Geometric double-perturbation expansion of the coupled Hartree–Fock second-order energy

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The second-order energy of the coupled perturbed Hartree–Fock (CHF) theory is expanded explicitly into the sum with respect to the electron–correlation corrections. In a *matrix* form, the expansion is exactly *geometric*. The correlation effect included in the CHF theory has two origins: one represents the so-called first-order correlation energies *intrinsic to the unperturbed ground and excited states*, and the other represents the correlation effect *induced by the external perturbation*. The matrix geometric expansion reduces under some approximation to an ordinary *scalar* geometric series. This gives a basis for the geometric approximation of the CHF energy proposed empirically by Schulman and Musher. Exactly the same arguments also apply to the second-order energy of the singly excited CI method, simply by neglecting the perturbation-induced correlation effect.

I. INTRODUCTION

Some properties of a many-electron system in the field of one-electron perturbation may be calculated using perturbation theory. The coupled perturbed Hartree–Fock (CHF) theory[1–9] is especially suitable for this purpose. As was shown previously,[10] it gives the best possible second-order energy based on the Hartree–Fock (HF) zeroth order wavefunction. When we use the double-perturbation technique,[11] the CHF energy may be expanded with respect to the order of the electron–correlation correction as

$$E^{\mathrm{CHF}}_{(2)} = E^0_{(2)} + \lambda E^1_{(2)} + \lambda^2 E^2_{(2)} + \cdots \quad . \tag{1}$$

The leading term $E^0_{(2)}$ corresponds to the uncoupled HF energy of Dalgarno,[1] and the explicit formula of the first-order term $E^1_{(2)}$ was given by Tuan, Epstein, and Hirschfelder.[4]

Some years ago, Kelly[12] and Schulman and Musher[13a] considered the polarizability α of the hydrogen atom as a HF double-perturbation expansion problem. (In this case, the CHF energy turns out to be an exact second-order energy.) They observed that the expansion (1) was *geometric* to a high degree of accuracy in that the ratio between two neighboring terms was nearly a constant.[13a] Schulman and Musher extended this observation, by analogy, to the many-electron system and proposed the following geometric approximation of the CHF polarizability:

$$\alpha_{\mathrm{CHF}} \simeq \alpha_{\mathrm{geom}} = \alpha_0 (1 - \alpha_1/\alpha_0)^{-1} \ , \tag{2}$$

where $\alpha_n = -\frac{1}{2} E^n_{(2)}$. Theoretical justifications of this approximation were given by Amos[13b] using the Feenberg–Goldhammer procedure[13c] and by Tuan[13d] as a result of the restrictive variation of the CHF orbitals. Various calculations hitherto made[13a,13d,13e] have confirmed the validity of this approximation.

It was shown in a previous paper[10] that the CHF energy can be written exactly in a simple sum-over-state perturbation formula. The resultant equation was very similar to that of the singly excited (SE) configuration interaction (CI) method and did not require an iterative solution. Based on this expression, we give here explicitly the double-perturbation expansion formula (1) of the CHF energy. The expansion is shown to be exactly *geometric* in a *matrix* form. The analysis clarifies the nature of the electron correlation included in the CHF theory. The condition under which the matrix geometric expansion reduces to an ordinary *scalar* geometric series is given. Similar behaviors of the second-order energy of the SE–CI method are also mentioned. Prior to these, we first examine in the next section the hydrogen atom case, because of its unique simplicity, even though this system is not general enough since it does not have actual electron correlation.

II. EXPANSION FORMULA FOR HYDROGEN ATOM

The exact zeroth order states of the hydrogen atom are specified by the following eigenvalue equation.

$$H_0 = -\tfrac{1}{2}\Delta_1 - 1/r_1 \ , \tag{3}$$

$$H_0 |n\rangle = \epsilon_n |n\rangle \ . \tag{4}$$

In the HF representation, we define the following HF operator,

$$H_{00} = -\tfrac{1}{2}\Delta_1 - 1/r_1 + V(r_1) \ , \tag{5}$$

$$V(r_1) = \int dr_2 \, \phi_0(r_2) \, r_{12}^{-1} (1 - P_{12}) \, \phi_0(r_2) \ , \tag{6}$$

and the following HF equation,

$$H_{00} |n'\rangle = \epsilon'_n |n'\rangle \ . \tag{7}$$

Since the operator V has no effect on the ground-state orbital, i.e., $V|0\rangle = 0$, the ground state is common to both representations.

$$\phi_0 = |0\rangle = |0'\rangle \ , \quad \epsilon_0 = \epsilon'_0 \ . \tag{8}$$

The "electron–correlation" operator is defined as

$$-\lambda V = H_0 - H_{00} \ , \tag{9}$$

where λ is a dummy parameter.

In the exact representation, an electron in the excited orbital $|n\rangle$ sees a bare nucleus, whereas in the HF representation, an electron in the excited orbital $|n'\rangle$ sees

a bare nucleus *and* an electron in the 1*s* orbital. The main effect of the potential V is thus to raise the orbital energy by the amount of the electron repulsion integral. In other words, going from the representation (4) to the representation (7) corresponds to going reverse the story of the "$N-1$" field.[14,15] Hence, in the language of many-electron systems, the exact excited orbitals $|n\rangle$ are just the *modified* HF virtual orbitals.[15] The corresponding modified HF operator is the exact Hamiltonian H_0, as the relation $V|0\rangle = 0$ implies. The two sets of the excited orbitals $\{n\}$ and $\{n'\}$ are therefore connected by the unitary transformation as[10,15b]

$$\mathbf{n} = \mathbf{n}'\mathbf{U} \ , \tag{10}$$

where $\mathbf{n}$ and $\mathbf{n}'$ are row vectors, and $\mathbf{U}$ is defined as diagonalizing the following matrix:

$$\mathbf{U}^* \langle \mathbf{n}' | H_0 - \epsilon_0 | \mathbf{n}' \rangle \mathbf{U} = \Delta\epsilon \ . \tag{11}$$

$\Delta\epsilon$ is a diagonal matrix composed of the exact transition energy $\epsilon_n - \epsilon_0$ ($n \geq 1$). Inserting Eq. (9) into Eq. (11), we obtain

$$\Delta\epsilon' - \lambda \mathbf{V}' = \mathbf{U}\,\Delta\epsilon\,\mathbf{U}^* \ , \tag{12}$$

where $\mathbf{V}'$ is the "correlation" matrix defined by

$$\mathbf{V}' = \langle \mathbf{n}' | \mathbf{V} | \mathbf{n}' \rangle \ . \tag{13}$$

The exact second-order energy of the hydrogen atom is written in a sum-over-state formula as

$$E_{(2)} = -\langle 0 | H_1 | \mathbf{n} \rangle (\Delta\epsilon)^{-1} \langle \mathbf{n} | H_1 | 0 \rangle \ , \tag{14}$$

where H_1 is the external one-electron perturbation and the reciprocal matrix $(\Delta\epsilon)^{-1}$ is diagonal with the elements $(\epsilon_n - \epsilon_0)^{-1}$. The expressions of the SE–CI and the CHF energies obtained previously[10] reduce to the above equation for a one-electron system.[16] In the HF representation, the exact second-order energy (14) is written as

$$E_{(2)} = -\langle 0 | H_1 | \mathbf{n}' \rangle (\Delta\epsilon')^{-1} [\mathbf{1} - \lambda \mathbf{V}' (\Delta\epsilon')^{-1}]^{-1} \langle \mathbf{n}' | H_1 | 0 \rangle \ , \tag{15}$$

where $(\Delta\epsilon')^{-1}$ is a diagonal matrix with the elements $(\epsilon_n' - \epsilon_0)^{-1}$. Expanding the term $[\mathbf{1} - \lambda \mathbf{V}'(\Delta\epsilon')^{-1}]^{-1}$ with respect to the "correlation" parameter λ, we obtain

$$E_{(2)} = E^0_{(2)} + \lambda E^1_{(2)} + \lambda^2 E^2_{(2)} + \cdots \ , \tag{16}$$

where

$$E^0_{(2)} = -\langle 0 | H_1 | \mathbf{n}' \rangle (\Delta\epsilon')^{-1} \langle \mathbf{n}' | H_1 | 0 \rangle \ , \tag{17a}$$

$$E^1_{(2)} = -\langle 0 | H_1 | \mathbf{n}' \rangle (\Delta\epsilon')^{-1} \mathbf{V}' (\Delta\epsilon')^{-1} \langle \mathbf{n}' | H_1 | 0 \rangle \ , \tag{17b}$$

$$E^2_{(2)} = -\langle 0 | H_1 | \mathbf{n}' \rangle (\Delta\epsilon')^{-1} \mathbf{V}' (\Delta\epsilon')^{-1} \mathbf{V}' (\Delta\epsilon')^{-1} \langle \mathbf{n}' | H_1 | 0 \rangle \ , \tag{17c}$$

$$\cdots \quad .$$

This expansion is *geometric* in a matrix form. The "ratio" matrix is

$$\lambda \mathbf{V}' (\Delta\epsilon')^{-1} = \lambda \langle \mathbf{n}' | V | \mathbf{n}' \rangle (\Delta\epsilon')^{-1} \tag{18}$$

Its diagonal element is the usual Coulomb minus exchange integral divided by the HF orbital energy difference $(J_{1s,n'} - K_{1s,n'})/(\epsilon_n' - \epsilon_0)$, which is positive and much smaller than unity. The off-diagonal elements are an order of magnitude smaller than the diagonal elements. Therefore, it is expected that the characteristic values[17] of the ratio matrix are smaller than unity, and then the above expansion converges[17] to the single formula (15), i.e., to the exact value.

If we can approximate in important excitation domains (see below) as

$$\mathbf{V}' (\Delta\epsilon')^{-1} \simeq a\mathbf{1} \ , \tag{19}$$

where a is a constant smaller than unity, the above geometric expansion reduces to an ordinary *scalar* geometric series, and Eq. (15) becomes

$$E_{(2)} \simeq E^{\mathrm{GEOM}}_{(2)} = E^0_{(2)} (1 - E^1_{(2)}/E^0_{(2)})^{-1} . \tag{20}$$

This is the geometric approximation proposed by Schulman and Musher.[13a] Due to their analysis, the approximation (19) holds in the important excitation domains. That is, in the regions of the excitations which give dominant contributions, the elements of the ratio matrix are well approximated by $a\delta_{ij}$. Kelly[12] also used essentially the same approximation as above.

III. EXPANSION OF THE COUPLED HF ENERGY

In a previous paper[10] the CHF energy was expressed in a simple sum-over-state perturbation formula. This expression is very suitable to study the correlation effects included in the CHF energy. The formulation is very similar to the hydrogen atom case.

First, we review briefly the previous results.[10] As an unperturbed wavefunction, we choose the HF closed-shell wavefunction Ψ_0 composed of doubly occupied orbitals $\{i\}$. The virtual orbitals are denoted as $\{m\}$. We introduce single excitation operators defined by

$$S^+_{mi} = (a^+_{m\alpha} a_{i\alpha} + a^+_{m\beta} a_{i\beta})/\sqrt{2} \ . \tag{21}$$

for spin-independent perturbations, and

$$S^+_{mi} = (a^+_{m\alpha} a_{i\alpha} - a^+_{m\beta} a_{i\beta})/\sqrt{2} \ , \tag{22}$$

for spin-linear perturbations.[18] $a^+_{m\alpha}$ and $a_{i\alpha}$ are the fermion creation and destruction operators. $S^+_{mi}\Psi_0$ is a singly excited singlet or triplet configuration, depending on Eqs. (21) or (22). As shown previously, the CHF energy is equivalent to the variational second-order energy associated with the wavefunction

$$\Psi_{\mathrm{CHF}} = \mathfrak{N}\left(1 + \sum_{mi} C_{mi} S^+_{mi} + \frac{1}{2} \sum_{mi} \sum_{nj} C_{mi} C_{nj} S^+_{mi} S^+_{nj}\right)\Psi_0 \ , \tag{23}$$

in the *exact* perturbed field, $H_0 + H_1$. $\mathfrak{N}$ is a normalization constant and C_{mi} is a variational parameter first order to H_1.[19] Let us define the following two matrices $\mathbf{A}$ and $\mathbf{B}$:

$$\mathbf{A} = \langle 0 | \mathbf{S} H_0 \mathbf{S}^+ | 0 \rangle \ , \tag{24}$$

$$\mathbf{B} = \langle 0 | H_0 (\mathbf{S}^+)^T \mathbf{S}^+ | 0 \rangle \ , \tag{25}$$

where $\mathbf{S}^+$ denotes a row vector composed of the excitation operators S^+_{mi}, and $|0\rangle$ denotes the HF Ψ_0. For closed-shell systems, both of the matrices $\mathbf{A}$ and $\mathbf{B}$ are real symmetric matrices. Then, we can define the orthogonal matrix $\mathbf{U}$ which diagonalize the sum of the matrices, $\mathbf{A} \pm \mathbf{B}$, as

$$\mathbf{U}^T (\mathbf{A} \pm \mathbf{B}) \mathbf{U} = \mathbf{T} \ , \tag{26}$$

where the plus and minus signs correspond to real and

pure imaginary perturbations, respectively.[19] $\mathbf{T}$ is a diagonal matrix with the element T_{mi}. Using this orthogonal matrix $\mathbf{U}$, we define the following transformation of the single excitation operators:

$$\mathbf{Q}^+ = \mathbf{S}^+ \mathbf{U} \ . \tag{27}$$

Thus, the variational second-order energy associated with the wavefunction (23) is written in a following sum-over-state perturbation formula:

$$E^{\mathrm{CHF}}_{(2)} = -\sum_{mi} \langle 0|H_1 Q^+_{mi}|0\rangle \langle 0|Q_{mi} H_1|0\rangle/(T_{mi} - E_0) \ , \tag{28}$$

where $E_0 = \langle 0|H_0|0\rangle$. This is an alternative equivalent expression of the CHF energy.

Now, let us introduce the HF operator H_{00} and the electron–correlation operator λV. The HF operator is defined as

$$H_{00} = \sum_\nu h(\nu) \ ,$$

$$h(\nu) = -\tfrac{1}{2}\Delta_\nu - \sum_A Z_A/r_{A\nu} + g(\nu) \ , \tag{29}$$

where $g(\nu)$ is the sum of the Coulomb and exchange operators. The electron–correlation operator λV is defined as

$$-\lambda V = H_0 - H_{00} = \sum_{\mu>\nu} 1/r_{\mu\nu} - \sum_\nu g(\nu) \ , \tag{30}$$

where the minus sign is attached for the later convenience. The HF operator H_{00} satisfies the following eigenvale equations:

$$\begin{aligned} &H_{00}|0\rangle = E_{00}|0\rangle \ , \qquad E_{00} = \sum_i^{\mathrm{occ}} 2\epsilon_i \ , \\ &H_{00} S^+_{mi}|0\rangle = (E_{00} - \epsilon_i + \epsilon_m) S^+_{mi}|0\rangle \ , \end{aligned} \tag{31}$$

where ϵ_i is the HF orbital energy.

Using the above definitions, the CHF energy (28) can be rewritten in the HF representation. The denominator is related with the HF quantities as

$$\mathbf{U}(\mathbf{T} - E_0\mathbf{1})\mathbf{U}^T = \Delta\boldsymbol{\epsilon} - \lambda\mathbf{V} \ , \tag{32}$$

where $\Delta\boldsymbol{\epsilon}$ is a diagonal matrix composed of the HF orbital energy difference, $\epsilon_m - \epsilon_i$. $\mathbf{V}$ is a *correlation matrix* defined by

$$\mathbf{V} = \langle 0|\mathbf{S}\, V\, \mathbf{S}^+|0\rangle - \langle 0|V|0\rangle \mathbf{1} \pm \langle 0|V(\mathbf{S}^+)^T \mathbf{S}^+|0\rangle \ , \tag{33}$$

where the plus and minus signs correspond again to real and imaginary perturbations, respectively. Using Eqs. (27) and (32), the CHF energy is rewritten as

$$E^{\mathrm{CHF}}_{(2)} = -\langle 0|H_1 \mathbf{S}^+|0\rangle (\Delta\boldsymbol{\epsilon})^{-1} [\mathbf{1} - \lambda\mathbf{V}(\Delta\boldsymbol{\epsilon})^{-1}]^{-1} \langle 0|\mathbf{S}H_1|0\rangle \ . \tag{34}$$

Expanding the term, $[\mathbf{1} - \lambda\mathbf{V}(\Delta\boldsymbol{\epsilon})^{-1}]^{-1}$ with respect to the correlation parameter λ, we obtain

$$E^{\mathrm{CHF}}_{(2)} = E^0_{(2)} + \lambda E^1_{(2)} + \lambda^2 E^2_{(2)} + \cdots \ , \tag{35}$$

where

$$E^0_{(2)} = -\langle 0|H_1 \mathbf{S}^+|0\rangle (\Delta\boldsymbol{\epsilon})^{-1} \langle 0|\mathbf{S}H_1|0\rangle \ , \tag{36a}$$

$$E^1_{(2)} = -\langle 0|H_1 \mathbf{S}^+|0\rangle (\Delta\boldsymbol{\epsilon})^{-1} \mathbf{V} (\Delta\boldsymbol{\epsilon})^{-1} \langle 0|\mathbf{S}H_1|0\rangle \ , \tag{36b}$$

$$E^2_{(2)} = -\langle 0|H_1 \mathbf{S}^+|0\rangle (\Delta\boldsymbol{\epsilon})^{-1} \mathbf{V} (\Delta\boldsymbol{\epsilon})^{-1} \mathbf{V} (\Delta\boldsymbol{\epsilon})^{-1} \langle 0|\mathbf{S}H_1|0\rangle \ ,$$

$$\cdots \ . \tag{36c}$$

This is the *geometric* expansion of the CHF energy in a *matrix* form. Due to the similar argument[20] to the hydrogen atom case, the above matrix geometric expansion is expected to converge to the single formula (34), i.e., to the CHF value.[21] This presumes that the HF approximation is meaningful.[20]

The leading term $E^0_{(2)}$ is identical with the uncoupled HF energy of Dalgarno,[1] and the first-order term $E^1_{(2)}$ is equivalent to that determined by Tuan, Epstein, and Hirschfelder.[4] The explicit formulas of the second- and higher-order correlation terms were not given elsewhere in the literature.

Tuan, Epstein, and Hirschfelder[4] proposed to approximate the CHF energy by the first two terms of the expansion (35), i.e., $E^0_{(2)} + E^1_{(2)}$. However, due to the calculations of Epstein and Johnson,[22] it was not a good approximation to the CHF polarizabilities of neutral atoms. This is also seen from the calculations reported by Caves and Karplus[9] (see Table I). The second- and higher-order correlation terms given by Eqs. (36c), etc., are therefore important for the CHF energy.

The above formulation clarifies the nature of the electron correlation included in the CHF energy. Referring to the correlation matrix defined by Eq. (33), we find that the first two terms represent the so-called first-order correlation energies *intrinsic to the unperturbed excited and ground states*, respectively. The last term of Eq. (33) originates from the second-order (with respect to H_1) doubly excited configurations in the wavefunction (23).[23] Namely, the origin of this term is that the doubly excited configurations induced by the external perturbation H_1 interact with the ground state through the correlation operator λV. Then, this term may be said to represent the correlation effect *induced by the external perturbation*. The diagonal element of this term reduces to the exchange repulsion integral of the appropriate sign,

$$\langle 0|VS^+_{mi} S^+_{mi}|0\rangle = \pm K_{mi} \ . \tag{37}$$

Here, the plus and minus signs correspond to the singlet and triplet excitations defined by Eqs. (21) and (22), respectively. Since there is another ± sign in front of the

TABLE I. Uncoupled, geometric, and coupled Hartree–Fock values of some properties of the Be atom and hydrogen molecule.[a]

Property[b]	Uncoupled $E^0_{(2)}$	$E^0_{(2)} + E^1_{(2)}$	Geometric $E^{\mathrm{GEOM}}_{(2)}$	Coupled $E^{\mathrm{CHF}}_{(2)}$	Expt.
Be α	4.51	5.97	6.67	6.73	⋯
H_2 $\langle\alpha\rangle$	0.566	0.715	0.768	0.775	0.823
$\alpha_\parallel$	0.725	0.896	0.949	0.960	1.03
$\alpha_\perp$	0.487	0.624	0.678	0.682	0.720
$\chi^p_\perp$	0.801	1.09	1.26	1.27	1.29

[a] These values are obtained from the calculations reported by Caves and Karplus (Ref. 9).

[b] α denotes electric dipole polarizability and χ^p high-frequency paramagnetic term in magnetic susceptibility. $\parallel$ and $\perp$ denote the directions parallel and perpendicular to the molecular axis.

TABLE II. Analysis of the correlation expansion of the singly excited CI values and its geometric approximation.[a]

Property[b]	Uncoupled[c] $E^0_{(2)}$	$E^0_{(2)}+E^{1\prime}_{(2)}$	Geometric $E^{GEOM'}_{(2)}$	SE–CI $E^{SECI}_{(2)}$	Expt.
Be α	4.51	6.59	8.37	8.45	···
H_2 $\langle\alpha\rangle$	0.566	0.758	0.855	0.856	0.823
$\alpha_{\parallel}$	0.725	0.970	1.10	1.10	1.03
$\alpha_{\perp}$	0.487	0.651	0.735	0.736	0.720
χ^2_1	0.801	1.04	1.14	1.15	1.29

[a]These values are obtained from the calculations reported by Caves and Karplus (Ref. 9).
[b]The notations are the same as those in Table I.
[c]The zeroth order values are common to both the CHF and SE–CI methods.

last term of Eq. (33), the sign of the final contribution of K_{mi} is plus for real singlet and imaginary triplet perturbations, and minus for real triplet and imaginary singlet perturbations. This shows a critical dependence of the second correlation effect on the nature of the external perturbation.

As shown in the previous report,[10] if we neglect the second perturbation-induced correlation effect, i.e., the last term of Eq. (33), the formulation given above turns out to be the formulation for the SE–CI method. That is, the second-order energy of the SE–CI method can also be expanded in a matrix geometric series having exactly the same form as Eqs. (34)–(36), simply by changing the definition of the correlation matrix as

$$\mathbf{V}_{SECI} = \langle 0|\mathbf{S}V\mathbf{S}^{+}|0\rangle - \langle 0|V|0\rangle \mathbf{1} \ . \tag{38}$$

In the hydrogen atom case studied in Sec. II, the correlation matrix is composed only of the first term. Hence, the formulation for the hydrogen atom is not general enough to extend the results to many electron systems.

The above geometric expansion in a matrix form can be written in an ordinary *scalar* geometric series, if the "ratio" matrix $\mathbf{V}(\Delta\epsilon)^{-1}$ can be approximated as

$$\mathbf{V}(\Delta\epsilon)^{-1} \simeq a\mathbf{1} \ , \tag{39}$$

in the important excitation domains (see the hydrogen atom case), where a is a constant which is smaller than unity.[20] Then, the CHF energy is approximated by

$$E^{CHF}_{(2)} \simeq E^{GEOM}_{(2)} = E^0_{(2)}(1 - E^1_{(2)}/E^0_{(2)})^{-1} \ . \tag{40}$$

This is a geometric approximation of the CHF energy. Tuan[13d] has shown that when we restrict the variation of the CHF first-order orbitals as $i^1_{CHF} = \mu i^1_{UCHF}$, where μ is a variational parameter, the approximation (40) results. Referring to Eqs. (34) and (36a), we understand that the Tuan's restriction is equivalent to the approximation (39), and that μ is given by $\mu = (1-a)^{-1}$. The present formulation clarifies the meaning of the parameter μ. The calculations carried out hitherto for atoms, small molecules, and some π-electron systems have supported this approximation.[13a,13d,13e] Table I gives some numerical results taken from the calculations reported by Caves and Karplus.[9] There, the error of the above approximation is within 2% for every case.

Similarly, replacing $\mathbf{V}$ by $\mathbf{V}_{SECI}$, we can also obtain the geometric approximation of the SE–CI energy as

$$E^{SECI}_{(2)} \simeq E^{GEOM'}_{(2)} = E^0_{(2)}(1 - E^{1\prime}_{(2)}/E^0_{(2)})^{-1} \ , \tag{41}$$

where $E^0_{(2)}$ is the uncoupled HF value and $E^{1\prime}_{(2)}$ is the first-order term calculated from Eq. (36). In Table II, we examined the validity of this approximation. It also holds to a good approximation. The differences between the geometric and SE–CI values are within 1%.

IV. SUMMARY

In the present paper, the double perturbation expansion of the CHF energy was given explicity. It was found *geometric* in a matrix form. The analysis has shown that the electron–correlation effect included in the CHF theory has two origins. One arises from the so-called first-order correlation energies *intrinsic to the unperturbed ground and excited states*, and the other arises from the correlation effect *induced by the external perturbation*. The magnitude of the latter is of the order of the exchange repulsion integral and its sign depends on the nature of the perturbation. For the SE–CI energy, its expansion is also geometric in a matrix form, but the second correlation effect is neglected. In comparison with the diagrammatic analysis given by Caves and Karplus,[9] the present analysis is much simpler and clearer.

The matrix geometric expansion of the CHF and the SE–CI energies reduce to scalar geometric series, if the approximation (39) holds for largely contributing excitations. This is a basis of the geometric approximations of the CHF and SE–CI energies. The numerical results support these approximations to a high degree of accuracy.

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[16]For the SE–CI method, see Eq. (25) of Ref. 10. For the CHF theory, see Eq. (50) of Ref. 10 and note that the **B** matrix does not appear for this system.

[17]For the matrix geometric expansion to converge, every characteristic value in the Jordan canonical form of the "ratio" matrix must be smaller than unity. See, for example, Chap. 10 of D. T. Finkbeiner, *Introduction to Matrices and Linear Transformations* (W. H. Freeman, San Francisco, 1965).

[18]The perturbation H_1 is assumed to commute with the z component of the total spin operator.

[19]Almost all the perturbations we encounter are either real or pure imaginary. When the perturbation H_1 is real, all the coefficients C_{mi} are real, and when H_1 is pure imaginary, C_{mi} are all pure imaginary.

[20]From Eq. (33), the diagonal element of the "ratio" matrix, $\mathbf{V}(\Delta\epsilon)^{-1}$ is written as $(J_{mi} - cK_{mi})/(\epsilon_n - \epsilon_i)$, where $c = 3, -1, 1$, and 1 for real singlet, real triplet, imaginary singlet, and imaginary triplet perturbations, respectively. Therefore, the diagonal element is smaller than unity, so long as the HF approximation is meaningful in that the HF *instability* does not occur. The off-diagonal elements of the ratio matrix are an order of magnitude smaller than the diagonal elements. Then, it is expected that the characteristic values of the ratio matrix are smaller than unity and the matrix geometric expansion (35) converges. (See also Refs. 17 and 21.)

[21]Even if the cases that the expansion does not converge may occur, it causes no problem for the calculation of the CHF energy, because the single formula (34) is valid even in these cases.

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[23]Although there is another independent doubly excited function which is not included in the CHF theory, it does not contribute to the second-order energy (with respect to H_1) based on the HF Ψ_0. See Appendix B of Ref. 10.