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Analytic expression of the second derivatives of electronic energy for full configuration interaction wave functions

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Summary. A new analytic second derivative expression of the electronic energy is derived for full configuration interaction (CI) wave functions. This formula is shown to be free from the derivative terms of both CI and MO coefficients. The second-order relationships between CI and MO coefficients for full CI wave functions are also presented.

Key words: Analytic energy second derivatives — Full CI wave functions

1. Introduction

In *ab initio* molecular orbital (MO) calculations, analytic derivative methods are now widely used in chemical applications [1, 2]. The analytic energy derivatives with respect to nuclear coordinate are indispensable in theoretical chemistry for determining molecular structures and chemical reaction pathways both accurately and economically. From the first derivative of total energy with respect to atomic positions, the equilibrium structure on the potential energy surface may easily be found. We can also look at the magnitudes of the energy second derivatives which give the force constant matrix in the vibrational analysis and/or in the Newton–Raphson search for stationary points such as transition-state structures [3, 4]. It is also important to characterize these stationary geometries by a normal coordinate analysis.

Analytic derivative techniques are well-established for the Hartree–Fock (HF) wave functions [1, 5–7]. The same is not true for second derivatives of correlated wave functions, such as those from configuration interaction (CI) [8, 9], multi-configuration self-consistent-field (MCSCF) [10–15] or many body perturbation (MBPT) wave functions [16], though analytic first derivative methods for these wave functions have been used for the last fifteen years. Inclusion of the effect of electron correlation is very important not only to obtain accurate theoretical results but also to enable us to treat excited states. We therefore wish to develop a practical, feasible way to compute the analytic energy derivatives of correlated wave functions. Although several groups have developed computer programs for analytic second derivative methods for correlated wave functions [10–15], it remains computationally complex to evaluate the derivative of a wave function itself. Note that in order to calculate the derivatives of the electronic energy of the system the derivatives of variational parameters (i.e., MO and CI coefficients) with respect to nuclear coordinates are necessary as well as the derivatives of atomic orbital (AO) integrals [16–18].

When the electronic energy is calculated with an HF or MCSCF wave function, all variational parameters are optimised. Because of this, one can reduce the order of the derivatives of the variational parameters required to evaluate the energy derivatives. The rule of the reduction of derivative order (which originates from Wigner's $2n + 1$ rule for perturbation order [20, 21]) has been well discussed by Pulay [19]. For example, the first derivative of HF or MCSCF energies with respect to nuclear coordinate does not require the derivative of the MO or CI coefficients. Only first order MO and/or CI coefficients are needed to evaluate the second derivative HF or MCSCF energies. The first derivative of an MO coefficient can be calculated by solving the coupled-perturbed Hartree–Fock (CPHF) equation [7, 22, 23] whose practical application in large dimension has been established by Pople et al. [7]. Since MO and CI coefficients are coupled for MCSCF wave functions, a large effort is required to solve the CPMCSCF equation [24].

When the CI wave function is used to evaluate the energy, it should be noted that the MO's used to construct the electron configurations are not optimum. This situation necessitates the explicit evaluation of derivatives of the MO coefficients, though the derivatives of the CI coefficients do obey the $2n + 1$ rule due to the variational condition. For the second derivative of the CI energy, however, one has to evaluate the first derivatives of the CI coefficients from solving the coupled-perturbed configuration interaction (CPCI) equation [25].

In the CI calculation, the large number of electron configurations constructed in the wave function in addition to the number of basis functions results in a computational difficulty. Since the Hamiltonian matrix of CI wave function is generally of large dimension, the ability to do energy derivative calculations would be determined by the limitation of the computational resources.

In light of the increasing need for quantum chemical calculations using accurate wave functions, one needs to aim to do the computation with full CI wave functions where all variational parameters are fully optimized. Once we obtain the full CI wave function, there is no need to optimize the MO's. This situation would provide an easy evaluation of the various kinds of molecular properties as well as the energy derivatives. In this paper we derive some of the relations about the energy derivatives up to second-order and present the reduced formula for the second derivative of full CI energy.

In the following section, the electronic energy expression and its first and second derivatives for CI and MCSCF wave functions, as well as the constraints involved in both MO and CI spaces, are briefly reviewed. In the third section, the derivation of a simplified expression specifically applicable to full CI wave functions will be presented.

2. Theoretical background [25]

2.1. CI wave function and its electronic energy

The electronic CI wave function is generally defined as the linear combination of a set of electronic configurations (CSF) Φ_I,

$$\Psi = \sum_I C_I \Phi_I. \tag{1}$$

Each electron configuration may be described by one or several combinations of Slater determinants, e.g.

$$\Phi_I = \| \varphi_1 \varphi_2 \cdots \|. \tag{2}$$

In the scheme of LCAO-MO (linear combination of atomic orbitals-molecular orbitals), each molecular orbital φ_i is written as

$$\varphi_i = \sum_\mu C^i_\mu \chi_\mu, \tag{3}$$

where C^i_μ is the ith MO coefficient of μth AO χ_μ. CI coefficients $\{C_I\}$ and MO coefficients $\{C^i_\mu\}$ are the variational parameters to determine the electronic wave function and energy. Hereafter, we use capital letters (I, J, K, L) for electronic configurations, small Roman letters (i, j, k, l) for molecular orbitals and small Greek letters (μ, ν, ρ, σ) for atomic orbitals. Defining the CI Hamiltonian matrix

$$\begin{aligned} H_{IJ} &\equiv \langle \Phi_I | H | \Phi_J \rangle \\ &= \sum_{ij} \gamma^{IJ}_{ij} h_{ij} + \sum_{ijkl} \Gamma^{IJ}_{ijkl} (ij \,|\, kl), \end{aligned} \tag{4}$$

the electronic energy is given by

$$E = \sum_{IJ} C_I C_J H_{IJ} \tag{5}$$

in configuration basis, or

$$E = \sum_{ij} \gamma_{ij} h_{ij} + \sum_{ijkl} \Gamma_{ijkl} (ij \,|\, kl) \tag{6}$$

in MO basis, where h_{ij} and $(ij \,|\, kl)$ are one- and two-electron MO integrals, and γ^{IJ}_{ij} and Γ^{IJ}_{ijkl} are the one- and two-electron coupling constants between electronic configurations and molecular orbitals. The one- and two-electron density matrices γ_{ij} and Γ_{ijkl} are connected with the following relations:

$$\gamma_{ij} = \sum_{IJ} C_I C_J \gamma_{ij}^{IJ} \tag{7}$$

and

$$\Gamma_{ijkl} = \sum_{IJ} C_I C_J \Gamma_{ijkl}^{IJ}. \tag{8}$$

Under the condition of the orthonormality of the CI wave function:

$$\sum_I C_I^2 = 1, \tag{9}$$

we have the variational condition,

$$\sum_J C_J (H_{IJ} - \delta_{IJ} E) = 0, \tag{10}$$

to determine the CI wave function and its energy.

Note that the electronic energy is the function of not only the variational parameters but also parameters involving the basis functions χ_μ. Examples of such variables considered in this paper are the nuclear coordinate R, electric field $\mathfrak{F}$, and orbital exponents ζ, i.e.,

$$\chi_\mu = \chi_\mu(R, \mathfrak{F}, \zeta), \tag{11}$$

We refer to such 'real' variables R, $\mathfrak{F}$, and ζ as "a" or "b" in the text.

2.2. *First derivatives of the energy*

The first derivative of a CI energy (5) with respect to a non-variational parameter "a" can be expressed as follows:

$$\frac{\partial E}{\partial a} = \sum_{IJ} C_I C_J \frac{\partial H_{IJ}}{\partial a}. \tag{12}$$

Here, we used condition (10) and the derivative form of Eq. (9). The first derivative of the Hamiltonian matrix H_{IJ} may be divided into two terms

$$\frac{\partial H_{IJ}}{\partial a} = H_{IJ}^a + 2 \sum_{im} U_{im}^a X_{im}^{IJ}, \tag{13}$$

where H_{IJ}^a involves the derivatives of AO integrals and the second term contains the derivative of MO coefficients. Defining the integral derivatives in the MO basis as

$$h_{ij}^a = \sum_{\mu\nu} C_\mu^i C_\nu^j \frac{\partial h_{\mu\nu}}{\partial a} \tag{14}$$

and

$$(ij\,|\,kl)^a = \sum_{\mu\nu\rho\sigma} C^i_\mu C^j_\nu C^k_\rho C^l_\sigma \frac{\partial(\mu\nu\,|\,\rho\sigma)}{\partial a}, \tag{15}$$

the first term of Eq. (13) becomes

$$H^a_{IJ} = \sum_{ij} \gamma^{IJ}_{ij} h^a_{ij} + \sum_{ijkl} \Gamma^{IJ}_{ijkl} (ij\,|\,kl)^a. \tag{16}$$

The matrix U^a, which appeared in the second term of Eq. (13), is related to the derivative of MO coefficients $\partial C^i_\mu / \partial a$ by

$$\sum_j U^a_{ji} C^j_\mu = \frac{\partial C^i_\mu}{\partial a}. \tag{17}$$

The "bare" Lagrangian matrix X^{IJ}_{im} in Eq. (13) may be expressed as follows:

$$X^{IJ}_{im} = \sum_j \gamma^{IJ}_{mj} h_{ij} + 2 \sum_{jkl} \Gamma^{IJ}_{mjkl} (ij\,|\,kl). \tag{18}$$

Using Eqs. (12)–(18), the first derivative of the CI energy may be obtained from

$$\frac{\partial E}{\partial a} = E^a + 2 \sum_{im} U^a_{im} X_{im}, \tag{19}$$

where

$$E^a = \sum_{ij} \gamma_{ij} h^a_{ij} + \sum_{ijkl} \Gamma_{ijkl} (ij\,|\,kl)^a. \tag{20}$$

The Lagrangian matrix X which appears in Eq. (19) is defined as

$$X_{im} = \sum_j \gamma_{mj} h_{ij} + 2 \sum_{jkl} \Gamma_{mjkl} (ij\,|\,kl). \tag{21}$$

2.3. *Second derivatives of the energy*

The second derivative of the CI energy (5) may be obtained by further differentiation of Eq. (12) with respect to the second variable "b". One may obtain the relationship between the derivatives of the CI coefficients and those of Hamiltonian matrix elements by differentiating Eq. (10)

$$\sum_J \frac{\partial C_J}{\partial a} (H_{IJ} - \delta_{IJ} E) + \sum_J C_J \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E}{\partial a} \right) = 0. \tag{22}$$

This relation is so-called CPCI equation. Using Eq. (22), the second derivative of CI energy may be expressed as follows:

$$\frac{\partial^2 E}{\partial a\,\partial b} = \sum_{IJ} C_I C_J \frac{\partial^2 H_{IJ}}{\partial a\,\partial b} - 2 \sum_{IJ} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} (H_{IJ} - \delta_{IJ} E). \tag{23}$$

Using the definition of the second order U^{ab} matrix

$$\sum_j U^{ab}_{ji} C^j_\mu = \frac{\partial^2 C^i_\mu}{\partial a\, \partial b}, \tag{24}$$

the second derivative of Hamiltonian matrix elements may be written as follows:

$$\frac{\partial^2 H_{IJ}}{\partial a\, \partial b} = H^{ab}_{IJ} + 2\sum_{im} (U^{ab}_{im} X^{IJ}_{im} + U^a_{im} X^{IJb}_{im} + U^b_{im} X^{IJa}_{im}) + 2\sum_{im}\sum_{jn} U^a_{im} U^b_{jn} Y^{IJ}_{imjn}, \tag{25}$$

where

$$H^{ab}_{IJ} = \sum_{ij} \gamma^{IJ}_{ij} h^{ab}_{ij} + \sum_{ijkl} \Gamma^{IJ}_{ijkl} (ij\,|\,kl)^{ab}, \tag{26}$$

$$X^{IJa}_{im} = \sum_j \gamma^{IJ}_{mj} h^a_{ij} + 2\sum_{jkl} \Gamma^{IJ}_{mjkl} (ij\,|\,kl)^a, \tag{27}$$

$$Y^{IJ}_{imjn} = \gamma^{IJ}_{mn} h_{ij} + 2\sum_{kl} \{\Gamma^{IJ}_{mnkl} (ij\,|\,kl) + 2\Gamma^{IJ}_{mkn l} (ik\,|\,jl)\}, \tag{28}$$

$$h^{ab}_{ij} = \sum_{\mu\nu} C^i_\mu C^j_\nu \frac{\partial^2 h_{\mu\nu}}{\partial a\, \partial b}, \tag{29}$$

and

$$(ij\,|\,kl)^{ab} = \sum_{\mu\nu\rho\sigma} C^i_\mu C^j_\nu C^k_\rho C^l_\sigma \frac{\partial^2 (\mu\nu\,|\,\rho\sigma)}{\partial a\, \partial b}. \tag{30}$$

The CI second derivative may now be explicitly given by combining Eqs. (22)–(30).

$$\frac{\partial^2 E}{\partial a\, \partial b} = E^{ab} + 2\sum_{im} U^{ab}_{im} X_{im} + 2\sum_{im} (U^a_{im} X^b_{im} + U^b_{im} X^a_{im})$$

$$+ 2\sum_{im}\sum_{jn} U^a_{im} U^b_{jn} Y_{imjn} - 2\sum_{IJ} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} (H_{IJ} - \delta_{IJ} E), \tag{31}$$

where

$$E^{ab} = \sum_{ij} \gamma_{ij} h^{ab}_{ij} + \sum_{ijkl} \Gamma_{ijkl} (ij\,|\,kl)^{ab}, \tag{32}$$

$$X^a_{im} = \sum_j \gamma_{mj} h^a_{ij} + 2\sum_{jkl} \Gamma_{mjkl} (ij\,|\,kl)^a \tag{33}$$

and

$$Y_{imjn} = \gamma_{mn} h_{ij} + 2\sum_{kl} \{\Gamma_{mnkl} (ij\,|\,kl) + 2\Gamma_{mknl} (ik\,|\,jl)\}. \tag{34}$$

2.4. Energy derivatives for MCSCF wave function

Before we discuss the analytic derivative formula of the full CI energy, let us review the derivative expression for MCSCF wave functions. The analytical expression for the MCSCF energy is a good starting point from which to derive the full CI energy derivative, since the full CI wave function may be considered as a special case of the MCSCF wave function. Noticing that both CI and MO coefficients are simultaneously optimized in the MCSCF procedure, the following two variational conditions hold: (i) the secular equation (10) for CI coefficients and (ii) the so-called generalized Brillouin theorem

$$X_{ij} - X_{ji} = 0, \tag{35}$$

which gives the optimum condition for orbital variation. Differentiating the orthonormalization condition for molecular orbitals

$$S_{ij} = \sum_{\mu\nu} C^i_\mu S_{\mu\nu} C^j_\nu = \delta_{ij}, \tag{36}$$

we have the self-relation of the matrix U^a from referring Eq. (17):

$$U^a_{ij} + U^a_{ji} + S^a_{ij} = 0, \tag{37}$$

where the overlap derivative matrix S^a is defined as

$$S^a_{ij} = \sum_{\mu\nu} C^i_\mu C^j_\nu \frac{\partial S_{\mu\nu}}{\partial a}. \tag{38}$$

In the case of an MCSCF wave function, the analytic first derivative of the energy (19) turns out to be

$$\frac{\partial E^{\mathrm{MCSCF}}}{\partial a} = E^a - \sum_{im} S^a_{im} X_{im} \tag{39}$$

from (35) and (37). Equation (39) is free from the derivatives of variational parameters, since the wave function is determined to be optimum in both CI and MO spaces.

The relation for the matrix U^{ab} given by Eq. (24) is similar to Eq. (37), which can be written as

$$U^{ab}_{ij} + U^{ab}_{ji} + \mathscr{S}^{ab}_{ij} = 0, \tag{40}$$

where

$$\mathscr{S}^{ab}_{ij} = S^{ab}_{ij} + \sum_m (U^a_{im} U^b_{jm} + U^a_{jm} U^b_{im} - S^a_{im} S^b_{jm} - S^a_{jm} S^b_{im}). \tag{41}$$

The overlap second derivative matrix, S^{ab}, which appeared in Eq. (41) is defined as

$$S^{ab}_{ij} = \sum_{\mu\nu} C^i_\mu C^j_\nu \frac{\partial S_{\mu\nu}}{\partial a\, \partial b}. \tag{42}$$

Substituting Eqs. (35) and (40) into Eq. (31), a final expression for the MCSCF energy second derivative becomes

$$\frac{\partial^2 E^{\mathrm{MCSCF}}}{\partial a\,\partial b} = E^{ab} - \sum_{ij}\left(S_{ij}^{ab} - 2\sum_{k} S_{ik}^{a} S_{jk}^{b}\right)X_{ij} + 2\sum_{ij}(U_{ij}^{a}X_{ij}^{b} + U_{ij}^{b}X_{ij}^{a}) + 2\sum_{ij}\sum_{kl} U_{ij}^{a}U_{kl}^{b}(Y_{ijkl} - \delta_{jl}X_{ik}) - 2\sum_{IJ}\frac{\partial C_I}{\partial a}\frac{\partial C_J}{\partial b}(H_{IJ} - \delta_{IJ}E). \tag{43}$$

3. Analytical second derivatives of the full CI energy

The first and second derivative expressions (39) and (43) derived for MCSCF energy also hold for the full CI energy, because the generalized Brillouin theorem (35) is automatically satisfied for full CI wave functions. The important aspect is that the MO's used in the calculation of the full CI energy are arbitrary under the orthonormality constraint (36) since all possible electron configurations are taken into account. Thus, the energy obtained by the full CI wave function does not change no matter how the MO's are determined to construct the electron configurations. Although there is no condition to be satisfied for the MO's except orthonormality, there must be some relations between the MO and CI coefficients so that the potential energy surfaces are smoothly connected. With respect to this, it is not necessary to determine the derivatives of the MO's when we evaluate the analytical energy derivatives for the full CI wave function.

Equation (39) for the energy first derivative does not include the derivatives of the MO coefficients as a result of the symmetric property of Lagrangian matrix X. The energy second derivative (43), however, explicitly involves both the first derivatives of the MO and CI coefficients. These derivative terms in Eq. (43) need to be re-expressed so that the analytic energy expression for the full CI energy is free from derivatives of variational parameters.

In the following subsections, we will try to eliminate the derivatives of MO and CI coefficients from the formula of the analytical second energy derivatives for the full CI wave function.

3.1. First derivatives of CI coefficients

Let us clarify how the first derivatives of CI coefficients are obtained. The CPCI equation (22), being formally a simultaneous equation, provides the first derivatives of the CI coefficients as the solution. Since Eq. (22) cannot be solved directly due to a singularity, it must be modified by including the orthonormality condition (9) as already shown elsewhere [24, 25]. By defining the augmented Hamiltonian matrix $\mathscr{H}$

$$\mathscr{H}_{IJ} \equiv H_{IJ} - \delta_{IJ}E + C_I C_J, \tag{44}$$

the CPCI equation may be written in matrix form as

$$\mathscr{H}\cdot\frac{\partial C}{\partial a}=-\frac{\partial\mathscr{H}}{\partial a}\cdot C. \tag{45}$$

Equation (45) is seen to be formally the same as the Eq. (22) since

$$\sum_I C_I\frac{\partial C_I}{\partial a}=0, \tag{46}$$

which is the first derivative of Eq. (9). Multiplying the inverse of the augmented Hamiltonian matrix on the left-hand side of Eq. (45), gives an expression for the first derivative of the CI coefficients without a singularity problem,

$$\frac{\partial C}{\partial a}=-\mathscr{H}^{-1}\cdot\frac{\partial\mathscr{H}}{\partial a}\cdot C. \tag{47}$$

The derivative term of the CI coefficients in the second derivative expression is formally eliminated by substituting Eq. (47) into Eq. (43). The last term of Eq. (43) becomes

$$\begin{aligned}-2\sum_{IJ}\frac{\partial C_I}{\partial a}\frac{\partial C_J}{\partial b}(H_{IJ}-\delta_{IJ}E)&=-2\frac{\partial C^+}{\partial a}\cdot\mathscr{H}\cdot\frac{\partial C}{\partial b}\\&=-2C^+\cdot\frac{\partial\mathscr{H}}{\partial a}\cdot\mathscr{H}^{-1}\cdot\mathscr{H}\cdot\mathscr{H}^{-1}\cdot\frac{\partial\mathscr{H}}{\partial b}\cdot C\\&=-2C^+\cdot\frac{\partial\mathscr{H}}{\partial a}\cdot\mathscr{H}^{-1}\cdot\frac{\partial\mathscr{H}}{\partial b}\cdot C,\end{aligned} \tag{48}$$

where the first derivative of augmented Hamiltonian matrix elements are written as follows:

$$\frac{\partial\mathscr{H}_{IJ}}{\partial a}=H^a_{IJ}+2\sum_{ij}U^a_{ij}X^{IJ}_{ij}-\delta_{IJ}\left(E^a+2\sum_{ij}U^a_{ij}X_{ij}\right). \tag{49}$$

3.2. Elimination of the term depending on derivatives of MO coefficients

The next step is to eliminate the first derivatives of the MO coefficients which should not be necessary for the expression of the second derivatives of the full CI energy. Noting that the first derivatives of the MO coefficients are included in Eq. (49), we collect the terms depending on the U^a and U^b matrices in Eq. (43).

Let us define the augmented derivative Lagrangian matrix, $\mathscr{X}^a$, and the augmented Y matrix, $\mathscr{Y}$, as follows:

$$\mathscr{X}^a_{ij}\equiv X^a_{ij}-2\sum_{IJKL}C_I(H^a_{IJ}-\delta_{IJ}E^a)\mathscr{H}^{-1}_{JK}(X^{KL}_{ij}-\delta_{KL}X_{ij})C_L, \tag{50}$$

$$\mathscr{Y}_{ijkl}\equiv Y_{ijkl}-\delta_{jl}X_{ik}-4\sum_{IJKL}C_I(X^{IJ}_{ij}-\delta_{IJ}X_{ij})\mathscr{H}^{-1}_{JK}(X^{KL}_{kl}-\delta_{KL}X_{kl})C_L. \tag{51}$$

By using Eqs. (48), (50), and (51), Eq. (43) becomes

$$\begin{aligned}\frac{\partial^2 E}{\partial a\,\partial b} &= E^{ab} - \sum_{ij} X_{ij}\left(S^{ab}_{ij} - 2\sum_{k} S^{a}_{ik} S^{b}_{jk}\right)\\ &\quad -2\sum_{IJKL} C_I (H^{a}_{IJ} - \delta_{IJ}E^{a})\mathscr{H}^{-1}_{JK}(H^{b}_{KL} - \delta_{KL}E^{b})C_L\\ &\quad +2\sum_{ij}(U^{a}_{ij}\mathscr{X}^{b}_{ij} + U^{b}_{ij}\mathscr{X}^{a}_{ij}) + 2\sum_{ij}\sum_{kl} U^{a}_{ij}U^{b}_{kl}\mathscr{Y}_{ijkl}. \qquad (52)\end{aligned}$$

Noticing that the energy and the relation (35) do not change under the unitary transformations of MO's in the case of full CI wave functions, the following relations,

$$\mathscr{X}^{a}_{ij} - \mathscr{X}^{a}_{ji} = 0, \qquad (53)$$

and

$$\mathscr{Y}_{ijkl} - \mathscr{Y}_{jikl} - \mathscr{Y}_{ijlk} + \mathscr{Y}_{jilk} = 0, \qquad (54)$$

must hold for full CI wave functions since they are the second-order expressions corresponding to the generalized Brillouin theorem (35). If Eqs. (53) and (54) are satisfied, the U^a and U^b matrices in the third line of Eq. (52) may be reduced to the S^a and S^b matrices. This is similar to the replacing of the first-order U^a matrix by the overlap derivative matrix S^a in the first derivative formulae of MCSCF or full CI energy (Eq. (39)).

Using the results of several full CI calculations, we have checked the identity relations among the values of the matrix elements of $\mathscr{X}^a$ and $\mathscr{Y}$ by numerical calculation. In addition to Eq. (53), all the values which appeared in Eq. (54) were found to be identical, i.e.,

$$\mathscr{Y}_{ijkl} = \mathscr{Y}_{jikl} = \mathscr{Y}_{ijlk} = \mathscr{Y}_{jilk}. \qquad (55)$$

Consequently, Eqs. (53) and (55) may be regarded as the second-order relations for the full CI wave functions corresponding to the first-order equation (35).

3.3. *Analytic expression of energy second derivatives for full CI wave functions*

Since we have found that the relations (53) and (55) hold in the case of full CI wave functions, the final expression for the second derivatives of the full CI energy may be described as

$$\begin{aligned}\frac{\partial^2 E}{\partial a\,\partial b} &= E^{ab} - \sum_{ij} X_{ij}\left(S^{ab}_{ij} - 2\sum_{k} S^{a}_{ik} S^{b}_{jk}\right)\\ &\quad -2\sum_{IJKL} C_I (H^{a}_{IJ} - \delta_{IJ}E^{a})\mathscr{H}^{-1}_{JK}(H^{b}_{KL} - \delta_{KL}E^{b})C_L\\ &\quad -\sum_{ij}(S^{a}_{ij}\mathscr{X}^{b}_{ij} + S^{b}_{ij}\mathscr{X}^{a}_{ij}) + \frac{1}{2}\sum_{ij}\sum_{kl} S^{a}_{ij}S^{b}_{kl}\mathscr{Y}_{ijkl}, \qquad (56)\end{aligned}$$

which does not contain derivatives of either MO or CI coefficients.

Since Eq. (56) involves the inverse of the augmented Hamiltonian matrix, we may re-express Eq. (56) in a practically accessible formula using a technique similar to the Z-vector approach proposed by Handy and Schaefer [26] for the calculation of CI first derivatives. Thus Eq. (56) becomes

$$\begin{aligned}\frac{\partial^2 E}{\partial a\,\partial b} &= E^{ab} - \sum_{ij} X_{ij}\left(S_{ij}^{ab} - 2\sum_{k} S_{ik}^{a} S_{jk}^{b}\right) \\ &\quad - \sum_{ij} (S_{ij}^{a}\mathscr{X}_{ij}^{b} + S_{ij}^{b}\mathscr{X}_{ij}^{a}) + \frac{1}{2}\sum_{ij}\sum_{kl} S_{ij}^{a} S_{kl}^{b}(Y_{ijkl} - \delta_{jl}X_{ik}) \\ &\quad + \sum_{I} [(B_I^a - \mathscr{B}_I^a)(\mathscr{Z}_I^b - Z_I^b) + (B_I^b - \mathscr{B}_I^b)(\mathscr{Z}_I^a - Z_I^a)], \end{aligned} \tag{57}$$

where the elements of the vector $\boldsymbol{B}^a$ and $\mathscr{B}^a$ are defined as follows:

$$B_I^a = \sum_{ij} S_{ij}^a \sum_{J} C_J (X_{ij}^{IJ} - \delta_{IJ} X_{ij}) \tag{58}$$

and

$$\mathscr{B}_I^a = \sum_{J} C_J (H_{IJ}^a - \delta_{IJ} E^a). \tag{59}$$

The elements of the vector $\boldsymbol{Z}^a$ and $\mathscr{Z}^a$ are the solutions of the following linear equations whose right-hand sides are the values of Eqs. (58) and (59) respectively,

$$\mathscr{H} \cdot \boldsymbol{Z}^a = \boldsymbol{B}^a. \tag{60}$$

and

$$\mathscr{H} \cdot \mathscr{Z}^a = \mathscr{B}^a. \tag{61}$$

4. Concluding remarks

The analytic expressions of the energy derivatives for full CI wave functions do not depend on the derivatives of the variational parameters (i.e. the MO and CI coefficients). In addition to the condition $X_{ij} = X_{ji}$, the relations (53) and (54) must be satisfied in order to eliminate the derivatives of CI and MO coefficients in the analytic energy second derivatives. We have tested these relations with numerical calculations, and have found that the relations (53) and (55) indeed hold when the full CI wave functions were used. It is interesting to know that the augmented Y matrix is symmetric to the interchange of MO indices, i.e.

$$\mathscr{Y}_{ijkl} = \mathscr{Y}_{jikl} = \mathscr{Y}_{ijlk} = \mathscr{Y}_{jilk} = \mathscr{Y}_{klij} = \mathscr{Y}_{lkij} = \mathscr{Y}_{klji} = \mathscr{Y}_{lkji}, \tag{62}$$

if and only if full CI wave functions are utilized. This relation is similar to that of two-electron quantities, such as integrals and density matrix. The final formula for the second energy derivatives is given by Eq. (56) or (57).

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