What is the best expression of the second-order sum-over-state perturbation energy based on the Hartree–Fock wavefunction?*

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(Received 4 March 1974)

We have improved in a stepwise manner the second-order sum-over-state perturbation energy which is written in the infinite sum over singly excited configurations based on the Hartree–Fock (HF) zeroth-order wavefunction. Firstly, the conventional equation [Eq. (10)] is shown to be *dependent* on the unitary transformations among singly excited configurations. The *best* unitary transformation gives the Tamm–Dancoff (or singly excited configuration interaction) approximation of the excited states. The resultant equation [Eq. (25)] includes in a simple form *all* of the coupling terms between different singly excited configurations. As a restrictive special case, this unitary transformation leads to the modified HF orbitals of Silverstone–Huzinaga and Morokuma–Iwata. Secondly, it is shown that the second-order energy of the coupled HF theory can also be written in a simple sum-over-state perturbation formula. The resultant equation [Eq. (50)] does *not* require an iterative solution. Moreover, it is shown that this is the *best possible* expression of the second-order energy based on the HF zeroth-order wavefunction. As a restrictive special case, this treatment produces *new* improved modified HF operators which are thought to be *superior* to those hitherto given.

I. INTRODUCTION

Some properties of a many-electron system undergoing a one-electron perturbation may be calculated using perturbation theory. When we have a complete set of eigenfunctions and eigenvalues of the zeroth-order Hamiltonian as

$$H_0 |n\rangle = E_n |n\rangle , \quad (n = 0, 1, \ldots) \tag{1}$$

$$H_0 = \sum_{\nu} \left(-\tfrac{1}{2} \Delta_{\nu} - \sum_{A} \frac{Z_A}{r_{A\nu}} \right) + \sum_{\mu > \nu} \frac{1}{r_{\mu\nu}} , \tag{2}$$

the second-order property of a system undergoing perturbation

$$H = H_0 + H_1 , \tag{3}$$

may be calculated using the following *sum-over-state perturbation formula*

$$E_{(2)} = \sum' \langle 0 | H_1 | n \rangle \langle n | H_1 | 0 \rangle / (E_0 - E_n) , \tag{4}$$

where the sum is over an infinite number of excited states (for continuum, it indicates integral).[1] However, since it is impossible to obtain a set of exact many-electron wavefunctions satisfying Eq. (1), some approximation must be made. The most frequent approximation to Eq. (4) is to replace $|0\rangle$ by the (closed-shell) Hartree–Fock (HF) wavefunction Ψ_0, $|n\rangle$ by the singly excited configuration Ψ_{mi} built up from HF occupied orbitals $\{i\}$ and virtual orbitals $\{m\}$, and E_0 and E_n by $E_0 = \langle \Psi_0 | H_0 | \Psi_0 \rangle$ and $E_{mi} = \langle \Psi_{mi} | H_0 | \Psi_{mi} \rangle$, respectively. However, this approximation has some intrinsic deficiencies.[2,3]

In the present paper, we seek for the best expression of the approximate second-order energy $\tilde{E}_{(2)}$ of the one-electron perturbation H_1 in the form as *simple* as Eq. (4). In the next section, it is shown that the $\tilde{E}_{(2)}$ approximated as above depends on the unitary transformations among singly excited configurations. Section III shows that the best unitary transformation gives the Tamm–Dancoff (or singly excited CI) approximation[4] of the excited states. The resultant $\tilde{E}_{(2)}$ includes all of the coupling terms in which different singly excited configura-

tions couple through H_0. As a restrictive special case, this unitary transformation leads to the modified HF orbitals proposed by Silverstone and Yin,[5a] Huzinaga and Arnau[5b] (SY–HA), and Morokuma and Iwata (MI).[6] In Sec. IV, it is shown that the second-order energy of the coupled HF theory[7] can also be written exactly in a simple sum-over-state perturbation formula. The resultant equation of $\tilde{E}_{(2)}$ is very similar to the above case and does not require an iterative solution. Moreover, this treatment gives new improved modified HF operators which are thought to be superior to those hitherto given.[5,6] In the last section, it is shown that the $\tilde{E}_{(2)}$ obtained in Sec. IV, which is equivalent to the coupled HF energy, is the best possible second-order sum-over-state perturbation energy based on the HF Ψ_0.

II. DEPENDENCE OF $\tilde{E}_{(2)}$ ON THE UNITARY TRANSFORMATIONS AMONG SINGLY EXCITED CONFIGURATIONS

First, we examine the approximation stated in Sec. I. Taking account of the one-electron property of the perturbation H_1, one may assume the form of the perturbed wavefunction as

$$\Psi = \Psi_0 + \sum_{mi} C_{mi} S^+_{mi} \Psi_0 , \tag{5}$$

where Ψ_0 is the HF single determinant composed of doubly occupied orbitals. S^+_{mi} is the single excitation operator defined by

$$S^+_{mi} = (a^+_{m\alpha} a_{i\alpha} + a^+_{m\beta} a_{i\beta})/\sqrt{2} , \tag{6}$$

for spin-less perturbations and

$$S^+_{mi} = (a^+_{m\alpha} a_{i\alpha} - a^+_{m\beta} a_{i\beta})/\sqrt{2} , \tag{7}$$

for spin-linear perturbations. $a^+_{m\alpha}$ and $a_{i\alpha}$ are the creation and destruction operators which satisfy Fermion anticommutation relation. $S^+_{mi} \Psi_0 (= \Psi_{mi})$ is a singly excited singlet or triplet configuration depending on Eq. (6) or (7). As seen from Eq. (7), the spin-dependent

perturbations are restricted here, for simplicity, to those which commute with the z component of the total spin operator. It is a simple matter to extend the following results to other kind of spin-dependent perturbations. The following formulations are valid for both excitation operators defined by Eqs. (6) and (7).

Using the Brillouin theorem for the HF Ψ_0, the approximate second-order energy is obtained from the secular equation for Eq. (5) as

$$\bar{E}_{(2)} = \sum_{mi} \langle 0 | H_1 S_{mi}^+ | 0 \rangle C_{mi} , \tag{8}$$

where C_{mi} is the solution of the first-order equation

$$(E_0 - E_{mi}) C_{mi} = \langle 0 | S_{mi} H_1 | 0 \rangle + \sum_{\substack{nj \\ (\neq mi)}} \langle 0 | S_{mi} H_0 S_{nj}^+ | 0 \rangle C_{nj} . \tag{9}$$

In the above equations and hereafter, Ψ_0 and $|0\rangle$ are the same and both denote the HF Ψ_0. E_0 and E_{mi} are the energies of the HF Ψ_0 and $S_{mi}^+ \Psi_0$.

$$E_0 = \langle 0 | H_0 | 0 \rangle , \quad E_{mi} = \langle 0 | S_{mi} H_0 S_{mi}^+ | 0 \rangle .$$

In the last term of Eq. (9), *different* singly excited configurations couple through H_0. *If one neglects these coupling terms*, one obtains

$$C_{mi} = \langle 0 | S_{mi} H_1 | 0 \rangle / (E_0 - E_{mi}) , \tag{9a}$$

and the expression of the second-order energy becomes

$$\bar{E}_{(2)} = \sum_{mi} \langle 0 | H_1 S_{mi}^+ | 0 \rangle \langle 0 | S_{mi} H_1 | 0 \rangle / (E_0 - E_{mi}) . \tag{10}$$

Equation (10) is an approximation to Eq. (4) as described in Sec. I.

It should be noted that our zeroth order Hamiltonian H_0 is *not* a HF Hamiltonian, but the exact Hamiltonian in the absence of perturbation, Eq. (2). If we start from the HF Hamiltonian H_{00}, namely from $H_{00} \Psi_0 = E_{00} \Psi_0$ (E_{00} is the sum of orbital energies, $E_{00} = \sum_i 2\epsilon_i$), Eq. (10) is obtained by summing up appropriate infinite correction terms with respect to $\lambda V = H_0 - H_{00}$ in the double perturbation expansions, using the relation of geometric expansion.[7a,8] The first term in this expansion, which is zeroth order with respect to λV, corresponds to the "uncoupled HF" second-order energy of Dalgarno.[7a]

$$\bar{E}_{(2,0)} = \sum_{mi} \langle 0 | H_1 S_{mi}^+ | 0 \rangle \langle 0 | S_{mi} H_1 | 0 \rangle / (\epsilon_i - \epsilon_m) . \tag{11}$$

The energy denominator of Eq. (11) does *not* correspond to the excitation energy in the HF approximation and the result is poorer than that of Eq. (10).

Now, let us consider the dependence of $\bar{E}_{(2)}$ on the unitary transformations among singly excited configurations given by

$$R^+ = S^+ U \tag{12}$$

where S^+ and R^+ are the row vectors composed of S_{mi}^+ and the new excitation operators R_{mi}^+. Since the new set of the singly excited configurations $R^+ \Psi_0$ forms, as an old set $S^+ \Psi_0$, an orthonormal (not complete) set which is orthogonal to the HF Ψ_0, it may *well* be used as a basis of expansion in Eq. (5) *in place of* $S^+ \Psi_0$. If we write the second-order energy thus obtained as $\bar{E}'_{(2)}$, it is given by

$$\bar{E}'_{(2)} = \sum_{mi} \langle 0 | H_1 R_{mi}^+ | 0 \rangle \langle 0 | R_{mi} H_1 | 0 \rangle / (E_0 - E'_{mi}) , \tag{13}$$

where $E'_{mi} = \langle 0 | R_{mi} H_0 R_{mi}^+ | 0 \rangle$. This is rewritten in the old representation as

$$\bar{E}'_{(2)} = \langle 0 | H_1 S^+ | 0 \rangle \sum_{mi} \frac{U_{(mi)} U_{(mi)}^*}{E_0 - U_{(mi)}^* A U_{(mi)}} \langle 0 | S H_1 | 0 \rangle , \tag{14}$$

where $U_{(mi)}$ is a column vector defined as $U = (\ldots, U_{(mi)}, \ldots)$ and A is a matrix defined by

$$A = \langle 0 | S H_0 S^+ | 0 \rangle . \tag{15}$$

Note that the matrix A is Hermitian and that the quantity $U_{(mi)}^* A U_{(mi)}$ in the denominator of Eq. (14) is the mith diagonal element of the matrix $U^* A U$.

As seen from Eq. (14), the approximate second-order energy in the conventional form *depends* on the unitary transformations among singly excited configurations. Different second-order energy is obtained if we use different set of singly excited configurations. Inspection of Eq. (14) shows that $\bar{E}_{(2)}$ is invariant to the unitary transformation *only when* $U = 1$ (no transformation) *or* $A = E_a 1$, where E_a is a constant. (Note the relations, $U_{(mi)}^* U_{(mi)} = 1$ and $\sum_{mi} U_{(mi)} U_{(mi)}^* = 1$.) The former case is trivial and the latter cannot be satisfied in actual problems, except when one forces this relation assuming the average-excitation-energy approximation.[9]

Hirao and Kato[10] calculated nuclear spin–spin coupling constants using *localized* orbitals as a basis which can be obtained in the above treatment by choosing special kind of U.[11] The calculated values were *more than twice* as large as those obtained with the usual canonical orbital basis. As seen in this example, one must be cautious when one uses the conventional equation (10). Many earlier calculations based on Eq. (10) stand in need of re-examinations.

As shown in the next section, the coupled equations (8) and (9) themselves are independent on the choice of U. The unitary dependence of $\bar{E}_{(2)}$ originates from neglecting the coupling terms in Eq. (9), the magnitude of which depends on the choice of U. Thus, we reach the following natural question, "What is the best choice of U?"

III. $\tilde{E}_{(2)}$ INCLUDING COUPLING TERMS COMPLETELY—$\tilde{E}_{(2)}$ BASED ON SINGLY EXCITED CI WAVEFUNCTIONS

In order to consider the above question, we return to Eqs. (8) and (9). They are rewritten in a matrix form as

$$\tilde{E}_{(2)} = \langle 0 | H_1 S^+ | 0 \rangle C , \tag{16}$$

$$\langle 0 | S H_1 | 0 \rangle + (A - E_0 1) C = 0 , \tag{17}$$

where C is a column vector composed of C_{mi}. The previous equation (10) was obtained by neglecting the off-diagonal elements of the matrix A, i.e. the coupling terms.

Now, let us choose the unitary transformation U as diagonalizing the Hermitian matrix A, or equivalently the matrix $A - E_0 1$ as

$$\mathbf{U}^* \mathbf{A} \mathbf{U} = \mathbf{D} \ , \tag{18}$$

where $\mathbf{D}$ is the diagonal matrix with real diagonal elements D_{mi}. Also, let us define the following unitary transformations of $\mathbf{S}^+$ and $\mathbf{C}$.

$$\mathbf{R}^+ = \mathbf{S}^+ \mathbf{U} \ , \quad \mathbf{C}' = \mathbf{U}^* \mathbf{C} \ . \tag{19}$$

Using these newly defined excitation operators R_{mi}^+, Eq. (18) is rewritten as

$$\langle 0 | R_{mi} H_0 R_{nj}^+ | 0 \rangle = \delta_{mn} \delta_{ij} D_{mi} \ , \tag{20a}$$

$$D_{mi} = \langle 0 | R_{mi} H_0 R_{mi}^+ | 0 \rangle \ . \tag{20b}$$

Thus, D_{mi} is the energy associated with the configuration $R_{mi}^+ \Psi_0$. Also, Eq. (5) is rewritten as

$$\Psi = \Psi_0 + \sum_{mi} C_{mi}' R_{mi}^+ \Psi_0 \ , \tag{21}$$

and Eqs. (16) and (17) are transformed to

$$\bar{E}_{(2)} = \langle 0 | H_1 \mathbf{R}^+ | 0 \rangle \mathbf{C}' \ , \tag{22}$$

$$\langle 0 | \mathbf{R} H_1 | 0 \rangle + (\mathbf{D} - E_0 \mathbf{1}) \mathbf{C}' = 0 \ . \tag{23}$$

Comparing Eqs. (21), (22), and (23) with Eqs. (5), (16), and (17), we understand that these coupled equations are *invariant* to the unitary transformations among singly excited configurations. Amos, Musher, and Roberts[12] showed a special case of this, limiting the unitary transformations to those among occupied and vacant orbitals.[11] Since $\mathbf{D}$ is a diagonal matrix, Eq. (23) is equivalent to

$$C_{mi}' = \langle 0 | R_{mi} H_1 | 0 \rangle / (E_0 - D_{mi}) \ , \tag{24}$$

without approximation [compare with Eq. (9a)]. Then, from Eq. (22), we obtain

$$\bar{E}_{(2)} = \sum_{mi} \langle 0 | H_1 R_{mi}^+ | 0 \rangle \langle 0 | R_{mi} H_1 | 0 \rangle / (E_0 - D_{mi}) \ . \tag{25}$$

This equation includes *all* of the coupling terms in spite of its similarlity to Eq. (10). Namely, by choosing $\mathbf{U}$ as diagonalizing the matrix $\mathbf{A}$, the second-order energy can be written in the same form as the conventional one *without* neglecting the coupling terms between singly excited configurations. To solve Eq. (25) is equivalent to solving the coupled equations (16) and (17). In other words, when we choose $\mathbf{U}$ as defined by Eq. (18), the coupling terms in Eq. (17) *vanish identically* without approximation.

Moreover, this choice of $\mathbf{U}$ is *physical*. The configuration $R_{mi}^+ \Psi_0$ and its energy D_{mi} appearing in Eq. (25) have realistic physical meanings as the energy and wavefunction of the excited *state* in the Tamm–Dancoff approximation.[4] This is because to solve Eq. (18) is equivalent to solving the secular equation of the singly excited configuration interaction (CI) method in the absence of perturbation. Thus, the $\bar{E}_{(2)}$ given by Eq. (25) is *identical with* the second-order energy based on the singly excited (SE) CI wavefunctions. The Brillouin relation $\langle 0 | H_0 R_{mi}^+ | 0 \rangle = 0$ and the relation (20a) mean that Ψ_0 and $R_{mi}^+ \Psi_0$ are the best possible approximations to the eigenfunctions of H_0 [Eq. (1)] *within* the space spanned by the HF and singly excited configurations. The energy difference denominator of Eq. (25) corresponds to the excitation energy in this approximation.

Murrell *et al.*[13] reported a calculation of the contact contribution to the nuclear spin–spin coupling constant of hydrogen fluoride. It was calculated as 502 Hz by Eq. (10),[3] but as 836 Hz by the SE-CI method, i.e., by Eq. (25). The difference as large as 334 Hz comes from the coupling terms and shows the importance of these terms.

Connection with the modified HF theories

A *restrictive* application of the above treatment leads to the *modified* HF theories of Silverstone–Yin,[5a] Huzinaga–Arnau[5b] (SY–HA), and Morokuma–Iwata (MI).[6] Let us consider the unitary transformations within the HF occupied orbitals **i** and/or the virtual orbitals **m** (**i** and **m** are row vectors)

$$\mathbf{i}' = \mathbf{i} \mathbf{U}^o \ , \quad \mathbf{m}' = \mathbf{m} \mathbf{U}^v \ , \tag{26}$$

and redefine the destruction and creation operators associated with $\mathbf{i}'$ and $\mathbf{m}'$, e.g.,

$$a_{i'\alpha} = \sum_j (\mathbf{U}^{o*})_{ij} a_{j\alpha} \ , \quad a_{m'\alpha}^+ = \sum_n a_{n\alpha}^+ U_{nm}^v \ . \tag{27}$$

Then, the new excitation operators $\mathbf{S}^{+\prime}$ which are defined using these new destruction and creation operators as in Eqs. (6) and (7) are connected with the old $\mathbf{S}^+$ by

$$\mathbf{S}^{+\prime} = \mathbf{S}^+ \mathbf{W} \ , \tag{28}$$

where $\mathbf{W}$ is the direct product of $\mathbf{U}^o$ and $\mathbf{U}^v$ defined by $W_{mi,nj} = \overline{U}_{ij}^o U_{mn}^v$ ($\overline{U}_{ij}^o$ is a complex conjugate of U_{ij}^o),

$$\mathbf{W} = \overline{\mathbf{U}^o} \times \mathbf{U}^v \ . \tag{29}$$

Because $\mathbf{U}^o$ and $\mathbf{U}^v$ are unitary, $\mathbf{W}$ is also unitary. However, the converse is not always true. Namely, an arbitrary unitary matrix can not always be written as a direct product of two unitary matrices of fixed dimensions. Therefore, it is *not* generally possible to diagonalize the matrix $\mathbf{A}$ by the direct product of the unitary transformations within the HF occupied and/or virtual manifolds. The freedom due to the HF orbital ambiguity is, as expected, insufficient to diagonalize the coupling terms included in the $\mathbf{A}$ matrix.

However, some simplifications of the $\mathbf{A}$ matrix is possible by the orbital unitary transformations $\mathbf{U}^o$ and $\mathbf{U}^v$. Let us restrict ourselves to consider only the excitation operators of the form $S_{mi_0}^+$ or $S_{m_0i}^+$, where i_0 and m_0 are the *one special* orbitals chosen from the occupied and virtual manifolds. Then the submatrix of $\mathbf{A}$ defined by

$$\mathbf{A}_{i_0} = \{ \langle 0 | S_{mi_0} H_0 S_{ni_0}^+ | 0 \rangle \} \ , \tag{30}$$

or

$$\mathbf{A}_{m_0} = \{ \langle 0 | S_{m_0i} H_0 S_{m_0j}^+ | 0 \rangle \} \ , \tag{31}$$

can be diagonalized, respectively, by the unitary transformation $\mathbf{U}^v$ or $\mathbf{U}^o$, since both $\mathbf{A}_{i_0}$ and $\mathbf{A}_{m_0}$ are Hermitian. The new orbitals $\mathbf{m}'$ or $\mathbf{i}'$ [Eq. (26)] thus obtained satisfy

$$\langle 0 | S_{m'i_0} H_0 S_{n'i_0}^+ | 0 \rangle = \delta_{m'n'} E_{m'i_0} \ , \tag{32}$$

or

$$\langle 0 | S_{m_0i'} H_0 S_{m_0j'}^+ | 0 \rangle = \delta_{i'j'} E_{m_0i'} \ , \tag{33}$$

where $E_{m'i_0}$ and $E_{m_0i'}$ are the energies of the singly excited configurations, $S_{m'i_0}^+ \Psi_0$ and $S_{m_0i'}^+ \Psi_0$, respectively.

$$E_{m'i_0} = \langle 0 | S_{m'i_0} H_0 S^+_{m'i_0} | 0 \rangle , \quad E_{m_0i'} = \langle 0 | S_{m_0i'} H_0 S^+_{m_0i'} | 0 \rangle .$$
(34)

Furthermore, since the above result is due to the unitary transformation within the virtual or occupied manifold, it is possible to select U^v and U^o in a self-consistent fashion so as to satisfy both of the equations (32) and (33).[14]

As studied by Morokuma and Iwata[6] and Hirao,[15] the transformed virtual orbitals m' satisfying Eq. (32) are equivalent to the SY–HA's modified virtual orbitals which are the solutions of the modified HF equation[16]

$$F' | k' \rangle = \epsilon'_k | k' \rangle ,$$

$$F' = F + P\Omega_0 P + (1 - P)\Omega_v(1 - P) ,$$
(35)

with the special selection of $\Omega_0 = 0$ and $\Omega_v = - J_{i_0} + K_{i_0} \pm K_{i_0}$ [the upper and lower signs correspond to the singlet and triplet excitations defined by Eqs. (6) and (7), respectively]. In Eq. (35), F is the conventional HF operator and $P = \sum_i^{occ} | i \rangle \langle i |$ is the projection operator onto the HF manifold. J_{i_0} and K_{i_0} are the Coulomb and exchange operators. On the other hand, the new set of occupied orbitals i' satisfying Eq. (33) is equivalent to the "electron potential" orbitals of MI[6] which are the solutions of Eq. (35) with $\Omega_0 = J_{m_0} - K_{m_0} \mp K_{m_0}$ and $\Omega_v = 0$. The orbitals which satisfy both Eqs. (32) and (33) are equivalent to the "electron–hole potential" orbitals[6] which are the solutions of Eq. (35) with $\Omega_0 = J_{m_0} - K_{m_0} \mp K_{m_0}$, $\Omega_v = - J_{i_0} + K_{i_0} \pm K_{i_0}$.[14]

Thus, the orbital unitary transformations in the modified HF orbital theory help to diagonalize some of the matrix elements of the A matrix as shown by Eqs. (32) and (33). However, there is no guarantee for the rest of the off-diagonal elements to be small. The excited states of this theory, which were originally devised so that the excited electron feels the appropriate field of the other $N-1$ electrons,[5,8a] correspond to the limited approximations to the excited states of the Tamm–Dancoff approximation. Note lastly that for a one-HF-orbital system like hydrogen[17] and helium atoms, the matrix U^v becomes identical with the matrix U of Eq. (18) since in this case $A = A_{i_0}$. Therefore, for this special case, the coupling terms can be completely included only by the unitary transformation among the virtual orbitals, and the resultant modified virtual orbitals become useful as the basic orbitals of perturbation theory.[18,19]

IV. $\tilde{E}_{(2)}$ OF THE COUPLED PERTURBED HF THEORY

The second-order energy of the coupled perturbed HF theory[7] may be considered to be the best possible value in the sense that it is based on the best possible orbitals for the perturbed Hamiltonian $H_0 + H_1$. Applications of the coupled HF theory are, however, still limited due to the existence of the self-consistency terms. Many variants of the "uncoupled" scheme have been proposed in order to eliminate the self-consistency terms.[7a,c,d,e]

In this section, we will show that the second-order energy of the coupled HF theory can also be written exactly in a simple sum-over-state perturbation formula. The resultant equation is very similar to the previous equation (25) and does not require an iterative solution.

The coupled perturbed HF theory is essentially a variational method in that it is based on the best possible single determinant (Hartree–Fock) wavefunction for the perturbed Hamiltonian $H_0 + H_1$.[20]

$$\Psi_{CHF} = \| 1^c 2^c \ldots i^c \ldots N^c \| .$$
(36)

The difference between the perturbed orbital i^c and the zeroth-order HF orbital i can be expanded with respect to the order of the perturbation H_1 as

$$i^c = i + i_1 + i_2 + \cdots ,$$
(37)

where i_1 and i_2 are the first- and second-order orbital corrections, respectively. In Eqs. (36) and (37), the orbitals are spin orbitals.

What we are interested in here is the second-order energy. This allows us some simplifications. Firstly, in Eq. (37), we need only the first- and second-order corrections i_1 and i_2. However, due to the Brillouin theorem, i_2 does not contribute to the second-order energy.[21] Thus, in Eq. (37), only the first-order correction i_1 contributes to the second-order energy. When we put the relation, $i^c = i + i_1$ into the perturbed wavefunction (36) and expand it, we obtain the sum of the determinants including the orbital correction i_1 never (HF Ψ_0), once (first order), twice (second order), etc. Again, we can make a simplification eliminating the determinants including more-than-three orbital corrections (higher than third order). Thus, using the previous notation, the resultant wavefunction is written as

$$\Psi = \mathfrak{N}\left(1 + \sum_{mi} C_{mi} S^+_{mi} + \frac{1}{2}\sum_{mi}\sum_{nj} C_{mi} C_{nj} S^+_{mi} S^+_{nj}\right)\Psi_0 .$$
(38)

$\mathfrak{N}$ is a normalization constant and S^+_{mi} is the excitation operator defined by Eqs. (6) or (7). In obtaining Eq. (38), we have expanded i_1 by means of the virtual orbitals $\{m\}$ [see Appendix A].

Thus, to solve the second-order energy from the coupled perturbed wavefunction (36)[20] is equivalent to solving the variational second-order energy from the trial wavefunction (38). That is, the $\bar{E}_{(2)}$ obtained variationally from the wavefunction (38) is identical with the second-order energy of the coupled HF theory. In Appendix A, the identity is shown more explicitly. It is also identical with the second-order energy of the method of Cohen and Roothaan[22a] and Pople, McIver, and Ostlund (finite perturbation method)[22b] in which the wavefunction (36) is directly solved variationally in the perturbed field $H_0 + H_1$.

The wavefunction (38) includes a contribution of the doubly excited configurations in the last term. It is a second-order correction and is written as a product of the first-order corrections. There is another independent doubly excited function which is not included in the present coupled HF scheme. However, fortunately, it does not contribute to the second-order energy based on the HF Ψ_0, as will be discussed in Sec. V and Appendix B [see also Ref. 7(i)]. When we neglect the contribution of the doubly excited configurations in Eq. (38), we reach the second-order energy obtained in Sec. III.

Now, let us solve the variational second-order energy

associated with the wavefunction (38). The trial form of the second-order energy is obtained from Eq. (38) as

$$\bar{E}^t_{(2)} = \sum_{mi} (C^*_{mi} \langle 0|S_{mi} H_1|0\rangle + C_{mi} \langle 0|H_1 S^+_{mi}|0\rangle)$$

$$+ \sum_{mi}\sum_{nj} C^*_{mi} C_{nj} (\langle 0|S_{mi} H_0 S^+_{nj}|0\rangle - \delta_{mn}\delta_{ij}E_0)$$

$$+ \frac{1}{2}\sum_{mi}\sum_{nj} (C^*_{mi} C^*_{nj} \langle 0|S_{mi} S_{nj} H_0|0\rangle$$

$$+ C_{mi} C_{nj} \langle 0|H_0 S^+_{nj} S^+_{mi}|0\rangle) . \tag{39}$$

Actually, almost all the perturbations we encounter are either real or pure imaginary, and in these cases all of the coefficients C_{mi} in Eq. (39) are either real or pure imaginary, respectively. Since we are dealing with closed-shell systems, all the integrals with respect to H_0 can be chosen as real. Therefore, Eq. (39) can be rewritten in a simple matrix form as

$$\bar{E}^t_{(2)} = 2\mathbf{C}^* \langle 0|\mathbf{S}H_1|0\rangle + \mathbf{C}^* (\mathbf{A} \pm \mathbf{B} - E_0 \mathbf{1})\mathbf{C} . \tag{40}$$

The matrix $\mathbf{A}$ is defined by Eq. (15) which is symmetric because it is real. The matrix $\mathbf{B}$ is also a real symmetric matrix defined by

$$\mathbf{B} = \langle 0|H_0(\mathbf{S}^+)^T \mathbf{S}^+|0\rangle = \langle 0|\mathbf{S}\mathbf{S}^T H_0|0\rangle , \tag{41}$$

where $(\mathbf{S}^+)^T$ is the transpose of the row vector $\mathbf{S}^+$. The plus and minus signs in front of the matrix $\mathbf{B}$ correspond to the real and pure imaginary perturbations, respectively. $\mathbf{C}^*$ is the Hermite conjugate of the column vector $\mathbf{C}$(when real, $\mathbf{C}^* = \mathbf{C}^T$ and when imaginary, $\mathbf{C}^* = -\mathbf{C}^T$).

Let us define the orthogonal matrix $\mathbf{V}$ which diagonalizes the sum of the matrices, $\mathbf{A} \pm \mathbf{B}$, or equivalently, $\mathbf{A} \pm \mathbf{B} - E_0 \mathbf{1}$ as

$$\mathbf{V}^T (\mathbf{A} \pm \mathbf{B}) \mathbf{V} = \mathbf{T} , \tag{42}$$

where $\mathbf{T}$ is the diagonal matrix with diagonal elements T_{mi}. Also, let us define the following orthogonal transformations of $\mathbf{S}^+$ and $\mathbf{C}$ as

$$\mathbf{Q}^+ = \mathbf{S}^+ \mathbf{V} , \quad \mathbf{C}' = \mathbf{V}^T \mathbf{C} . \tag{43}$$

Using these newly defined excitation operators Q^+_{mi}, Eq. (42) is rewritten as

$$\langle 0|Q_{mi} H_0 Q^+_{nj}|0\rangle \pm \langle 0|H_0 Q^+_{mi} Q^+_{nj}|0\rangle = \delta_{mn}\delta_{ij}(D'_{mi} \pm K'_{mi}) , \tag{44}$$

where the plus and minus signs correspond to those in Eq. (40). D'_{mi} and K'_{mi} are the integrals defined by[23]

$$T_{mi} = D'_{mi} \pm K'_{mi} , \tag{45}$$

$$D'_{mi} = \langle 0|Q_{mi} H_0 Q^+_{mi}|0\rangle ,$$

$$K'_{mi} = \langle 0|H_0 Q^+_{mi} Q^+_{mi}|0\rangle . \tag{46}$$

D'_{mi} denotes the energy associated with the singly excited configuration $Q^+_{mi} \Psi_0$. The integral, $\langle 0|H_0 Q^+_{mi} Q^+_{mi}|0\rangle$ is denoted as K'_{mi} because if Q^+_{mi} is replaced by S^+_{mi}, this integral is just the ordinary exchange integral $\pm K_{mi}$ between the orbitals m and i.

$$\langle 0|H_0 S^+_{mi} S^+_{mi}|0\rangle = \pm K_{mi} . \tag{47}$$

Thus, the integral K'_{mi} may be referred to as *generalized exchange integral*. In Eq. (47), the plus and minus signs correspond to the singlet and triplet excitation operators defined by Eqs. (6) and (7), respectively. These plus and minus signs should not be confused with the previous ones in Eqs. (40) and (44).

Using the orthogonal transformations given by Eqs. (42) and (43), equation (40) is rewritten equivalently as

$$\bar{E}^t_{(2)} = 2\mathbf{C}'^* \langle 0|\mathbf{Q}H_1|0\rangle + \mathbf{C}'^*(\mathbf{T} - E_0 \mathbf{1})\mathbf{C}' . \tag{48}$$

Making the energy given by Eq. (48) stationary to small changes in C'_{mi} and using the fact that $\mathbf{T}(= \mathbf{D}' + \mathbf{K}')$ is diagonal, we obtain the variational solution,

$$C'_{mi} = \langle 0|Q_{mi} H_1|0\rangle/(E_0 - D'_{mi} \mp K'_{mi}) . \tag{49}$$

Inserting Eq. (49) into Eq. (48), we obtain the variational solution of the second-order energy associated with the wavefunction (38) as

$$\bar{E}_{(2)} = \sum_{mi} \langle 0|H_1 Q^+_{mi}|0\rangle \langle 0|Q_{mi} H_1|0\rangle/(E_0 - D'_{mi} \mp K'_{mi}) , \tag{50}$$

where the minus sign corresponds to real perturbation and the plus sign to the imaginary perturbation.

In spite of its simplicity, Eq. (49) is *equivalent* to the ordinary coupled HF equation [Eq. (A1) or (A2) of Appendix A].[7] In Appendix A, the equivalence is shown explicitly. Equation (50) is an alternative expression of the second-order energy of the coupled HF theory. It is written in a simple sum-over-state perturbation formula. The calculation of Eq. (50) does *not* require an iterative procedure, although it can also be calculated iteratively. The procedure is simply a single diagonalization shown by Eq. (42) and the summation shown by Eq. (50). The labor is almost the same as for the previous singly excited CI case [Eq. (25)]. Therefore, the terminology, the "self-consistency" terms, in the ordinary coupled HF theory becomes inadequate in this representation. They are included here automatically in the terms D'_{mi} and K'_{mi} of Eq. (50). Moreover, as will be shown elsewhere,[24] this expression is suitable for expanding the coupled HF energy into the sum with respect to the correlation correction, $\lambda V = H_0 - H_{00}$[7d,g,1] [see Eq. (A4) of Appendix A]. This will clarify the nature of the electron correlation included in the coupled HF theory[24] and give a support to the geometric approximation of the coupled HF energy.[17,24]

In comparison with the previous singly excited CI result, Eq. (25), the coupled HF result, Eq. (50), includes an additional term K'_{mi} in the denominator, though the configuration $Q^+_{mi} \Psi_0$ and its energy D'_{mi} are also different from $R^+_{mi} \Psi_0$ and D_{mi} in Eq. (25). The generalized exchange integral K'_{mi} originates from the $\mathbf{B}$ matrix which represents the electron correlation (λV) interactions of the HF Ψ_0 with the second-order doubly excited configurations. Therefore, this integral K'_{mi} may be said to represent the effect of the electron correlation *induced* by the perturbation.[24] The sign of this integral depends on the nature of perturbation [plus for singlet perturbation and minus for triplet perturbation as shown in Eq. (47)], and its magnitude is of the order of ordinary exchange repulsion integral.

The appearance of the *ordinary* exchange repulsion integral in the energy difference demoninator was pointed out previously by Caves and Karplus[71] in the diagrammatic double perturbation analysis of the coupled HF theory, by Ditchfield *et al.*[25] in the analysis of the finite perturbation theory,[22] and by Nakatsuji[26] in the analysis of the spin-polarization corrections in various open-shell orbital theories. However, the previous analyses correspond essentially to neglecting the coupling terms appearing in both **A** and **B** matrices. Nevertheless, the differences in the numerical values between the singly excited CI and the coupled HF theories were well understood from this exchange integral.[71,25] The situation is very similar to the previous analysis of the various open-shell orbital theories.[26]

Caves and Karplus[71] analyzed the coupled HF theory using the diagrammatic double perturbation technique and compared it with the singly excited CI method. In comparison with the present results expressed by Eq. (25) (singly excited CI) and Eq. (50) (coupled HF), their presentations are much more complicated (see also Ref. 24).

New modified HF orbitals

As in Sec. III, the above treatment produces *new* modified HF orbitals as a *restrictive* special case. Let us consider the orthogonal transformations of the HF occupied orbitals **i** and the virtual orbitals **m**.

$$\mathbf{i'} = \mathbf{iV^o}, \quad \mathbf{m'} = \mathbf{mV^v} . \tag{51}$$

The orthogonal matrix $\mathbf{V^v}$ or $\mathbf{V^o}$ is defined as diagonalizing the *submatrix* of $\mathbf{A} \pm \mathbf{B}$ given by

$$(\mathbf{A} \pm \mathbf{B})_{i_0} = \{\langle 0|S_{mi_0}H_0 S^+_{ni_0}|0\rangle \pm \langle 0|H_0 S^+_{mi_0}S^+_{ni_0}|0\rangle\} , \tag{52}$$

or

$$(\mathbf{A} \pm \mathbf{B})_{m_0} = \{\langle 0|S_{m_0 i}H_0 S^+_{m_0 j}|0\rangle \pm \langle 0|H_0 S^+_{m_0 i}S^+_{m_0 j}|0\rangle\} , \tag{53}$$

respectively, where i_0 and m_0 are the *one special* orbitals chosen from the occupied and virtual manifolds. From the above definitions of $\mathbf{U^v}$ and $\mathbf{U^o}$ and from Eq. (47), the new orbitals $\mathbf{m'}$ or $\mathbf{i'}$ are shown to satisfy

$$\langle 0|S_{m'i_0}H_0 S^+_{n'i_0}|0\rangle \pm \langle 0|H_0 S^+_{m'i_0}S^+_{n'i_0}|0\rangle$$
$$= \delta_{m'n'}[E_{m'i_0} \pm (\pm K_{m'i_0})] . \tag{54}$$

or

$$\langle 0|S_{m_0 i'}H_0 S^+_{m_0 j'}|0\rangle \pm \langle 0|H_0 S^+_{m_0 i'}S^+_{m_0 j'}|0\rangle$$
$$= \delta_{i'j'}[E_{m_0 i'} \pm (\pm K_{m_0 i'})] . \tag{55}$$

In Eqs. (54) and (55), note the double $\pm$ signs in front of the exchange integrals $K_{m'i_0}$ and $K_{m_0 i'}$. The first plus and minus signs correspond to real and imaginary perturbations, respectively, and the second signs to spinless and spin-linear perturbations, respectively. $E_{m'i_0}$ and $E_{m_0 i'}$ are defined similarly to Eq. (34) and represent the energies of the configurations $S^+_{m'i_0}\Psi_0$ and $S^+_{m_0 i'}\Psi_0$, respectively. Moreover, since the above result is due to the orthogonal transformation within virtual *or* occupied manifold, we can select $\mathbf{V^v}$ *and* $\mathbf{V^o}$ in a self-consistent fashion so as to satisfy *both* Eqs. (54) and (55).[14]

The above new orbitals $\mathbf{i'}$ and $\mathbf{m'}$ can also be expressed as the solutions of the modified HF equation[16]

$$F'|k'\rangle = \epsilon'_k|k'\rangle ,$$
$$F' = F + P\Omega'_o P + (1 - P)\Omega'_v(1 - P) . \tag{56}$$

The new set of the virtual orbitals $\mathbf{m'}$ which satisfy Eq. (54) is equivalent to the solutions of Eq. (56) with $\Omega'_o = 0$, $\Omega'_v = -J_{i_0} + cK_{i_0}$, where $c = 3, -1, 1, 1$ for real singlet, real triplet, imaginary singlet, and imaginary triplet perturbations, respectively. Similarly, the new set of the occupied orbitals $\mathbf{i'}$ satisfy Eq. (56) with $\Omega'_o = J_{m_0} - cK_{m_0}$, $\Omega'_v = 0$. The orbitals which satisfy both Eqs. (54) and (55) are the solutions of Eq. (56) with $\Omega'_o = J_{m_0} - cK_{m_0}$, $\Omega'_v = -J_{i_0} + cK_{i_0}$.[14]

As shown by Eqs. (54) and (55), these modified orbitals $\mathbf{i'}$ and $\mathbf{m'}$ diagonalize some of the off-diagonal elements of the matrix, $\mathbf{A} \pm \mathbf{B}$. Therefore, these modified orbitals are thought to be superior, as the basis of perturbation theory, to the SY-HA's and MI's modified orbitals[5,6] which diagonalize some of the off-diagonal elements of the **A** matrix only (see also Sec. V). However, there is no guarantee that the off-diagonal elements other than those shown by Eqs. (54) and (55) are small in magnitude. Note that for a one-HF-orbital system like helium atom, the matrix $(\mathbf{A} \pm \mathbf{B})_{i_0}$ turns out to be identical with the matrix $\mathbf{A} \pm \mathbf{B}$ in Eq. (42) and then the matrix $\mathbf{V^v}$ becomes identical with $\mathbf{V}$. That is, for this special case, the coupled HF second-order energy can be obtained *only by* the orthogonal transformation of the virtual orbitals. In fact, when the solutions of the modified HF equation (56) are inserted into the "uncoupled HF" equation of Dalgarno, Eq. (11), it becomes identical, in this special case, with Eq. (50), i.e. the coupled HF value. Therefore, these virtual orbitals are very useful as the basis of perturbation theory.

V. DISCUSSION AND CONCLUSION

The second-order energy given by Eq. (50) is identical with the coupled HF second-order energy. This identity may suggest that it is the best possible expression of the approximate second-order energy based on the HF Ψ_0 and expressed as the sum over singly excited configurations. This point is discussed in this section.

Let us write the approximate perturbed wavefunction as $\tilde{\Psi}$. The variational principle requires $\bar{E} = \langle\tilde{\Psi}|H|\tilde{\Psi}\rangle/\langle\tilde{\Psi}|\tilde{\Psi}\rangle$ be minimum, where H is the perturbed Hamiltonian given by Eq. (3). Expanding this expression with respect to the order of perturbation, we obtain the variational principles for individual order corrections as[27]

$$\bar{E}_{(0)} = \langle\tilde{\Psi}_{(0)}|H_0|\tilde{\Psi}_{(0)}\rangle , \quad \delta\bar{E}_{(0)} = 0 , \tag{57}$$

$$\bar{E}_{(1)} = \langle\tilde{\Psi}_{(0)}|H_1|\tilde{\Psi}_{(0)}\rangle + \langle\tilde{\Psi}_{(1)}|H'_0|\tilde{\Psi}_{(0)}\rangle + \langle\tilde{\Psi}_{(0)}|H'_0|\tilde{\Psi}_{(1)}\rangle,$$
$$\delta\bar{E}_{(1)} = 0 , \tag{58}$$

$$\bar{E}_{(2)} = \langle\tilde{\Psi}_{(1)}|H'_1|\tilde{\Psi}_{(0)}\rangle + \langle\tilde{\Psi}_{(0)}|H'_1|\tilde{\Psi}_{(1)}\rangle + \langle\tilde{\Psi}_{(1)}|H'_0|\tilde{\Psi}_{(1)}\rangle$$
$$+ \langle\tilde{\Psi}_{(2)}|H'_0|\tilde{\Psi}_{(0)}\rangle + \langle\tilde{\Psi}_{(0)}|H'_0|\tilde{\Psi}_{(2)}\rangle , \quad \delta\bar{E}_{(2)} = 0 , \tag{59}$$

where $H'_0 = H_0 - \bar{E}_{(0)}$, $H'_1 = H_1 - \bar{E}_{(1)}$, and $\tilde{\Psi}_{(0)}$ is taken to be normalized. These equations are used as the basis of the following discussions.

Although the HF Ψ_0 is not an eigenfunction of H_0, it does satisfy Eq. (57) in a limited sense. Then, we choose the HF Ψ_0 as the zeroth-order wavefunction $\tilde{\Psi}_{(0)}$

and *fix* this choice *throughout* Eqs. (57)–(59), although, generally speaking, the $\bar{\Psi}_{(0)}$'s determined from Eqs. (58) and (59) are not necessarily required to be identical with the $\bar{\Psi}_{(0)}$ obtained from Eq. (57).[27] Similarly, we restrict $\bar{\Psi}_{(1)}$ in Eq. (58) to be identical with that in Eq. (59).

Taking into account the one-electron property of H_1, the above choice of $\bar{\Psi}_{(0)}$ leads naturally to the choice of the first-order wavefunction $\bar{\Psi}_{(1)}$ as the sum of the *singly* excited configurations. In fact, in this choice, the second and third terms of Eq. (58) vanish identically due to the Brillouin theorem and the natural expression, $\bar{E}_{(1)} = \langle \Psi_0 | H_1 | \Psi_0 \rangle$ results. Moreover, this choice of $\bar{\Psi}_{(1)}$ is shown to be *unique*.[28] It is written by means of the single excitation operators given by Eq. (6) or Eq. (7), depending on the property of the perturbation.

After the above choice of the $\bar{\Psi}_{(0)}$ and $\bar{\Psi}_{(1)}$, only possible choice of the second-order wavefunction $\bar{\Psi}_{(2)}$ in Eq. (59) is the sum of *doubly* excited configurations. In fact, second-order singly excited configurations do not contribute to $\bar{E}_{(2)}$ due to the Brillouin theorem, and triply and more highly excited configurations can not contribute in Eq. (59). Moreover, the form of the doubly excited terms of $\bar{\Psi}_{(2)}$ is restricted. It can *never be free* from that of the singly excited terms of $\bar{\Psi}_{(1)}$.[29] The dependence of the doubly excited terms of $\bar{\Psi}_{(2)}$ on the singly excited terms of $\bar{\Psi}_{(1)}$ is represented in the coupled HF framework by the last term of Eq. (38). Although there is another doubly excited singlet function [only singlet function contribute to $\bar{E}_{(2)}$ of Eq. (59)] independent from $S_{mi}^+ S_{nj}^+ \Psi_0$, it does *not* contribute to $\bar{E}_{(2)}$ given by Eq. (59), as shown in Appendix B. This fact is very *fortunate* for the coupled HF theory, since its framework is the one which can not include the other independent doubly excited function.

Thus, the variation of the $\bar{E}_{(2)}$ of Eq. (59), starting from the restriction of $\bar{\Psi}_{(0)}$ to the HF Ψ_0, reduces to the variation of the second-order energy associated with the wavefunction (38). That is, the second-order energy given by Eq. (50), which is identical with the coupled HF energy, is the *best possible* second-order energy *based on* the HF Ψ_0. Moreover, Eq. (50) is written in the sum over singly excited configurations. Therefore, the answer of the question, "What is the best expression of the second-order sum-over-state perturbation energy based on the HF Ψ_0?" may be said to be *the equation* (50).

Referring to Eq. (59), we understand that the coupling terms between different singly excited configurations appear in the third term. If one neglects these coupling terms and the last two terms, the variation of Eq. (59) leads to the conventional equation (10) of Sec. II. If we include these coupling terms but neglect the last two terms,[30] we obtain Eq. (25) of Sec. III, which is identical with the second-order energy based on the singly excited CI wavefunctions. If we include all of the terms of Eq. (59), we reach Eq. (50) of Sec. IV, which is identical with the second-order energy of the coupled HF theory. All of these second-order energies are written in the sum over singly excited configurations. The equation (50) is the best possible expression.

The present formulation has also shown that the modified HF theory can be obtained as a *restrictive* application of the present theory. Each step of the above stepwise improvements gives a different stage of the modified HF theory. The HF theory associated with Eq. (10) of Sec. II is actually a standard one. The modified HF orbitals of SY–HA[5] and MI[6] are all associated with the treatment given in Sec. III. The treatment of Sec. IV gives, as a by-product, new modified HF operators given by Eq. (56), which are thought from the above discussions to be superior to the modified HF operators hitherto given.[5,6]

ACKNOWLEDGMENTS

APPENDIX A

This appendix gives an explicit proof of the identity between the second-order energy given by Eq. (50) of Sec. IV and that of the coupled HF theory. For simplicity, we consider only the spin-free perturbation.

The coupled HF equation for the first-order orbital correction i_1 of Eq. (37) is written as[7]

$$[h_0(\mu) - \epsilon_i^0] i_1(\mu) + [h_1(\mu) + g_1(\mu) - \epsilon_i^1] i(\mu) = 0 , \qquad (A1)$$

where h_0 is the unperturbed HF operator, ϵ_i the orbital energy, h_1 the one-electron perturbation defined by $H_1 = \sum_\mu h_1(\mu)$, and g_1 the operator defined by

$$g_1(\mu) = \sum_j^{occ} \left[\int d\tau_\nu j_1^*(\nu) r_{\mu\nu}^{-1} (2 - P_{\mu\nu}) j(\nu) \right.$$
$$\left. + \int d\tau_\nu j^*(\nu) r_{\mu\nu}^{-1} (2 - P_{\mu\nu}) j_1(\nu) \right] ,$$

which is the origin of the so-called self-consistency term. When we expand the first-order correction i_1 by means of the virtual orbitals

$$i_1 = \sum_m c_{mi} m ,$$

the coupled HF equation (A1) is rewritten as

$$(\epsilon_m^0 - \epsilon_i^0) c_{mi} + \langle m | h_1 | i \rangle + \sum_{nj} [c_{nj}(2\langle mj | in \rangle - \langle mj | ni \rangle)$$
$$+ c_{nj}^* (2\langle mn | ij \rangle - \langle mn | ji \rangle)] = 0 . \qquad (A2)$$

where $\langle mj | in \rangle = \langle m^*(1) j^*(2) | r_{12}^{-1} | i(1) n(2) \rangle$. The coupled HF second-order energy is calculated using the solutions of Eq. (A2) as

$$\bar{E}_{(2)}^{CHF} = \sum_{mi} (c_{mi} \langle i | h_1 | m \rangle + c_{mi}^* \langle m | h_1 | i \rangle) . \qquad (A3)$$

In order to rewrite Eq. (A2) by means of the notations used in the text, we introduce the following HF and electron-correlation operators.

$$H_{00} = \sum_\mu h_0(\mu)$$

$$V = H_0 - H_{00} = \sum_{\mu > \nu} 1/r_{\mu\nu} - \sum_{\mu} g_0(\mu) \ . \tag{A4}$$

g_0 is the usual Coulomb minus exchange operator in the unperturbed HF operator. Using these operators, the quantities appearing in Eq. (A2) are rewritten as

$$\epsilon_m^0 - \epsilon_i^0 = \langle 0 | S_{mi} H_{00} S_{mi}^+ | 0 \rangle - \langle 0 | H_{00} | 0 \rangle \ ,$$

$$\langle m | h_1 | i \rangle = \langle 0 | S_{mi} H_1 | 0 \rangle / \sqrt{2} \ ,$$

$$2\langle mj | in \rangle - \langle mj | ni \rangle = \langle 0 | S_{mi} V S_{nj}^+ | 0 \rangle - \delta_{mn} \delta_{ij} \langle 0 | V | 0 \rangle \ ,$$

$$2\langle mn | ij \rangle - \langle mn | ji \rangle = \langle 0 | S_{mi} S_{nj} V | 0 \rangle \ . \tag{A5}$$

where S_{mi}^+ is the singlet excitation operator defined by Eq. (6), and $|0\rangle$ is the HF Ψ_0. Inserting Eq. (A5) into Eq. (A2) and using Eq. (A4), we can rewrite the coupled HF equation (A2) as

$$\langle 0 | S_{mi} H_1 | 0 \rangle + \sum_{nj} C_{nj} (\langle 0 | S_{mi} H_0 S_{nj}^+ | 0 \rangle - \delta_{mn} \delta_{ij} E_0)$$

$$+ \sum_{nj} C_{nj}^* \langle 0 | S_{mi} S_{nj} H_0 | 0 \rangle = 0 \ , \tag{A6}$$

where $E_0 = \langle 0 | H_0 | 0 \rangle$ and we have scaled the coefficient as

$$C_{mi} = \sqrt{2} \, c_{mi} \ . \tag{A7}$$

Using the definition of the **A** and **B** matrices given by Eqs. (15) and (41), Eq. (A6) is rewritten in a matrix form as

$$\langle 0 | \mathbf{S} H_1 | 0 \rangle + (\mathbf{A} \pm \mathbf{B} - E_0 \mathbf{1}) \mathbf{C} = 0 \ , \tag{A8}$$

where we have restricted H_1 to be real (plus sign) or pure imaginary (minus) perturbation. This equation can be further simplified using the orthogonal transformation defined by Eqs. (42) and (43) as

$$\langle 0 | \mathbf{Q} H_1 | 0 \rangle + (\mathbf{T} - E_0 \mathbf{1}) \mathbf{C}' = 0 \ ,$$

which is equivalent to

$$C_{mi}' = \langle 0 | Q_{mi} H_1 | 0 \rangle / (E_0 - T_{mi}) \ , \tag{A9}$$

namely to Eq. (49) of the text. Thus, Eq. (49) of the text is identical with the coupled HF equation (A1) or (A2) in spite of its simplicity. The coupled HF second-order energy given by Eq. (A3) is rewritten as

$$\bar{E}_{(2)}^{\mathrm{CHF}} = \sum_{mi} \langle 0 | H_1 Q_{mi}^+ | 0 \rangle \langle 0 | Q_{mi} H_1 | 0 \rangle / (E_0 - T_{mi}) \ , \tag{A10}$$

which is identical with Eq. (50) of the text. Thus, the theory developed in Sec. IV is exactly equivalent to the coupled HF theory.

APPENDIX B

This appendix shows that the other doubly excited singlet function which is not included in the coupled HF scheme does not contribute to the second-order energy based on the HF Ψ_0.

Since doubly excited function corresponds to four-spin case, there are two independent doubly excited singlet functions. They are written explicitly as

$$\Psi_{ij}^{mn}(1) = \tfrac{1}{2} \| \cdots min\, j (\alpha\beta\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta + \beta\alpha\beta\alpha) \cdots \| \ , \tag{B1}$$

$$\Psi_{ij}^{mn}(2) = \frac{1}{2\sqrt{3}} \| \cdots min\, j (\alpha\beta\alpha\beta + \alpha\beta\beta\alpha + \beta\alpha\alpha\beta + \beta\alpha\beta\alpha$$

$$- 2\alpha\alpha\beta\beta - 2\beta\beta\alpha\alpha) \cdots \| \ . \tag{B2}$$

For notational convenience, let us rewrite the single excitation operators given by Eqs. (6) and (7) as S_{mi}^+ and $T_{mi}^+(0)$, respectively, and introduce following two triplet excitation operators $T_{mi}^+(1)$ and $T_{mi}^+(-1)$ as

$$T_{mi}^+(1) = a_{m\alpha}^+ a_{i\beta} \ , \quad T_{mi}^+(-1) = a_{m\beta}^+ a_{i\alpha} \ . \tag{B3}$$

Using these notations, the two independent doubly excited functions are written as

$$\Psi_{ij}^{mn}(1) = S_{mi}^+ S_{nj}^+ \Psi_0 \ , \tag{B4}$$

$$\Psi_{ij}^{mn}(2) = (1/\sqrt{3}) [T_{mi}^+(0) T_{nj}^+(0) + T_{mi}^+(1) T_{nj}^+(-1)$$

$$+ T_{mi}^+(-1) T_{nj}^+(1)] \Psi_0 \ . \tag{B5}$$

When we consider the spin-free perturbation, the first-order correction $\tilde{\Psi}_{(1)}$ is expressed by the singlet excitation operator as

$$\tilde{\Psi}_{(1)} = \sum_{mi} C_{mi} S_{mi}^+ \Psi_0 \tag{B6}$$

It can never include the triplet excitation operators because of spin-conservation. In the second-order correction $\tilde{\Psi}_{(2)}$, the contribution of the doubly excited function $\Psi_{ij}^{mn}(1)$ may be written as $\sum_{mi} \sum_{nj} C_{mi} C_{nj} S_{mi}^+ S_{nj}^+ \Psi_0$ which is *dependent* on $\tilde{\Psi}_{(1)}$ given by Eq. (B6). However, the contribution of the other function $\Psi_{ij}^{mn}(2)$ is *independent* of $\tilde{\Psi}_{(1)}$, since the $\tilde{\Psi}_{(1)}$ given by Eq. (B6) does not include the term composed of the triplet excitation operators. When we write the latter contribution as, e.g., $\sum_{mi} \sum_{nj} \times G_{mi} G_{nj} T_{mi}^+(0) T_{nj}^+(0) \Psi_0$ and apply the variational principle to the $\bar{E}_{(2)}$ given by Eq. (59), we obtain

$$\sum_{nj} G_{nj} \langle 0 | H_0 T_{mi}^+(0) T_{nj}^+(0) | 0 \rangle = 0 \ . \tag{B7}$$

This relation means that the contribution of $\Psi_{ij}^{mn}(2)$ to the $\bar{E}_{(2)}$ of Eq. (59), $\sum_{mi} \sum_{nj} G_{mi} G_{nj} \langle 0 | H_0 T_{mi}^+(0) T_{nj}^+(0) | 0 \rangle$, vanishes identically. Therefore, for the spin-free perturbation, the doubly excited function $\Psi_{ij}^{mn}(2)$ does not contribute to the second-order energy $\bar{E}_{(2)}$ based on the HF Ψ_0. This result is closely related to the discussion given in Ref. 29. For the spin-dependent perturbation, the roles of the functions (B4) and (B5) are interchanged.

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[19]In the case of hydrogen atom, this unitary transformation of the HF virtual orbitals leads to the ordinary exact excited orbitals. Namely, in this case, the modified HF orbitals are equivalent to the exact excited orbitals (see Ref. 24).

[20]In the ordinary coupled HF formalism,[7] one obtains first the perturbed HF equation $F^c i^c = \epsilon^c i^c$ by applying the *variational* principle to the wavefunction (36) in the perturbed field $H_0 + H_1$. Then, one expands F^c, i^c, and ϵ^c with respect to the order of perturbation and obtain the coupled HF equation from the first-order relation. This leads to the second-order energy of the coupled HF theory.

[21]The second-order orbital correction i_2 contributes to the second-order energy in the form $\langle 0 | H_0 | \| 1 \cdots i_2 \cdots N \| \rangle$ which vanishes identically due to the Brillouin theorem.

[22](a) H. D. Cohen and C. C. J. Roothaan, J. Chem. Phys. 43, S34 (1965); H. D. Cohen, *ibid.* 43, 3558 (1965); (b) J. A. Pople, J. W. McIver, and N. S. Ostlund, *ibid.* 49, 2960 (1968); (c) See also, H. Nakatsuji, K. Hirao, H. Kato, and T. Yonezawa, Chem. Phys. Lett. 6, 541 (1970).

[23]In comparison with the **D** matrix in Sec. III, Eq. (20a), the matrices **D′** and **K′** are not diagonal, but the sum, **D′** + **K′** = **T** is a diagonal matrix as defined by Eq. (42).

[24]H. Nakatsuji and J. I. Musher, J. Chem. Phys. 61, 3737 (1974), following paper.

[25]R. Ditchfield, N. S. Ostlund, J. N. Murrell, and M. A. Turpin, Mol. Phys. 18, 433 (1970).

[26]H. Nakatsuji, J. Chem. Phys. 59, 2586 (1973). See also, H. Nakatsuji, H. Kato, and T. Yonezawa, *ibid.* 51, 3175 (1969).

[27]See Eq. (V.1)–(V.4) of Ref. 1.

[28]*If* we include, e.g., *doubly* excited configurations into $\bar{\Psi}_{(1)}$ of Eq. (58), a peculiar result occurs. Let us denote these doubly excited terms as $\sum C_{ij}^{mn} \Psi_{ij}^{mn}$. The variation of these terms depends only on the last two terms of Eq. (58), and the minimization of $\bar{E}_{(1)}$ with respect to C_{ij}^{mn} leads to

$$\langle \Psi_{ij}^{mn} | H_0' | \Psi_0 \rangle + \langle \Psi_0 | H_0' | \Psi_{ij}^{mn} \rangle = 0, \tag{A}$$

where Ψ_0 is the HF Ψ_0. However, the left-hand-side integrals, which reduce to electron repulsion integrals, are not generally zero. This contradiction arises from the restriction of the zeroth-order function $\bar{\Psi}_{(0)}$ in Eq. (58) to the HF Ψ_0. In other words, doubly excited terms as well as other higher terms are allowed to appear in the first-order correction $\bar{\Psi}_{(1)}$ *only when* the zeroth-order wavefunction $\bar{\Psi}_{(0)}$ is an exact wavefunction or some over-HF wavefunction which satisfies the *generalized Brillouin* relation like Eq. (A). However, this is not the present case. Therefore, the first-order wavefunction $\bar{\Psi}_{(1)}$ is written *uniquely* by the sum of the singly excited configurations, *so long as* we choose the HF Ψ_0 as the zeroth order wavefunction $\bar{\Psi}_{(0)}$ in Eq. (58).

[29]*If* the form of the doubly excited terms of $\bar{\Psi}_{(2)}$ is *free* from the singly excited terms of $\bar{\Psi}_{(1)}$, it may be written as $\sum C_{ij}^{mn} \Psi_{ij}^{mn}$, where C_{ij}^{mn} is an independent parameter from the coefficients of the singly excited terms of $\bar{\Psi}_{(1)}$. The variation of $\bar{E}_{(2)}$ given by Eq. (59) with respect to C_{ij}^{mn} leads, as in Ref. 28, to the equation

$$\langle \Psi_{ij}^{mn} | H_0' | \Psi_0 \rangle + \langle \Psi_0 | H_0' | \Psi_{ij}^{mn} \rangle = 0,$$

which can never be satisfied actually. As discussed in Ref. 28, this contradiction means that the doubly excited second-order terms *free from* $\bar{\Psi}_{(1)}$ do *not* occur in the $\bar{\Psi}_{(2)}$ of Eq. (59), *so long as* we restrict the $\bar{\Psi}_{(0)}$ in Eq. (59) to the HF Ψ_0.

[30]This corresponds to the Hylleraas variational principle[1] of the second-order energy, which is applicable *only when* the zeroth order wavefunction is an eigenfunction of the zeroth-order Hamiltonian.