E_0 - (1/s) \sum_m^o (K_{mk} + K_{mt}) - K_{kt} \}}$	0
SEHF	$\frac{(1/2)^{1/2} \sum_m^o (mt   km)}{[s/(s+2)]^{1/2} \{ {}^s E_k^t(2) - E_0 \} - [(s+2)/s]^{1/2} K_{kt}}$	0

<sup>a</sup>The coefficients are defined by,

$$\Psi = {}^s \Psi_0 + \sum_k^c \sum_t^v s a_k^t {}^s \Psi_k^t(2) + \sum_k^c \sum_t^v s^{s+2} a_k^t {}^{s+2} \Psi_k^t.$$

<sup>b</sup>The energies  ${}^s E_k^t(2)$  and  ${}^{s+2} E_k^t$  are connected by the following equation:

$${}^{s+2} E_k^t = {}^s E_k^t(2) - [(s+2)/2s] \sum_m^o (K_{mk} + K_{mt}).$$

wavefunction  ${}^s \Psi_0$  of Eq. (1). They all have the same spin-multiplicity  $s+1$ .<sup>18</sup> However, since our present interest lies in the first order spin-correlation correction, we have only to consider the configuration  ${}^s \Psi_k^t(2)$  of Eq. (14) among these  $s$  spin-functions.<sup>9</sup> Then, from the first order perturbation theory,

$${}^s \Psi_{\text{SOS}} = {}^s \Psi_0 + \sqrt{2} \sum_k^c \sum_t^v a_k^t(\text{SOS}) {}^s \Psi_k^t(2), \quad (33)$$

where the coefficient  $a_k^t(\text{SOS})$  is given by

$$a_k^t(\text{SOS}) = \frac{\frac{1}{2} \sum_m^o (mt | km)}{[s/(s+2)]^{1/2} \{ {}^s E_k^t(2) - E_0 \}}. \quad (34)$$

Since the FO-SOSP coefficient given by Eq. (34) is essentially the uncoupled one, it is compared in Table I with the UHF, PUHF, and SEHF coefficients obtained by the uncoupled approximation. These coefficients are defined by the equation

$$\Psi = {}^s \Psi_0 + \sum_k^c \sum_t^v s a_k^t {}^s \Psi_k^t(2) + \sum_k^c \sum_t^v s^{s+2} a_k^t {}^{s+2} \Psi_k^t, \quad (35)$$

where the last configuration is the spin-contaminating configuration. In the UHF method, there exists the following relation,

$$s a_k^t = (s/2)^{1/2} s^{s+2} a_k^t,$$

coming from Eq. (12). In Table I, the term  $(1/s) \sum_m^o (K_{mk} + K_{mt})$  in the denominators of the UHF and PUHF coefficients arises from the spin-contaminating configuration  ${}^{s+2} \Psi_k^t$  [see Eqs. (12) and (23)]. The exchange integral  $K_{kt}$  common to the denominators of the UHF, PUHF, and SEHF coefficients but missing in the FO-SOSP coefficient comes from the second order two-electron excited configuration  ${}^s \Psi_{kk}^t$ , which is usually one of the most important configurations in the electron correlation corrections<sup>11,17</sup> [see Eq. (18)]. When  $s$  approaches

to infinity as in some solid states, the UHF, PUHF, and SEHF theories become identical.<sup>19</sup> This fact may be considered as a justification of the UHF theory in infinite systems. Interestingly, even when  $s = \infty$ , these UHF, PUHF, and SEHF coefficients are different from the FO-SOSP coefficient by  $K_{kt}$  in the denominator. The physical meaning of the appearance of  $K_{kt}$  will be fully discussed in Sec. V.

Since spin density is a good manifestation of the spin-correlation effects in open-shell electronic systems, it is useful to compare these four methods with respect to this property. By applying the normalized spin-density operator,<sup>20</sup>

$$\rho(r) = \langle S_z \rangle^{-1} \sum_\nu S_{z\nu} \delta(r_\nu - r),$$

to the uncoupled equation (35), and by using the following relation,<sup>9</sup>

$$\langle {}^s \Psi_0 | \rho(r) | {}^{s+2} \Psi_k^t \rangle = (2/s)^{1/2} \langle {}^s \Psi_0 | \rho(r) | {}^s \Psi_k^t(2) \rangle,$$

we obtain the following equations for the first order spin density,

$$\rho = \rho_{\text{SD}} + \rho_{\text{SP}}, \quad (36)$$

where

$$\rho_{\text{SD}} = \langle {}^s \Psi_0 | \rho(r) | {}^s \Psi_0 \rangle, \quad (37)$$

$$\rho_{\text{SP}} = \sum_k^c \sum_t^v \{ s a_k^t + (2/s)^{1/2} s^{s+2} a_k^t \} \langle {}^s \Psi_0 | \rho(r) | {}^s \Psi_k^t(2) \rangle.$$

In Eq. (36),  $\rho_{\text{SD}}$  and  $\rho_{\text{SP}}$  are the contributions due to the spin-delocalization (SD) and spin-polarization (SP) mechanisms.<sup>9,10</sup> From Eqs. (35) and (37),  $\rho_{\text{SD}}$  is shown to be always positive and has the same value in the FO-SOSP, UHF, PUHF, and SEHF methods to the first order uncoupled approximation:

TABLE II.  $\rho_{SP}$  in the uncoupled approximation.

Method	$\rho_{SP}$
FO-SOSP	$\sum_s \sum_k^c \sum_t^v \frac{\sum_m^o (mt km)}{sE_k^t(2) - E_0} \psi_k(r)\psi_t(r)$
UHF	$\sum_s \sum_k^c \sum_t^v \frac{\sum_m^o (mt km)}{sE_k^t(2) - E_0 - (1/s)\sum_m^o (K_{mk} \cdot K_{mt}) - K_{kt}} \psi_k(r)\psi_t(r)$
PUHF <sup>a</sup>	$[s/(s+2)](\rho_{UHF})_{SP}$
SEHF	$\sum_s \sum_k^c \sum_t^v \frac{\sum_m^o (mt km)}{sE_k^t(2) - E_0 - (1+2/s)K_{kt}} \psi_k(r)\psi_t(r)$

<sup>a</sup>Reference 9.

$$(\rho_{SOS})_{SD} = (\rho_{UHF})_{SD} = (\rho_{PUHF})_{SD} = (\rho_{SEHF})_{SD} \quad (38)$$

However,  $\rho_{SP}$  is different for different methods and offers a good measure of the spin-correlation effects included in these methods. In Table II, the formula of  $\rho_{SP}$  calculated from the uncoupled equation (35) are compared among the FO-SOSP, UHF, PUHF, and SEHF theories. In the UHF method,  $\rho_{SP}$  includes the contribution due to the spin-contaminating configuration  $s+2\Psi_k^t$ , although it is easily picked out by the projection<sup>4</sup> or annihilation<sup>5</sup> method.

Referring to Table II, we notice that the differences in  $\rho_{SP}$  among the FO-SOSP, UHF, and SEHF theories lie in their denominators. Since the exchange integrals  $K_{mk}$ ,  $K_{mt}$  and  $K_{kt}$  are always positive, the relations,

$$|(\rho_{SOS})_{SP}| < |(\rho_{UHF})_{SP}|, \quad (39)$$

$$|(\rho_{SOS})_{SP}| < |(\rho_{SEHF})_{SP}| \quad (40)$$

are expected in the first order uncoupled approximation. The relative magnitude between  $(\rho_{UHF})_{SP}$  and  $(\rho_{SEHF})_{SP}$  depends upon the relative magnitude between  $\sum_m^o (K_{mk} + K_{mt})$  and  $2K_{kt}$ . As to the relation between  $(\rho_{UHF})_{SP}$  and  $(\rho_{PUHF})_{SP}$ , we have already reported previously<sup>9,10a</sup>,

$$(\rho_{PUHF})_{SP} \approx [s/(s+2)](\rho_{UHF})_{SP} \quad (41)$$

Note that when  $s$  approaches to infinity, the spin densities calculated from the UHF, PUHF, and SEHF theories become identical, although they are still different from that obtained from the FO-SOSP method.

To examine the reliability of the above relations (39), (40), and (41) in actual calculations, we summarize in Tables III and IV spin densities calculated by these various methods. The spin densities of the first-row atoms shown in Table III were obtained by Goddard<sup>21</sup> except those calculated by the FO-SOSP method.<sup>22</sup> As seen from the RHF values, all the spin densities except those of Li( $2^2S$ ) and Li( $3^2S$ ) are due only to the SP mechanism. The

spin densities of the doublet alternant hydrocarbon radicals shown in Table IV were calculated by the Pariser-Parr-Pople method with the same integral values.<sup>23,24</sup> In the position of negative spin density, only the SP mechanism is important.

In both Tables III and IV, the relations (39), (40), and (41) hold satisfactorily for all the SP contributions. Although one exception to relation (39) is found for Li( $2^2P$ ), the reason is probably due to the differences in the basis functions between the FO-SOSP<sup>22c</sup> and UHF<sup>21</sup> calculations. For the spin densities where both of the SD and SP mechanisms are important, both contributions are positive in the cases shown in Tables III and IV. Then, from Eqs. (38), (39), and (40), the relations  $\rho_{SOS} < \rho_{UHF}$  and  $\rho_{SOS} < \rho_{SEHF}$  are expected. These relations hold in both tables with an exception of the latter relation at the 3 position of the pentadienyl radical shown in Table IV. This is perhaps due to the crudeness of the uncoupled approximation.

As to the relative magnitude between  $(\rho_{UHF})_{SP}$  and  $(\rho_{SEHF})_{SP}$ , the relative magnitude between  $\sum_m^o (K_{mk} + K_{mt})$  and  $2K_{kt}$  becomes a subject of discussion (refer Table II). Generally speaking, the more similar the orbitals  $\psi_i$  and  $\psi_j$  are, the larger is the exchange integral  $K_{ij}$ . If both orbitals  $\psi_i$  and  $\psi_j$  belong to the same partial symmetry (e.g., both are  $s$ -AO's or  $p$ -AO's in atoms, or both are  $\sigma$ -MO's or  $\pi$ -MO's in molecules), the similarity (e.g., in nodal property) between the orbitals  $\psi_i$  and  $\psi_j$  is closely related to the level splitting between the orbitals  $\psi_i$  and  $\psi_j$ . Then, for example in the alternant hydrocarbon radicals, we can expect the relation,  $K_{mk} + K_{mt} \geq 2K_{kt}$  and then,  $\sum_m^o (K_{mk} + K_{mt}) \geq 2K_{kt}$  which results in the relation,  $|(\rho_{SEHF})_{SP}| \leq |(\rho_{UHF})_{SP}|$ . Moreover, in the positions where the SD contribution is also important, the SP contribution is positive for the cases shown in Table IV. Then, from Eq. (38), this relation is rewritten as,

$$|\rho_{SEHF}| \leq |\rho_{UHF}| \quad (42)$$

The above relation holds actually in Table IV with the few exceptions of the 3 and 5 positions of the benzyl radical. On the other hand, if the partial symmetry of the orbitals  $\psi_k$  and  $\psi_t$  are the same but different from that of the orbital  $\psi_m$  as in the  $P$  and  $D$  states shown in Table III, the reverse relation,  $K_{mk} + K_{mt} \leq 2K_{kt}$  is expected for similar reasons as above. Although this leads to the relation  $|(\rho_{UHF})_{SP}| \leq |(\rho_{SEHF})_{SP}|$  for doublet radicals ( $s=1$ ), we can not deduce any general relation between  $\sum_m^o (K_{mk} + K_{mt})$  and  $2K_{kt}$ , and then between  $(\rho_{UHF})_{SP}$  and  $(\rho_{SEHF})_{SP}$ . Actually in Table III, we can see the relation,  $\rho_{UHF} < \rho_{SEHF}$  for the doublet  $P$  and  $D$  states.

TABLE III. Spin densities of the first-row atoms calculated by the various methods.<sup>a</sup>

Atom	State	RHF	FO-SOSP	UHF	PUHF	SEHF(GF)	Exptl.
Li	$2^2S$	0.1667	0.2065 <sup>b</sup>	0.2248	0.1866	0.2406	0.2313
	$3^2S$	0.03864	...	0.05253	0.04335	0.05622	...
	$2^2P$	0.0	-0.02222 <sup>c</sup>	-0.01747	-0.00582	-0.02304	-0.0182
	$3^2P$	0.0	...	-0.005531	-0.001843	-0.007318	...
	$3^2D$	0.0	...	-0.000036	-0.000012	-0.000053	...
B	$2^2P_{3/2}$	0.0	0.0073 <sup>d</sup>	0.0192	0.0067	0.0362	(0.0003)
C	$3^2P_2$	0.0	0.0227 <sup>d</sup>	0.0753	0.0398	0.0733	0.00889
N	$4^4S_{3/2}$	0.0	0.0730 <sup>d</sup>	0.1853	0.1179	0.1579	0.0970505
O	$3^2P_2$	0.0	0.0610 <sup>d</sup>	0.1944	0.1013	0.2137	0.11398
F	$2^2P_{3/2}$	0.0	0.0470 <sup>d</sup>	0.1298	0.0444	0.2454	0.071835

<sup>a</sup>Reference 21.<sup>b</sup>A. W. Weiss, Phys. Rev. 122, 1826 (1961).<sup>c</sup>R. W. B. Ardill and A. L. Stewart, Proc. Phys. Soc. (London) 92, 296 (1967); A. W. Weiss, Astrophys. J. 138, 1262 (1963).<sup>d</sup>H. F. Schaefer III, R. A. Klemm, and F. E. Harris, Phys. Rev. 176, 49 (1968).

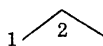
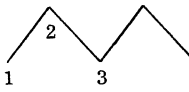
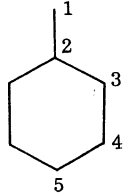
### V. THE NATURES OF THE UHF AND SEHF THEORIES IN THE SPIN-CORRELATION PROBLEMS

In this section, the natures of the UHF and SEHF theories in the spin-correlation problems for open-shell electronic systems are discussed in the light of the physical visuality of the Sinanoğlu's many-electron theory.<sup>2b,11</sup> As in the previous section, our starting point is the RHF wavefunction.

In the closed-shell systems, the orbitals are de-

termined by the average Coulombic field, where the effect of spin (the Pauli antisymmetric condition) functions to modify this field. However, in the open-shell systems where the numbers of the  $\alpha$ - and  $\beta$ -spin electrons are different ( $s \neq 0$ ), the effects of spins are not cancelled out and the field becomes spin-dependent. This is the physical reason of the different orbitals for different spins (DODS).<sup>1,6</sup> However, in the RHF theory, two electrons of different spins are forced on the same

TABLE IV. Spin densities of the doublet alternant hydrocarbon radicals calculated by the various methods.<sup>a</sup>

Radical	Position	FO-SOSP <sup>b</sup>	UHF	PUHF	SEHF	Full-CI
Allyl 	1	0.584	0.651	0.547	0.584	0.578
	2	-0.167	-0.302	-0.093	-0.167	-0.156
Pentadienyl 	1	0.405	0.545	0.383	0.452	0.413
	2	-0.127	-0.307	-0.094	-0.159	-0.140
	3	0.444	0.524	0.422	0.415	0.452
Benzyl <sup>c</sup> 	1	...	0.771	0.718	0.602	0.715
	2	...	-0.189	-0.060	-0.134	-0.110
	3	...	0.254	0.157	0.279	0.185
	4	...	-0.158	-0.050	-0.143	-0.070
	5	...	0.225	0.128	0.260	0.165

<sup>a</sup>References 23 and 24.<sup>b</sup>These values are obtained by the present author.<sup>c</sup>The values for the PUHF method of benzyl radical are obtained by the single annihilation of the spin-contaminating quartet state.

spatial orbital, by neglecting the spin-dependent character of the field. Therefore, in the theory of the electron correlation starting from the RHF wavefunction, the orbital correction term  $\hat{f}_i$  represents chiefly the orbital spin-polarization  $\pi_i$  shown for example in Eqs. (7) and (26).<sup>11</sup> Although the closed and open orbital shifts,  $\sigma_i$  and  $f_i^\sigma$  are also included in  $\hat{f}_i$ , they are expected to be small from the Brillouin theorem, Eq. (3).<sup>10a</sup> Note that in the closed-shell systems,  $\hat{f}_i$  is always very small. It appears only from the third order correction. Thus,  $\hat{f}_i$  gains simple physical reality only in open-shell electronic systems.

As shown by Sinanoğlu and Silverstone,<sup>11</sup> the two-electron correlation effect  $\hat{U}'_{ij}$  is also very important. It is expressed as the sum,

$$\hat{U}'_{ij} = \mathcal{G}(\hat{f}_i \hat{f}_j) + \hat{U}_{ij} = \circ \circ + \circ - \circ \quad (43)$$

where  $\mathcal{G}$  is the two-electron antisymmetrizer. The first term,  $\mathcal{G}(\hat{f}_i \hat{f}_j)$  (the unlinked cluster  $\circ \circ$  in the Sinanoğlu's notation) represents chiefly the "coupling" of the orbital spin-polarizations which is important only in the open-shell electronic systems. The second term  $\hat{U}_{ij}$  ( $\circ - \circ$ ) represents mainly the correlation correction due to the binary "collision" of two electrons. This belongs essentially to the two-body phenomena and its importance is common to both closed- and open-shell electronic systems. Moreover,  $\hat{U}_{ij}$  represents a large part of the correlation energy.<sup>11</sup>

In the orbital theories like the UHF and SEHF theories, one introduces first rather formally the orbital correction  $\hat{f}_i$  as in Eq. (5) and then makes it optimum to all orders by the variation method. In this sense, the orbital theory may be considered as the orbital (one-electron function)-constrained variation method. However, since the first order correction to the wavefunction is determined by varying at least the energy correct to second order in orbital corrections,<sup>15</sup> there comes out the coupling terms  $\mathcal{G}(\hat{f}_i \hat{f}_j)$  in the energy expression. These are seen in Eq. (9). Among these coupling terms, the most important term is  $\sum_k^c \sum_t^v (a_k^t)^2 {}^s\Psi_{kk}^{tt}$  arising from the sixth term of Eq. (9). On the other hand, these two-electron excited configurations, especially  ${}^s\Psi_{kk}^{tt}$ , are also important in describing the correlation effect  $\hat{U}_{ij}$ , which is expressed as the sum of terms like  $\sum_k^c \sum_t^v d_{kk}^{tt} {}^s\Psi_{kk}^{tt}$ .<sup>11,17</sup> The important difference between these CI expressions of  $\mathcal{G}(\hat{f}_i \hat{f}_j)$  and  $\hat{U}_{ij}$  lies in their coefficients; although the coefficients in the former term are constrained as the product of the orbital corrections like  $(a_k^t)^2$ , those in the latter term are the free variational parameter like  $d_{kk}^{tt}$ . Since in the UHF and SEHF theories only the former term appears, the effect of the latter will be incorporated "effectively" through the variation method into the con-

strained former term. In other words, in the UHF and SEHF theories, the real spin-polarization  $f_i$  is distorted to some extent by the "effective" inclusion of the correlation effect essentially due to  $\hat{U}_{ij}$ . Owing to the particular importance of the configuration  ${}^s\Psi_{kk}^{tt}$ , it appears even in the uncoupled equations of the UHF and SEHF theories shown in Table I as the exchange integral  $K_{kt}$  in the denominator. (Recall that  $\langle \Psi_0 | \mathcal{H} | {}^s\Psi_{kk}^{tt} \rangle = K_{kt}$ .) As a result, the spin densities due to the SP mechanism calculated by the UHF and SEHF theories are always larger (in absolute magnitude) not only than those calculated by the FO-SOSP method [Eqs. (39) and (40)], but also than those obtained by the full-CI method and experiments.

Some manifestations of the relations expected from the above conclusion and Eq. (38) are seen in Tables III and IV except the UHF spin densities of Li(2<sup>2</sup>S) and Li(2<sup>2</sup>P) and the SEHF spin densities of the 3 and 1 positions of the pentadienyl and benzyl radicals, respectively.

Before completing this section, some discussions are necessary about the alternant molecular orbital (AMO) method<sup>1,6</sup> for the closed-shell electronic systems. In this theory, the orbital correction  $f_i^{\text{AMO}}$  formally similar to  $\pi_k$  in Eq. (7) is first introduced in order to represent the "alternant" correlation effect trying to keep the two  $\alpha$ - and  $\beta$ -spin electrons on separate positions.<sup>1</sup> By applying this method to benzene, one can obtain 78% (one parameter) and 90.4% (two parameters) of the best possible improvement in energy within the  $\pi$ -electron treatment.<sup>6b</sup> However, this "alternant" effect is essentially a manifestation of the binary correlation effect  $\hat{U}_{ij}$ . This is clear from the fact that all the first order configurations linear in  $f_i^{\text{AMO}}$  are completely projected out by the projection operator.<sup>6b</sup> It functions only in the coupling form  $\mathcal{G}(f_i^{\text{AMO}} f_j^{\text{AMO}})$  as a relief of the binary correlation effect  $\hat{U}_{ij}$ . In this sense, the orbital correction  $f_i^{\text{AMO}}$  introduced intuitively in the AMO method is more imaginary than real. However, in the open-shell electronic systems, the statements given for the SEHF method apply also to the AMO method. Namely, in both cases, the orbital spin polarization effect and the "alternant" correlation effect disturb each other.

## VI. CONCLUDING REMARKS

As shown in the previous section, in the UHF and SEHF theories, the real spin-polarization correction  $\hat{f}_i$  is distorted to some extent through the "effective" inclusion of the correlation effect due essentially to  $\hat{U}_{ij}$ . Moreover, the fact that in the SEHF theory, the error in the expectation value of the one-electron operator begins from the first order term in the error function<sup>25</sup> seems to support the above conclusion. Since both of the corrections,  $\hat{f}_i$  and  $\hat{U}_{ij}$  are important in the open-shell electronic systems, it seems necessary for the fu-



ture theories of spin-correlation to include both of these corrections explicitly in a relevant framework, or to exclude reasonably the effect due to the correction  $\hat{U}_{ij}$ .

In order to keep  $f_i$  from the effect of  $\hat{U}_{ij}$ , Meyer<sup>26</sup> dropped off from the SEHF function the configurations  ${}^s\Psi_{kk}^{tt}$  and  ${}^s\Psi_{kk}^{tu}(1)$  coming from the sixth term of Eq. (9) and considered only the polarization interaction term arising from the eighth term of Eq. (9). Although he considered only the spin-polarization correction  $\pi_i^t$  in Eq. (26) in an approximate way, his results were satisfactory in the calculations of the hfs constants of the first-row atoms. Since in atoms, the energetically most important correlation effect is the intra-shell (pair) correlation effect expressed mainly by the configurations like  ${}^s\Psi_{kk}^{tt}$  and  ${}^s\Psi_{kk}^{tu}(1)$ , his treatment may be justified. However, it seems still questionable whether the configurations  ${}^s\Psi_{kk}^{tt}$  and  ${}^s\Psi_{kk}^{tu}(1)$  are purely  $\hat{U}_{ij}$  origin and can be omitted completely. The relative weight in their origins between  $\hat{f}_i$  and  $\hat{U}_{ij}$  should be examined if we adhere to the framework of the SEHF theory. On the other hand, taking account of the considerations given in the present paper, we may rather set up more direct method which covers both correlation effects  $\hat{f}_i$  and  $\hat{U}_{ij}$  in the possible simplest but unconstrained framework. In this sense, the multiconfigurational (MC) SCF method seems promising.<sup>27</sup> This point is the problem to be discussed in the future studies.

#### ACKNOWLEDGMENTS

The author wishes to acknowledge Professors Teiji Yonezawa and Hiroshi Kato for encouragement and valuable discussions.

#### APPENDIX

First, by differentiating  ${}^2E_{\text{UHF}}$ , the UHF total energy correct up to second order in the orbital corrections, with respect to  $a_k^t$ , we obtain

$$\begin{aligned} \frac{1}{2} d^2 E_{\text{UHF}} / da_k^t &= 2a_k^t \{ [s/(s+2)] {}^sE_k^t(2) + [2/(s+2)] {}^{s+2}E_k^t \\ &\quad - E_0 - K_{kt} \} \\ &\quad - \sum_m^o (mt | km) \\ &\quad + \sum_{l(\neq k)}^c a_l^t \{ \sum_m^o (km | lm) - (kl | tt) - (kt | lt) \} \\ &\quad + \sum_{u(\neq t)}^v a_k^u \{ \sum_m^o (tm | um) - (tu | kk) - (tk | uk) \} \\ &\quad - \sum_{l(\neq k) u(\neq t)}^c a_l^u \{ (tu | lk) + (ku | lt) \} \\ &\quad + b_k^t \sum_m^o (K_{mk} - K_{mt}) \\ &\quad + \sum_{l(\neq k)}^c b_l^t \{ \sum_m^o (km | lm) - \sum_{u(\neq t)}^v b_k^u \sum_m^o (tm | um) \\ &\quad + \sum_m^o c_m^t \{ \sum_n^o (mn | kn) - (mk | tt) - (kt | mt) \} \\ &\quad - \sum_{m(\neq k)}^o \sum_{u(\neq t)}^v c_m^u \{ (tu | mk) + (ku | mt) \} \} \end{aligned}$$

$$= 0. \quad (\text{A1})$$

Second, by differentiating with respect to  $b_k^t$ , we obtain

$$\begin{aligned} \frac{1}{2} d^2 E_{\text{UHF}} / db_k^t &= 2b_k^t \{ {}^sE_k^t(1) - E_0 + K_{kt} \} \\ &\quad + \sum_{l(\neq k)}^c b_l^t \{ \sum_m^o (km | lm) - (kl | tt) + 3(lt | kt) \} \\ &\quad + \sum_{u(\neq t)}^v b_k^u \{ \sum_m^o (tm | um) - (tu | kk) + 3(kt | uk) \} \\ &\quad + \sum_{l(\neq k) u(\neq t)}^c \sum_{u(\neq t)}^v b_l^u \{ 4(tk | lu) - (tu | lk) - (ku | lt) \} \\ &\quad + a_k^t \sum_m^o (K_{mk} - K_{mt}) \\ &\quad + \sum_{l(\neq k)}^c a_l^t \sum_m^o (lm | km) - \sum_{u(\neq t)}^v a_k^u \sum_m^o (um | tm) \\ &\quad + \sum_m^o c_m^t \{ \sum_n^o (mn | kn) - (mk | tt) + 3(kt | mt) \} \\ &\quad + \sum_m^o \sum_{u(\neq t)}^v c_m^u \{ 4(kt | mu) - (tu | mk) - (mt | ku) \} \\ &= 0. \quad (\text{A2}) \end{aligned}$$

Third, by differentiating with respect to  $c_m^t$ , we obtain

$$\begin{aligned} d^2 E_{\text{UHF}} / dc_m^t &= 2c_m^t ({}^sE_m^t - E_0) \\ &\quad + \sum_{n(\neq m)}^o c_n^t \left\{ \frac{1}{2} \sum_i^o (im | in) - (mn | tt) + (mt | nt) \right\} \\ &\quad + \sum_{u(\neq t)}^v c_m^u \left\{ \frac{1}{2} \sum_n^o (nt | nu) - (tu | mm) + (mt | mu) \right\} \\ &\quad + \sum_{n(\neq m) u(\neq t)}^o \sum_{u(\neq t)}^v c_n^u \{ 2(mt | nu) - (mn | tu) - (mu | nt) \} \\ &\quad + 2 \sum_k^c a_k^t \{ \sum_n^o (mn | kn) - (mk | tt) - (kt | mt) \} \\ &\quad - 2 \sum_k^c \sum_{u(\neq t)}^v a_k^u \{ (tu | mk) - (kt | mu) \} \\ &\quad + 2 \sum_k^c b_k^t \{ \sum_n^o (mn | kn) - (mk | tt) + 3(kt | mt) \} \\ &\quad + 2 \sum_k^c \sum_{u(\neq t)}^v b_k^u \{ 4(ku | mt) - (tu | mk) - (mu | kt) \} \\ &= 0. \quad (\text{A3}) \end{aligned}$$

In the above equations,  $(ij | kl)$  is defined by,

$$(ij | kl) = \int \int \psi_i(1) \psi_j(1) (1/r_{12}) \psi_k(2) \psi_l(2) d\tau_1 d\tau_2,$$

and  $E_0$ ,  ${}^sE_k^t(1)$ ,  ${}^sE_k^t(2)$ ,  ${}^{s+2}E_k^t$ , and  ${}^sE_m^t$  are energies

corresponding to the configurations  ${}^s\Psi_0$ ,  ${}^s\Psi_k^t(1)$ ,  ${}^s\Psi_k^t(2)$ ,  ${}^{s+2}\Psi_k^t$ , and  ${}^s\Psi_m^t$ , respectively. [See Eqs. (1), (2), (14) and (15).]

Similarly, by differentiating  ${}^2E_{\text{SEHF}}$ , the SEHF energy correct up to second order in the orbital corrections, with respect to  $a_k^t$ , we obtain

$$\begin{aligned} \frac{1}{2} d {}^2E_{\text{SEHF}} / da_k^t &= 2a_k^t \left[ \frac{S}{S+2} \{ {}^sE_k^t(2) - E_0 \} - K_{kt} \right] \\ &- \sum_m^o (mt | km) \\ &+ \sum_{l(\neq k)}^o a_l^t \left\{ \frac{S+1}{S+2} \sum_m^o (km | lm) - \frac{S}{S+2} (kl | tt) - (kt | lt) \right\} \\ &+ \sum_{u(\neq t)}^o a_u^t \left\{ \frac{S+1}{S+2} \sum_m^o (tm | um) - \frac{S}{S+2} (tu | kk) - (tk | uk) \right\} \\ &- \sum_{l(\neq k)}^o \sum_{u(\neq t)}^o a_l^t a_u^t \left\{ \frac{S}{S+2} (tu | lk) + (ku | lt) \right\} \\ &+ b_k^t \sum_m^o (K_{mk} - K_{mt}) \\ &+ \sum_{l(\neq k)}^o b_l^t \sum_m^o (km | lm) - \sum_{u(\neq t)}^o b_u^t \sum_m^o (tm | um) \\ &+ \sum_m^o c_m^t \left\{ \sum_n^o (mn | kn) - (mk | tt) - (kt | mt) \right\} \\ &- \sum_m^o \sum_{u(\neq t)}^o c_m^t a_u^t \{ (tu | mk) + (ku | mt) \} \\ &= 0. \end{aligned} \quad (\text{A4})$$

The results for  $b_k^t$  and  $c_m^t$  have exactly the same forms as those given in Eqs. (A2) and (A3) except that  $a_k^t$ ,  $b_k^t$  and  $c_m^t$  appearing in these equations are substituted by  $a_k^t$ ,  $b_k^t$  and  $c_m^t$ , respectively.

\*Based on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Kyoto University, December 1970.

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