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Correspondence between higher order energy derivative formalisms for restricted Hartree–Fock and correlated wavefunctions

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This paper takes the form of a review including some original contributions. Analytic higher energy derivative expressions for configuration interaction (CI) wavefunctions have been used to obtain the corresponding energy derivative formulae for multi-configuration self-consistent-field (MCSCF), general open-shell and closed-shell restricted Hartree-Fock (RHF) wavefunctions by explicitly imposing the variational and orthonormality conditions on the molecular orbital (MO) space. The general structure of the reduction procedure used here is thus

CI → MCSCF → General RHF → Closed-shell HF.

The equations expressing the correspondence among correlated and RHF wavefunctions have been presented to interrelate various conditions and definitions involved in the energy derivative expressions. Practical formulae for the energy derivatives of the above mentioned wavefunctions up to fourth order are explicitly given.

Key words: Analytic energy derivatives — MCSCF and RHF wavefunctions

1. Introduction

The energy derivative expressions for a configuration interaction (CI) wavefunction shown in the preceding paper [1] are general formulae in the sense that there are no restrictions involved therein except the variational condition on the CI space. We may take advantage of this fact to obtain expressions for energy derivatives in the general framework of self-consistent-field (SCF) molecular orbital (MO) theory. A fruitful avenue to reliable wavefunctions is the multi-configuration self-consistent-field (MCSCF) method [2, 3] in which the CI and MO coefficients are simultaneously optimized by the variational principle. Recent advances in the quadratically convergent MCSCF and complete active space SCF (CASSCF) methods have made it possible to obtain MCSCF wavefunctions in a more efficient manner [4–24].

The format for this paper is primarily that of a review, but also presenting some new insights concerning the structure of analytic energy derivative expressions. Here we present a formalism for MCSCF energy derivatives by taking into account the correspondence with the more general CI formalism. We also show that derivative expressions for the MCSCF energy may be easily simplified to obtain energy derivatives for the restricted Hartree–Fock (RHF) wavefunction.

In the following section the derivative results for the CI wavefunction in the previous paper [1] are briefly reviewed. The electronic energy expression and the variational condition for the CI wavefunction are first described. Second, several variables and matrices involved in the higher energy derivative formulae are explicitly defined. Then the energy derivative expressions for the CI wavefunction from first to fourth order are given in a manner symmetric with respect to the differential variables. Also shown are unambiguous expressions for the first, second and third derivative CI Hamiltonian matrices.

In Sect. 3 the derivative expressions for the orthonormality condition on the molecular orbitals within the SCF formalism are carefully examined. The augmented S matrices, $\mathcal{S}$, are introduced to explicitly show linear relationships among elements of the U matrices, which are related to the derivatives of the MO coefficients.

The variational condition on the MO space and the derivative forms of the orthonormality condition are explicitly included to yield energy derivative expressions for the MCSCF wavefunction from the more general CI formalism in Sect. 4. It will be demonstrated that the introduction of these two (variational and orthonormality) conditions greatly simplifies the derivative formulae for the MCSCF wavefunction and substantially reduces the amount of work involved in the practical applications.

Starting from equations suitable to the MCSCF formalism, energy derivative expressions for the general open-shell SCF wavefunction will be pursued in Sect. 5. For one configuration SCF wavefunctions the terms involve the CI coefficients and their derivatives may of course be dropped. Furthermore the diagonality of the one-electron and two-electron reduced density matrices significantly simplifies the entire formalism involved in the higher energy derivatives for general open-shell wavefunctions.

In Sect. 6 energy derivative expressions for the simplest and most frequently used case, the closed-shell SCF wavefunction, will be derived to show the effectiveness of the correspondence manipulation. There the one- and two-electron density matrices have elements with constant values, and consequently the energy derivative formulae become even simpler. The reformulation of energy derivative expressions from both the MCSCF and the open-shell SCF formalisms will be presented.

2. Review of energy derivatives based on the CI formalism

Let us briefly review the CI energy derivative expressions before we discuss the correspondence among MCSCF, RHF and CI formalisms.

2.1. Wavefunction, electronic energy, and the variational condition [25]

The CI (or MCSCF wavefunction), Ψ, is constructed as a linear combination of electronic configurations Φ_I

$$|\Psi\rangle = \sum_I C_I |\Phi_I\rangle. \tag{2.1}$$

The electronic energy of the system may be expressed in terms of a configuration basis, or molecular orbital (MO) basis, or atomic orbital (AO) basis,

$$E = \sum_{IJ} C_I C_J H_{IJ} \tag{2.2}$$

$$= \sum_{ij} \gamma_{ij} h_{ij} + \sum_{ijkl} \Gamma_{ijkl}(ij|kl) \tag{2.3}$$

$$= \sum_{\mu\nu} \gamma_{\mu\nu} h_{\mu\nu} + \sum_{\mu\nu\rho\sigma} \Gamma_{\mu\nu\rho\sigma}(\mu\nu|\rho\sigma). \tag{2.4}$$

We assume that the indices using capital letters I, J denote the electronic configurations, the roman letters i, j, k, l the MO's, and the greek letters the AO's. The Hamiltonian matrix elements H_{IJ} may be defined using the coupling constants, γ_{ij}^{IJ} and Γ_{ijkl}^{IJ}, and MO integrals, h_{ij} and $(ij|kl)$,

$$H_{IJ} = \langle\Phi_I|H|\Phi_J\rangle = \sum_{ij} \gamma_{ij}^{IJ} h_{ij} + \sum_{ijkl} \Gamma_{ijkl}^{IJ}(ij|kl). \tag{2.5}$$

The relations between integrals and density matrices, γ and Γ, in the AO and MO basis are as follows,

$$h_{ij} = \sum_{\mu\nu} C_\mu^i C_\nu^j h_{\mu\nu}, \tag{2.6}$$

$$(ij|kl) = \sum_{\mu\nu\rho\sigma} C_\mu^i C_\nu^j C_\rho^k C_\sigma^l (\mu\nu|\rho\sigma), \tag{2.7}$$

$$\gamma_{\mu\nu} = \sum_{ij} C_\mu^i C_\nu^j \gamma_{ij}, \tag{2.8}$$

$$\Gamma_{\mu\nu\rho\sigma} = \sum_{ijkl} C_\mu^i C_\nu^j C_\rho^k C_\sigma^l \Gamma_{ijkl}, \tag{2.9}$$

where the one- and two-electron (reduced) density matrix elements [26] are defined by

$$\gamma_{ij} = \sum_{IJ} C_I C_J \gamma_{ij}^{IJ} \tag{2.10}$$

and

$$\Gamma_{ijkl} = \sum_{IJ} C_I C_J \Gamma_{ijkl}^{IJ}. \tag{2.11}$$

The variational condition on the CI space is given by

$$\sum_J (H_{IJ} - \delta_{IJ} E) C_J = 0. \tag{2.12}$$

2.2. The Lagrangian, Y and Z matrices and their derivatives

The Lagrangian matrix X [2, 27] and the derivative Lagrangian matrices are defined as

$$X_{im}=\sum_j \gamma_{mj}h_{ij}+2\sum_{jkl}\Gamma_{mjkl}(ij|kl), \tag{2.13}$$

$$X^a_{im}=\sum_j \gamma_{mj}h^a_{ij}+2\sum_{jkl}\Gamma_{mjkl}(ij|kl)^a, \tag{2.14}$$

$$X^{ab}_{im}=\sum_j \gamma_{mj}h^{ab}_{ij}+2\sum_{jkl}\Gamma_{mjkl}(ij|kl)^{ab}, \tag{2.15}$$

$$X^{abc}_{im}=\sum_j \gamma_{mj}h^{abc}_{ij}+2\sum_{jkl}\Gamma_{mjkl}(ij|kl)^{abc}. \tag{2.16}$$

The matrix Y [28] which relates to the second order variation of the CI energy with respect to the MO's and the derivative Y matrices are expressed as follows

$$Y_{imjn}=\gamma_{mn}h_{ij}+2\sum_{kl}\{\Gamma_{mnkl}(ij|kl)+2\Gamma_{mknl}(ik|jl)\}, \tag{2.17}$$

$$Y^a_{imjn}=\gamma_{mn}h^a_{ij}+2\sum_{kl}\{\Gamma_{mnkl}(ij|kl)^a+2\Gamma_{mknl}(ik|jl)^a\}, \tag{2.18}$$

$$Y^{ab}_{imjn}=\gamma_{mn}h^{ab}_{ij}+2\sum_{kl}\{\Gamma_{mnkl}(ij|kl)^{ab}+2\Gamma_{mknl}(ik|jl)^{ab}\}. \tag{2.19}$$

Furthermore, it is convenient to define the matrix Z and its derivatives for later use,

$$Z_{imjnko}=4\sum_l\{\Gamma_{mnol}(ij|kl)+\Gamma_{monl}(ik|jl)+\Gamma_{mlno}(il|jk)\}, \tag{2.20}$$

$$Z^a_{imjnko}=4\sum_l\{\Gamma_{mnol}(ij|kl)^a+\Gamma_{monl}(ik|jl)^a+\Gamma_{mlno}(il|jk)^a\}. \tag{2.21}$$

The transformed one- and two-electron derivative integrals in the MO basis appearing in these equations are given by

$$h^a_{ij}=\sum_{\mu\nu} C^i_\mu C^j_\nu \frac{\partial h_{\mu\nu}}{\partial a}, \tag{2.22}$$

$$h^{ab}_{ij}=\sum_{\mu\nu} C^i_\mu C^j_\nu \frac{\partial^2 h_{\mu\nu}}{\partial a\,\partial b}, \tag{2.23}$$

$$h^{abc}_{ij}=\sum_{\mu\nu} C^i_\mu C^j_\nu \frac{\partial^3 h_{\mu\nu}}{\partial a\,\partial b\,\partial c}, \tag{2.24}$$

$$h^{abcd}_{ij}=\sum_{\mu\nu} C^i_\mu C^j_\nu \frac{\partial^4 h_{\mu\nu}}{\partial a\,\partial b\,\partial c\,\partial d}, \tag{2.25}$$

$$(ij|kl)^a=\sum_{\mu\nu\rho\sigma} C^i_\mu C^j_\nu C^k_\rho C^l_\sigma \frac{\partial(\mu\nu|\rho\sigma)}{\partial a}, \tag{2.26}$$

$$(ij|kl)^{ab}=\sum_{\mu\nu\rho\sigma} C^i_\mu C^j_\nu C^k_\rho C^l_\sigma \frac{\partial^2(\mu\nu|\rho\sigma)}{\partial a\,\partial b}, \tag{2.27}$$

$$(ij|kl)^{abc}=\sum_{\mu\nu\rho\sigma} C^i_\mu C^j_\nu C^k_\rho C^l_\sigma \frac{\partial^3(\mu\nu|\rho\sigma)}{\partial a\,\partial b\,\partial c}, \tag{2.28}$$

$$(ij|kl)^{abcd}=\sum_{\mu\nu\rho\sigma} C^i_\mu C^j_\nu C^k_\rho C^l_\sigma \frac{\partial^4(\mu\nu|\rho\sigma)}{\partial a\,\partial b\,\partial c\,\partial d}. \tag{2.29}$$

2.3. *The U matrices*

Finally, we introduce the U matrices [29] (which express the changes in the molecular orbitals with respect to nuclear displacements) for future use. They are related to the derivatives of the MO coefficients as

$$\frac{\partial C_{\mu}^{i}}{\partial a}=\sum_{m} U_{mi}^{a} C_{\mu}^{m}, \tag{2.30}$$

$$\frac{\partial^2 C_{\mu}^{i}}{\partial a\, \partial b}=\sum_{m} U_{mi}^{ab} C_{\mu}^{m}, \tag{2.31}$$

$$\frac{\partial^3 C_{\mu}^{i}}{\partial a\, \partial b\, \partial c}=\sum_{m} U_{mi}^{abc} C_{\mu}^{m}, \tag{2.32}$$

$$\frac{\partial^4 C_{\mu}^{i}}{\partial a\, \partial b\, \partial c\, \partial d}=\sum_{m} U_{mi}^{abcd} C_{\mu}^{m}. \tag{2.33}$$

2.4. *First derivative*

The first derivative of CI energy [27, 28, 30, 31] is given by

$$\frac{\partial E}{\partial a}=\sum_{IJ} C_I C_J \frac{\partial H_{IJ}}{\partial a} \tag{2.34}$$

$$=\sum_{ij} \gamma_{ij} h_{ij}^{a}+\sum_{ijkl} \Gamma_{ijkl}(ij\,|\,kl)^{a}+2\sum_{im} U_{im}^{a} X_{im}. \tag{2.35}$$

2.5. *Second derivative*

The second derivative [32, 33] includes not only the derivatives of molecular orbitals but also the derivative of CI coefficients as follows.

$$\frac{\partial^2 E}{\partial a\, \partial b}=\sum_{IJ} C_I C_J \frac{\partial^2 H_{IJ}}{\partial a\, \partial b}-2\sum_{IJ} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b}(H_{IJ}-\delta_{IJ} E) \tag{2.36}$$

where the first term in Eq. (2.36) may be expressed in the MO basis as

$$\sum_{IJ} C_I C_J \frac{\partial^2 H_{IJ}}{\partial a\, \partial b}=\sum_{ij} \gamma_{ij} h_{ij}^{ab}+\sum_{ijkl} \Gamma_{ijkl}(ij\,|\,kl)^{ab}+2\sum_{im} U_{im}^{ab} X_{im}$$
$$+2\sum_{im}(U_{im}^{a} X_{im}^{b}+U_{im}^{b} X_{im}^{a})+2\sum_{im}\sum_{jn} U_{im}^{a} U_{jn}^{b} Y_{imjn}. \tag{2.37}$$

2.6. *Third derivative*

The third derivative of the CI energy may be written in the configuration description as

$$\frac{\partial^3 E}{\partial a\, \partial b\, \partial c}=\sum_{IJ} C_I C_J \frac{\partial^3 H_{IJ}}{\partial a\, \partial b\, \partial c}$$
$$+2\sum_{I} C_I \sum_{J}\left(\frac{\partial C_J}{\partial a} \frac{\partial^2 H_{IJ}}{\partial b\, \partial c}+\frac{\partial C_J}{\partial b} \frac{\partial^2 H_{IJ}}{\partial c\, \partial a}+\frac{\partial C_J}{\partial c} \frac{\partial^2 H_{IJ}}{\partial a\, \partial b}\right)$$

$$+2\sum_{IJ}\left[\frac{\partial C_I}{\partial a}\frac{\partial C_J}{\partial b}\left(\frac{\partial H_{IJ}}{\partial c}-\delta_{IJ}\frac{\partial E}{\partial c}\right)+\frac{\partial C_I}{\partial b}\frac{\partial C_J}{\partial c}\left(\frac{\partial H_{IJ}}{\partial a}-\delta_{IJ}\frac{\partial E}{\partial a}\right)+\frac{\partial C_I}{\partial c}\frac{\partial C_J}{\partial a}\left(\frac{\partial H_{IJ}}{\partial b}-\delta_{IJ}\frac{\partial E}{\partial b}\right)\right] \tag{2.38}$$

where the first term may be explicitly given as

$$\begin{aligned}\sum_{IJ} C_I C_J \frac{\partial^3 H_{IJ}}{\partial a\,\partial b\,\partial c} &= \sum_{ij} \gamma_{ij} h_{ij}^{abc} + \sum_{ijkl} \Gamma_{ijkl}(ij|kl)^{abc} + 2\sum_{im} U_{im}^{abc} X_{im} \\ &\quad + 2\sum_{im} (U_{im}^{ab} X_{im}^{[c]} + U_{im}^{bc} X_{im}^{[a]} + U_{im}^{ca} X_{im}^{[b]}) \\ &\quad + 2\sum_{im} (U_{im}^{a} X_{im}^{bc} + U_{im}^{b} X_{im}^{ca} + U_{im}^{c} X_{im}^{ab}) \\ &\quad + 2\sum_{im}\sum_{jn} (U_{im}^{a} U_{jn}^{b} Y_{imjn}^{c} + U_{im}^{b} U_{jn}^{c} Y_{imjn}^{a} + U_{im}^{c} U_{jn}^{a} Y_{imjn}^{b}) \\ &\quad + 2\sum_{im}\sum_{jn}\sum_{ko} U_{im}^{a} U_{jn}^{b} U_{ko}^{c} Z_{imjnko}. \end{aligned} \tag{2.39}$$

Here, we defined the modified Lagrangian first derivative matrices $X^{[a]}$ by combining the Lagrangian derivative (2.14) and Y matrix (2.17) as

$$X_{im}^{[a]} = X_{im}^{a} + \sum_{jn} U_{jn}^{a} Y_{imjn}. \tag{2.40}$$

The last term including the matrix Z in Eq. (2.39) may be expressed as

$$\begin{aligned} &2\sum_{im}\sum_{jn}\sum_{ko} U_{im}^{a} U_{jn}^{b} U_{ko}^{c} Z_{imjnko} \\ &= 8\sum_{im}\sum_{jn}\sum_{ko} (U_{im}^{a} U_{jn}^{b} U_{ko}^{c} + U_{im}^{b} U_{jn}^{c} U_{ko}^{a} + U_{im}^{c} U_{jn}^{a} U_{ko}^{b}) \sum_{l} \Gamma_{mnol}(ij|kl). \end{aligned} \tag{2.41}$$

2.7. Fourth derivative

The fourth energy derivative for the CI wavefunction is given by

$$\begin{aligned} \frac{\partial^4 E}{\partial a\,\partial b\,\partial c\,\partial d} &= \sum_{IJ} C_I C_J \frac{\partial^4 H_{IJ}}{\partial a\,\partial b\,\partial c\,\partial d} + 2\sum_I C_I \sum_J \left(\frac{\partial C_J}{\partial a}\frac{\partial^3 H_{IJ}}{\partial b\,\partial c\,\partial d} + \frac{\partial C_J}{\partial b}\frac{\partial^3 H_{IJ}}{\partial c\,\partial d\,\partial a} + \frac{\partial C_J}{\partial c}\frac{\partial^3 H_{IJ}}{\partial d\,\partial a\,\partial b} + \frac{\partial C_J}{\partial d}\frac{\partial^3 H_{IJ}}{\partial a\,\partial b\,\partial c}\right) \\ &\quad + 2\sum_{IJ}\left[\frac{\partial C_I}{\partial a}\frac{\partial C_J}{\partial b}\left(\frac{\partial^2 H_{IJ}}{\partial c\,\partial d} - \delta_{IJ}\frac{\partial^2 E}{\partial c\,\partial d}\right) + \frac{\partial C_I}{\partial a}\frac{\partial C_J}{\partial c}\left(\frac{\partial^2 H_{IJ}}{\partial b\,\partial d} - \delta_{IJ}\frac{\partial^2 E}{\partial b\,\partial d}\right)\right. \\ &\quad + \frac{\partial C_I}{\partial a}\frac{\partial C_J}{\partial d}\left(\frac{\partial^2 H_{IJ}}{\partial b\,\partial c} - \delta_{IJ}\frac{\partial^2 E}{\partial b\,\partial c}\right) + \frac{\partial C_I}{\partial b}\frac{\partial C_J}{\partial c}\left(\frac{\partial^2 H_{IJ}}{\partial a\,\partial d} - \delta_{IJ}\frac{\partial^2 E}{\partial a\,\partial d}\right) \\ &\quad \left. + \frac{\partial C_I}{\partial b}\frac{\partial C_J}{\partial d}\left(\frac{\partial^2 H_{IJ}}{\partial a\,\partial c} - \delta_{IJ}\frac{\partial^2 E}{\partial a\,\partial c}\right) + \frac{\partial C_I}{\partial c}\frac{\partial C_J}{\partial d}\left(\frac{\partial^2 H_{IJ}}{\partial a\,\partial b} - \delta_{IJ}\frac{\partial^2 E}{\partial a\,\partial b}\right)\right] \end{aligned}$$

$$-2\sum_{IJ}\left(\frac{\partial^2 C_I}{\partial a\,\partial b}\frac{\partial^2 C_J}{\partial c\,\partial d}+\frac{\partial^2 C_I}{\partial a\,\partial c}\frac{\partial^2 C_J}{\partial b\,\partial d}+\frac{\partial^2 C_I}{\partial a\,\partial d}\frac{\partial^2 C_J}{\partial b\,\partial c}\right)(H_{IJ}-\delta_{IJ}E). \quad (2.42)$$

The first term including the fourth derivative of Hamiltonian matrix elements may be expressed as follows

$$\begin{aligned}
&\sum_{IJ} C_I C_J \frac{\partial^4 H_{IJ}}{\partial a\,\partial b\,\partial c\,\partial d}\\
&\quad=\sum_{ij}\gamma_{ij}h_{ij}^{abcd}+\sum_{ijkl}\Gamma_{ijkl}(ij\,|\,kl)^{abcd}+2\sum_{im}U_{im}^{abcd}X_{im}\\
&\quad+2\sum_{im}(U_{im}^{abc}X_{im}^{[d]}+U_{im}^{bcd}X_{im}^{[a]}+U_{im}^{cda}X_{im}^{[b]}+U_{im}^{dab}X_{im}^{[c]})\\
&\quad+2\sum_{im}(U_{im}^{ab}X_{im}^{[cd]}+U_{im}^{ac}X_{im}^{[bd]}+U_{im}^{ad}X_{im}^{[bc]}+U_{im}^{bc}X_{im}^{[ad]}\\
&\qquad\quad+U_{im}^{bd}X_{im}^{[ac]}+U_{im}^{cd}X_{im}^{[ab]})\\
&\quad+2\sum_{im}\sum_{jn}(U_{im}^{ab}U_{jn}^{cd}+U_{im}^{ac}U_{jn}^{bd}+U_{im}^{ad}U_{jn}^{bc})Y_{imjn}\\
&\quad+2\sum_{im}(U_{im}^{a}X_{im}^{bcd}+U_{im}^{b}X_{im}^{cda}+U_{im}^{c}X_{im}^{dab}+U_{im}^{d}X_{im}^{abc})\\
&\quad+2\sum_{im}\sum_{jn}(U_{im}^{a}U_{jn}^{b}Y_{imjn}^{cd}+U_{im}^{a}U_{jn}^{c}Y_{imjn}^{bd}+U_{im}^{a}U_{jn}^{d}Y_{imjn}^{bc}\\
&\qquad\quad+U_{im}^{b}U_{jn}^{c}Y_{imjn}^{ad}+U_{im}^{b}U_{jn}^{d}Y_{imjn}^{ac}+U_{im}^{c}U_{jn}^{d}Y_{imjn}^{ab})\\
&\quad+2\sum_{im}\sum_{jn}\sum_{ko}(U_{im}^{a}U_{jn}^{b}U_{ko}^{c}Z_{imjnko}^{d}+U_{im}^{b}U_{jn}^{c}U_{ko}^{d}Z_{imjnko}^{a}\\
&\qquad\quad+U_{im}^{c}U_{jn}^{d}U_{ko}^{a}Z_{imjnko}^{b}+U_{im}^{d}U_{jn}^{a}U_{ko}^{b}Z_{imjnko}^{c})\\
&\quad+8\sum_{im}\sum_{jn}\sum_{ko}\sum_{lp}(U_{im}^{a}U_{jn}^{b}U_{ko}^{c}U_{lp}^{d}+U_{im}^{a}U_{jn}^{c}U_{ko}^{b}U_{lp}^{d}\\
&\qquad\quad+U_{im}^{a}U_{jn}^{d}U_{ko}^{b}U_{lp}^{c})\Gamma_{mnop}(ij\,|\,kl)
\end{aligned} \quad (2.43)$$

where the modified Lagrangian second derivative matrices are defined by

$$X_{im}^{[ab]}=X_{im}^{ab}+\sum_{jn}(U_{jn}^{a}Y_{imjn}^{b}+U_{jn}^{b}Y_{imjn}^{a})+\sum_{jn}\sum_{ko}U_{jn}^{a}U_{ko}^{b}Z_{imjnko}. \quad (2.44)$$

2.8. The derivatives of the CI *Hamiltonian matrix elements*

In this subsection the derivatives of the CI Hamiltonian matrix appearing in preceding subsections are explicitly defined. We first introduce the "skeleton" derivative Hamiltonian matrices

$$H_{IJ}^{a}=\sum_{ij}\gamma_{ij}^{IJ}h_{ij}^{a}+\sum_{ijkl}\Gamma_{ijkl}^{IJ}(ij\,|\,kl)^{a} \quad (2.45)$$

$$H_{IJ}^{ab}=\sum_{ij}\gamma_{ij}^{IJ}h_{ij}^{ab}+\sum_{ijkl}\Gamma_{ijkl}^{IJ}(ij\,|\,kl)^{ab} \quad (2.46)$$

$$H_{IJ}^{abc}=\sum_{ij}\gamma_{ij}^{IJ}h_{ij}^{abc}+\sum_{ijkl}\Gamma_{ijkl}^{IJ}(ij\,|\,kl)^{abc} \quad (2.47)$$

and the "bare" Lagrangian matrix [28], X^{IJ}, and its derivatives,

$$X^{IJ}_{im} = \sum_{j} \gamma^{IJ}_{mj} h_{ij} + 2 \sum_{jkl} \Gamma^{IJ}_{mjkl}(ij|kl) \tag{2.48}$$

$$X^{IJ^a}_{im} = \sum_{j} \gamma^{IJ}_{mj} h^a_{ij} + 2 \sum_{jkl} \Gamma^{IJ}_{mjkl}(ij|kl)^a \tag{2.49}$$

$$X^{IJ^{ab}}_{im} = \sum_{j} \gamma^{IJ}_{mj} h^{ab}_{ij} + 2 \sum_{jkl} \Gamma^{IJ}_{mjkl}(ij|kl)^{ab}. \tag{2.50}$$

Similarly, we also define the "bare" Y matrix and its derivatives as

$$Y^{IJ}_{imjn} = \gamma^{IJ}_{mn} h_{ij} + 2 \sum_{kl} \{\Gamma^{IJ}_{mnkl}(ij|kl) + 2\Gamma^{IJ}_{mknl}(ik|jl)\} \tag{2.51}$$

$$Y^{IJ^a}_{imjn} = \gamma^{IJ}_{mn} h^a_{ij} + 2 \sum_{kl} \{\Gamma^{IJ}_{mnkl}(ij|kl)^a + 2\Gamma^{IJ}_{mknl}(ik|jl)^a\}. \tag{2.52}$$

There are the following relationships between the "bare" and "parent" quantities for the Lagrangian and Y matrices;

$$X_{im} = \sum_{IJ} C_I C_J X^{IJ}_{im}, \tag{2.53}$$

$$X^a_{im} = \sum_{IJ} C_I C_J X^{IJ^a}_{im}, \tag{2.54}$$

$$X^{ab}_{im} = \sum_{IJ} C_I C_J X^{IJ^{ab}}_{im}, \tag{2.55}$$

$$Y_{imjn} = \sum_{IJ} C_I C_J Y^{IJ}_{imjn}, \tag{2.56}$$

$$Y^a_{imjn} = \sum_{IJ} C_I C_J Y^{IJ^a}_{imjn}. \tag{2.57}$$

Using these definitions, the derivatives of the Hamiltonian matrix elements may be explicitly expressed as follows

$$\frac{\partial H_{IJ}}{\partial a} = H^a_{IJ} + 2 \sum_{im} U^a_{im} X^{IJ}_{im} \tag{2.58}$$

$$\frac{\partial^2 H_{IJ}}{\partial a\, \partial b} = H^{ab}_{IJ} + 2 \sum_{im} (U^{ab}_{im} X^{IJ}_{im} + U^a_{im} X^{IJ^b}_{im} + U^b_{im} X^{IJ^a}_{im}) + 2 \sum_{im} \sum_{jn} U^a_{im} U^b_{jn} Y^{IJ}_{imjn} \tag{2.59}$$

$$\begin{aligned}\frac{\partial^3 H_{IJ}}{\partial a\, \partial b\, \partial c} = H^{abc}_{IJ} + 2 \sum_{im} (& U^{abc}_{im} X^{IJ}_{im} + U^{ab}_{im} X^{IJ^c}_{im} + U^{bc}_{im} X^{IJ^a}_{im} + U^{ca}_{im} X^{IJ^b}_{im} \\ & + U^a_{im} X^{IJ^{bc}}_{im} + U^b_{im} X^{IJ^{ca}}_{im} + U^c_{im} X^{IJ^{ab}}_{im}) \\ + 2 \sum_{im} \sum_{jn} \{ & (U^{ab}_{im} U^c_{jn} + U^{bc}_{im} U^a_{jn} + U^{ca}_{im} U^b_{jn}) Y^{IJ}_{imjn} \\ & + U^a_{im} U^b_{jn} Y^{IJ^c}_{imjn} + U^b_{im} U^c_{jn} Y^{IJ^a}_{imjn} + U^c_{im} U^a_{jn} Y^{IJ^b}_{imjn}\}\end{aligned}$$

$$+8\sum_{im}\sum_{jn}\sum_{ko}(U^a_{im}U^b_{jn}U^c_{ko}+U^b_{im}U^c_{jn}U^a_{ko}$$
$$+U^c_{im}U^a_{jn}U^b_{ko})\sum_l \Gamma^{IJ}_{mnol}(ij|kl). \qquad (2.60)$$

3. Derivatives of the molecular orbital coefficients

Let us describe the properties of the U matrices defined in Eqs. (2.30)-(2.33) before making a reduction in the formulae of CI energy derivatives to the special case of SCF wavefunctions. Since the U matrices are related to the derivatives of the MO coefficients, they are closely connected to the condition from which the molecular orbitals are determined in the SCF procedure. The equations obtained from the differentiation of the SCF variational condition are called the coupled-perturbed Hartree–Fock (CPHF) equations [29, 30, 34] and solving them produces the derivatives of the MO coefficients.

While one may use $\partial C^i_\mu/\partial a$ instead of the U^a matrix to derive the energy derivative expression [46], formulae based on the latter are much simpler to derive and it is easy to remove the redundancy due to the orthonormality condition of the MO's, i.e.,

$$S_{ij}=\sum_{\mu\nu} C^i_\mu C^j_\nu S_{\mu\nu}=\delta_{ij} \qquad (3.1)$$

where $S_{\mu\nu}$ is an AO overlap integral.

A series of differentiations of Eq. (3.1) gives the self-dependency of the U matrices [29, 30, 34] and provides the following very useful expressions:

$$U^a_{ij}+U^a_{ji}+S^a_{ij}=0, \qquad (3.2)$$

$$U^{ab}_{ij}+U^{ab}_{ji}+\mathcal{S}^{ab}_{ij}=0, \qquad (3.3)$$

$$U^{abc}_{ij}+U^{abc}_{ji}+\mathcal{S}^{abc}_{ij}=0, \qquad (3.4)$$

$$U^{abcd}_{ij}+U^{abcd}_{ji}+\mathcal{S}^{abcd}_{ij}=0, \qquad (3.5)$$

where the augmented S matrices, $\mathcal{S}$, are defined by

$$\mathcal{S}^{ab}_{ij}=S^{ab}_{ij}+\sum_m(U^a_{im}U^b_{jm}+U^a_{jm}U^b_{im}-S^a_{im}S^b_{jm}-S^a_{jm}S^b_{im}), \qquad (3.6)$$

$$\mathcal{S}^{abc}_{ij}=S^{abc}_{ij}+\sum_m(U^{ab}_{im}U^c_{jm}+U^{ab}_{jm}U^c_{im}+U^{ca}_{im}U^b_{jm}+U^{ca}_{jm}U^b_{im}$$
$$+U^{bc}_{im}U^a_{jm}+U^{bc}_{jm}U^a_{im})$$
$$-\sum_m(S^{ab}_{im}S^c_{jm}+S^{ab}_{jm}S^c_{im}+S^{ca}_{im}S^b_{jm}+S^{ca}_{jm}S^b_{im}+S^{bc}_{im}S^a_{jm}+S^{bc}_{jm}S^a_{im})$$
$$+\sum_{mn}(S^a_{im}S^b_{jn}S^c_{mn}+S^a_{jm}S^b_{in}S^c_{mn}+S^b_{im}S^c_{jn}S^a_{mn}+S^b_{jm}S^c_{in}S^a_{mn}$$
$$+S^c_{im}S^a_{jn}S^b_{mn}+S^c_{jm}S^a_{in}S^b_{mn}), \qquad (3.7)$$

$$\mathcal{S}^{abcd}_{ij}=S^{abcd}_{ij}$$
$$+\sum_m(U^{abc}_{im}U^d_{jm}+U^{abc}_{jm}U^d_{im}+U^{abd}_{im}U^c_{jm}+U^{abd}_{jm}U^c_{im}+U^{acd}_{im}U^b_{jm}$$

$$
\begin{aligned}
&+U^{acd}_{jm}U^{b}_{im}+U^{bcd}_{im}U^{a}_{jm}+U^{bcd}_{jm}U^{a}_{im})\\
&+\sum_m (U^{ab}_{im}U^{cd}_{jm}+U^{ab}_{jm}U^{cd}_{im}+U^{ac}_{im}U^{bd}_{jm}+U^{ac}_{jm}U^{bd}_{im}+U^{bc}_{im}U^{ad}_{jm}+U^{bc}_{jm}U^{ad}_{im})\\
&-\sum_m (S^{abc}_{im}S^{d}_{jm}+S^{abc}_{jm}S^{d}_{im}+S^{abd}_{im}S^{c}_{jm}+S^{abd}_{jm}S^{c}_{im}+S^{acd}_{im}S^{b}_{jm}+S^{acd}_{jm}S^{b}_{im}\\
&\qquad +S^{bcd}_{im}S^{a}_{jm}+S^{bcd}_{jm}S^{a}_{im})\\
&-\sum_m (S^{ab}_{im}S^{cd}_{jm}+S^{ab}_{jm}S^{cd}_{im}+S^{ac}_{im}S^{bd}_{jm}+S^{ac}_{jm}S^{bd}_{im}+S^{bc}_{im}S^{ad}_{jm}+S^{bc}_{jm}S^{ad}_{im})\\
&+\mathcal{Q}^{abcd}_{ij}.
\end{aligned}
\tag{3.8}
$$

The augmented Q matrices, $\mathcal{Q}$, in Eq. (3.8) are given by

$$
\begin{aligned}
\mathcal{Q}^{abcd}_{ij} =&\sum_m (S^{ab}_{im}\mathcal{O}^{cd}_{jm}+S^{ab}_{jm}\mathcal{O}^{cd}_{im}+S^{ac}_{im}\mathcal{O}^{bd}_{jm}+S^{ac}_{jm}\mathcal{O}^{bd}_{im}+S^{ad}_{im}\mathcal{O}^{bc}_{jm}+S^{ad}_{jm}\mathcal{O}^{bc}_{im}\\
&\qquad +S^{bc}_{im}\mathcal{O}^{ad}_{jm}+S^{bc}_{jm}\mathcal{O}^{ad}_{im}+S^{bd}_{im}\mathcal{O}^{ac}_{jm}+S^{bd}_{jm}\mathcal{O}^{ac}_{im}+S^{cd}_{im}\mathcal{O}^{ab}_{jm}+S^{cd}_{jm}\mathcal{O}^{ab}_{im})\\
&+\sum_{mn} [(S^{ab}_{mn}-\mathcal{O}^{ab}_{mn})(S^{c}_{im}S^{d}_{jn}+S^{c}_{jm}S^{d}_{in})+(S^{ac}_{mn}-\mathcal{O}^{ac}_{mn})(S^{b}_{im}S^{d}_{jn}+S^{b}_{jm}S^{d}_{in})\\
&\qquad +(S^{ad}_{mn}-\mathcal{O}^{ad}_{mn})(S^{b}_{im}S^{c}_{jn}+S^{b}_{jm}S^{c}_{in})+(S^{bc}_{mn}-\mathcal{O}^{bc}_{mn})(S^{a}_{im}S^{d}_{jn}+S^{a}_{jm}S^{d}_{in})\\
&\qquad +(S^{bd}_{mn}-\mathcal{O}^{bd}_{mn})(S^{a}_{im}S^{c}_{jn}+S^{a}_{jm}S^{c}_{in})\\
&\qquad +(S^{cd}_{mn}-\mathcal{O}^{cd}_{mn})(S^{a}_{im}S^{b}_{jn}+S^{a}_{jm}S^{b}_{in})]
\end{aligned}
\tag{3.9}
$$

where

$$\mathcal{O}^{ab}_{mn}=\sum_k (S^{a}_{mk}S^{b}_{nk}+S^{b}_{mk}S^{a}_{nk}). \tag{3.10}$$

The transformed derivative overlap integrals appearing in these equations are defined by

$$S^{a}_{ij}=\sum_{\mu\nu} C^{i}_{\mu}C^{j}_{\nu}\frac{\partial S_{\mu\nu}}{\partial a}, \tag{3.12}$$

$$S^{ab}_{ij}=\sum_{\mu\nu} C^{i}_{\mu}C^{j}_{\nu}\frac{\partial^2 S_{\mu\nu}}{\partial a\,\partial b}. \tag{3.13}$$

$$S^{abc}_{ij}=\sum_{\mu\nu} C^{i}_{\mu}C^{j}_{\nu}\frac{\partial^3 S_{\mu\nu}}{\partial a\,\partial b\,\partial c}, \tag{3.14}$$

$$S^{abcd}_{ij}=\sum_{\mu\nu} C^{i}_{\mu}C^{j}_{\nu}\frac{\partial^4 S_{\mu\nu}}{\partial a\,\partial b\,\partial c\,\partial d}. \tag{3.15}$$

It should be noted that the matrices $\mathcal{S}$ involve not only the transformed derivative overlap integrals but also the U matrices of lower orders. In the first order relation (3.2), $\mathcal{S}^{a}_{ij}$ simply becomes S^{a}_{ij}.

4. Energy derivatives for MCSCF wavefunctions

Given the general formulae for CI energy derivatives as reviewed in Sect. 2, we can easily perform the resolution to the case of SCF wavefunctions by introducing the additional variational condition used to determine the SCF wavefunctions. In this section, we discuss the MCSCF energy derivatives.

4.1. *The electronic energy and the variational condition for the* MCSCF *wavefunction* [2–24]

The energy expression for MCSCF wavefunctions is formally the same as for CI, namely,

$$E^{\mathrm{MC}}=\sum_{ij} \gamma_{ij}h_{ij}+\sum_{ijkl} \Gamma_{ijkl}(ij\,|\,kl). \tag{4.1}$$

One of the conditions used to determine the MCSCF wavefunction (2.1) is the variational condition for the configuration space; this has already been stated in Eq. (2.12). The other condition is the variational condition for the determination of optimum molecular orbitals. This condition may be represented as the symmetric property of the Lagrangian matrix defined in Eq. (2.13),

$$X_{ij}-X_{ji}=0. \tag{4.2}$$

When this condition is satisfied, the derivative expression may greatly be simplified, as will be demonstrated below.

4.2. *First derivatives*

The energy gradient for the MCSCF wavefunction [35, 36] may be derived from Eq. (2.35) by reference to the relations (3.2) and (4.2),

$$\frac{\partial E^{\mathrm{MC}}}{\partial a}=\sum_{ij} \gamma_{ij}h_{ij}^{a}+\sum_{ijkl} \Gamma_{ijkl}(ij\,|\,kl)^{a}-\sum_{im} S_{im}^{a}X_{im}. \tag{4.3}$$

4.3. *Second derivatives*

The second derivative of the MCSCF energy [37–42] may be obtained combining Eqs. (2.36) and (2.37),

$$\begin{aligned}\frac{\partial^2 E^{\mathrm{MC}}}{\partial a\,\partial b}=&\sum_{ij} \gamma_{ij}h_{ij}^{ab}+\sum_{ijkl} \Gamma_{ijkl}(ij\,|\,kl)^{ab}-\sum_{im} \mathcal{S}_{im}^{ab}X_{im}\\ &+2\sum_{im}(U_{im}^{a}X_{im}^{b}+U_{im}^{b}X_{im}^{a})+2\sum_{im}\sum_{jn} U_{im}^{a}U_{jn}^{b}Y_{imjn}\\ &-2\sum_{IJ}\frac{\partial C_I}{\partial a}\frac{\partial C_J}{\partial b}(H_{IJ}-\delta_{IJ}E^{\mathrm{MC}}).\end{aligned} \tag{4.4}$$

Here, again Eqs. (3.3) and (4.2) were used to re-express the term involving U^{ab} in terms of $\mathcal{S}^{ab}$. In order to evaluate the second derivative of the MCSCF wavefunction, one should determine the first derivatives of the molecular orbitals and CI coefficients by solving the coupled-perturbed multi-configuration Hartree-Fock (CPMCHF) equations [28, 38–46]. The CPMCHF equation may be derived by differentiating the variational conditions (2.12) and (4.2) for configuration space and molecular orbital space, respectively.

4.4. Third derivatives

The third derivative of the MCSCF energy [46, 47] may be obtained from the CI third derivative expressions (2.38) and (2.39). For this purpose it is necessary to introduce the first derivative form of the variational condition (4.2),

$$\frac{\partial X_{ij}}{\partial a}-\frac{\partial X_{ji}}{\partial a}=0. \tag{4.5}$$

The derivative of the Lagrangian matrix in Eq. (4.5) may be expressed by using the definitions (2.40) and (2.48) as

$$\frac{\partial X_{im}}{\partial a}=X_{im}^{[a]}+\sum_{k} U_{ki}^{a}X_{km}+2\sum_{IJ} C_I\frac{\partial C_J}{\partial a}X_{im}^{IJ}. \tag{4.6}$$

In Eqs. (2.38) and (2.39), those terms potentially including the second and third derivatives of the MO coefficients are

$$2\sum_{im} U_{im}^{abc}X_{im}+2\sum_{im}(U_{im}^{ab}X_{im}^{[c]}+U_{im}^{bc}X_{im}^{[a]}+U_{im}^{ca}X_{im}^{[b]})$$
$$+2\sum_{I} C_I\sum_{J}\left(\frac{\partial C_J}{\partial a}\frac{\partial^2 H_{IJ}}{\partial b\,\partial c}+\frac{\partial C_J}{\partial b}\frac{\partial^2 H_{IJ}}{\partial c\,\partial a}+\frac{\partial C_J}{\partial c}\frac{\partial^2 H_{IJ}}{\partial a\,\partial b}\right). \tag{4.7}$$

Combining Eqs. (3.7) and (2.59) with Eq. (4.7) the second and third derivatives of the MO coefficients may be eliminated. Most importantly the terms involving the second order U matrices are manipulated as follows,

$$2\sum_{im} U_{im}^{ab}\left[X_{im}^{[c]}-\sum_{k} U_{km}^{c}X_{ki}+2\sum_{IJ} C_I\frac{\partial C_J}{\partial c}X_{im}^{IJ}\right] \tag{4.8}$$

$$=2\sum_{im} U_{im}^{ab}\left[\frac{\partial X_{im}}{\partial c}-\sum_{k}(U_{ki}^{c}X_{km}+U_{km}^{c}X_{ki})\right] \tag{4.9}$$

$$=-\sum_{im}\mathcal{S}_{im}^{ab}\left[\frac{\partial X_{im}}{\partial c}-\sum_{k}(U_{ki}^{c}X_{km}+U_{km}^{c}X_{ki})\right]. \tag{4.10}$$

The definition (4.6) is used for the first equality from Eq. (4.8) to Eq. (4.9) and the relationships (3.3) and (4.5) are introduced for the second equality to get Eq. (4.10).

Finally, the third derivative expression for the MCSCF energy is found to be

$$\frac{\partial^3 E^{\mathrm{MC}}}{\partial a\,\partial b\,\partial c}=\sum_{ij}\gamma_{ij}h_{ij}^{abc}+\sum_{ijkl}\Gamma_{ijkl}(ij|kl)^{abc}$$
$$-\sum_{im}X_{im}\left[S_{im}^{abc}-2\sum_{k}(S_{ik}^{ab}S_{mk}^{c}+S_{ik}^{bc}S_{mk}^{a}+S_{ik}^{ca}S_{mk}^{b})\right.$$
$$\left.+2\sum_{kl}(S_{ik}^{a}S_{ml}^{b}S_{kl}^{c}+S_{ik}^{b}S_{ml}^{c}S_{kl}^{a}+S_{ik}^{c}S_{ml}^{a}S_{kl}^{b})\right]$$

$$
\begin{aligned}
&+2\sum_{im}(U_{im}^{a}X_{im}^{bc}+U_{im}^{b}X_{im}^{ca}+U_{im}^{c}X_{im}^{ab})\\
&+2\sum_{im}\sum_{jn}(U_{im}^{a}U_{jn}^{b}Y_{imjn}^{c}+U_{im}^{b}U_{jn}^{c}Y_{imjn}^{a}+U_{im}^{c}U_{jn}^{a}Y_{imjn}^{b})\\
&+8\sum_{im}\sum_{jn}\sum_{ko}(U_{im}^{a}U_{jn}^{b}U_{ko}^{c}+U_{im}^{b}U_{jn}^{c}U_{ko}^{a}\\
&\qquad+U_{im}^{c}U_{jn}^{a}U_{ko}^{b})\sum_{l}\Gamma_{mnol}(ij|kl)\\
&-\sum_{im}\left[\mathcal{S}_{im}^{ab}\left(X_{im}^{[c]}-\sum_{k}U_{km}^{c}X_{ki}\right)+\mathcal{S}_{im}^{bc}\left(X_{im}^{[a]}-\sum_{k}U_{km}^{a}X_{ki}\right)\right.\\
&\qquad\left.+\mathcal{S}_{im}^{ca}\left(X_{im}^{[b]}-\sum_{k}U_{km}^{b}X_{ki}\right)\right]\\
&+2\sum_{IJ}C_{I}\frac{\partial C_{J}}{\partial a}\left[H_{IJ}^{bc}-\sum_{im}\mathcal{S}_{im}^{bc}X_{im}^{IJ}+2\sum_{im}(U_{im}^{b}X_{im}^{IJ^{c}}+U_{im}^{c}X_{im}^{IJ^{b}})\right.\\
&\left.+2\sum_{im}\sum_{jn}U_{im}^{b}U_{jn}^{c}Y_{imjn}^{IJ}\right]\\
&+2\sum_{IJ}C_{I}\frac{\partial C_{J}}{\partial b}\left[H_{IJ}^{ca}-\sum_{im}\mathcal{S}_{im}^{ca}X_{im}^{IJ}+2\sum_{im}(U_{im}^{c}X_{im}^{IJ^{a}}+U_{im}^{a}X_{im}^{IJ^{c}})\right.\\
&\left.+2\sum_{im}\sum_{jn}U_{im}^{c}U_{jn}^{a}Y_{imjn}^{IJ}\right]\\
&+2\sum_{IJ}C_{I}\frac{\partial C_{J}}{\partial c}\left[H_{IJ}^{ab}-\sum_{im}\mathcal{S}_{im}^{ab}X_{im}^{IJ}+2\sum_{im}(U_{im}^{a}X_{im}^{IJ^{b}}+U_{im}^{b}X_{im}^{IJ^{a}})\right.\\
&\left.+2\sum_{im}\sum_{jn}U_{im}^{a}U_{jn}^{b}Y_{imjn}^{IJ}\right]\\
&+2\sum_{IJ}\left[\frac{\partial C_{I}}{\partial a}\frac{\partial C_{J}}{\partial b}\left(\frac{\partial H_{IJ}}{\partial c}-\delta_{IJ}\frac{\partial E^{\mathrm{MC}}}{\partial c}\right)+\frac{\partial C_{I}}{\partial b}\frac{\partial C_{J}}{\partial c}\left(\frac{\partial H_{IJ}}{\partial a}-\delta_{IJ}\frac{\partial E^{\mathrm{MC}}}{\partial a}\right)\right.\\
&\qquad\left.+\frac{\partial C_{I}}{\partial c}\frac{\partial C_{J}}{\partial a}\left(\frac{\partial H_{IJ}}{\partial b}-\delta_{IJ}\frac{\partial E^{\mathrm{MC}}}{\partial b}\right)\right].
\end{aligned}
\tag{4.11}
$$

4.5. Fourth derivatives

The fourth derivative of the MCSCF energy [47] may be derived from the corresponding expressions (2.42) and (2.43) for the CI wavefunction. In these equations the terms that potentially include the third and fourth derivatives of the MO coefficients are

$$
\begin{aligned}
&2\sum_{im}U_{im}^{abcd}X_{im}+2\sum_{im}(U_{im}^{abc}X_{im}^{[d]}+U_{im}^{bcd}X_{im}^{[a]}+U_{im}^{cda}X_{im}^{[b]}+U_{im}^{dab}X_{im}^{[c]})\\
&+2\sum_{I}C_{I}\sum_{J}\left(\frac{\partial C_{J}}{\partial a}\frac{\partial^{3}H_{IJ}}{\partial b\,\partial c\,\partial d}+\frac{\partial C_{J}}{\partial b}\frac{\partial^{3}H_{IJ}}{\partial c\,\partial d\,\partial a}+\frac{\partial C_{J}}{\partial c}\frac{\partial^{3}H_{IJ}}{\partial d\,\partial a\,\partial b}+\frac{\partial C_{J}}{\partial d}\frac{\partial^{3}H_{IJ}}{\partial a\,\partial b\,\partial c}\right).
\end{aligned}
\tag{4.12}
$$

Combining Eqs. (3.8) and (2.60) with Eq. (4.12) the third and fourth derivatives of the MO coefficients may be removed in a similar manner as for the third derivative case. Most importantly the terms involving the third derivative U matrices are treated as

$$2\sum_{im} U_{im}^{abc}\left[X_{im}^{[d]}-\sum_{k} U_{km}^{d}X_{ki}+2\sum_{IJ} C_I\frac{\partial C_J}{\partial d}X_{im}^{IJ}\right]$$

$$=-\sum_{im} \mathcal{S}_{im}^{abc}\left[X_{im}^{[d]}-\sum_{k} U_{km}^{d}X_{ki}+2\sum_{IJ} C_I\frac{\partial C_J}{\partial d}X_{im}^{IJ}\right]. \tag{4.13}$$

In deriving this relationship the symmetric property about the exchange of the indices i and m through Eq. (4.5) is utilized.

A final expression for the MCSCF fourth energy derivative may be written

$$\frac{\partial^4 E^{\text{MC}}}{\partial a\,\partial b\,\partial c\,\partial d}=\sum_{ij}\gamma_{ij}h_{ij}^{abcd}+\sum_{ijkl}\Gamma_{ijkl}(ij\,|\,kl)^{abcd}$$

$$-\sum_{im}X_{im}\Bigg[S_{im}^{abcd}-2\sum_{k}(S_{ik}^{abc}S_{mk}^{d}+S_{ik}^{bcd}S_{mk}^{a}+S_{ik}^{cda}S_{mk}^{b}+S_{ik}^{dab}S_{mk}^{c})$$

$$-2\sum_{k}(S_{ik}^{ab}S_{mk}^{cd}+S_{ik}^{ac}S_{mk}^{bd}+S_{ik}^{ad}S_{mk}^{bc})$$

$$+2\sum_{k}(U_{ik}^{ab}U_{mk}^{cd}+U_{ik}^{ac}U_{mk}^{bd}+U_{ik}^{ad}U_{mk}^{bc})+\mathcal{Q}_{im}^{abcd}\Bigg]$$

$$+2\sum_{im}\sum_{jn}(U_{im}^{ab}U_{jn}^{cd}+U_{im}^{ac}U_{jn}^{bd}+U_{im}^{ad}U_{jn}^{bc})Y_{imjn}$$

$$+2\sum_{im}(U_{im}^{ab}X_{im}^{[cd]}+U_{im}^{ac}X_{im}^{[bd]}+U_{im}^{ad}X_{im}^{[bc]}+U_{im}^{bc}X_{im}^{[ad]}+U_{im}^{bd}X_{im}^{[ac]}$$

$$+U_{im}^{cd}X_{im}^{[ab]})$$

$$+2\sum_{im}(U_{im}^{a}X_{im}^{bcd}+U_{im}^{b}X_{im}^{cda}+U_{im}^{c}X_{im}^{dab}+U_{im}^{d}X_{im}^{abc})$$

$$+2\sum_{im}\sum_{jn}(U_{im}^{a}U_{jn}^{b}Y_{imjn}^{cd}+U_{im}^{a}U_{jn}^{c}Y_{imjn}^{bd}+U_{im}^{a}U_{jn}^{d}Y_{imjn}^{bc}$$

$$+U_{im}^{b}U_{jn}^{c}Y_{imjn}^{ad}+U_{im}^{b}U_{jn}^{d}Y_{imjn}^{ac}+U_{im}^{c}U_{jn}^{d}Y_{imjn}^{ab})$$

$$+2\sum_{im}\sum_{jn}\sum_{ko}(U_{im}^{a}U_{jn}^{b}U_{ko}^{c}Z_{imjnko}^{d}+U_{im}^{b}U_{jn}^{c}U_{ko}^{d}Z_{imjnko}^{a}$$

$$+U_{im}^{c}U_{jn}^{d}U_{ko}^{a}Z_{imjnko}^{b}+U_{im}^{d}U_{jn}^{a}U_{ko}^{b}Z_{imjnko}^{c})$$

$$+8\sum_{im}\sum_{jn}\sum_{ko}\sum_{lp}(U_{im}^{a}U_{jn}^{b}U_{ko}^{c}U_{lp}^{d}+U_{im}^{a}U_{jn}^{c}U_{ko}^{b}U_{lp}^{d}$$

$$+U_{im}^{a}U_{jn}^{d}U_{ko}^{b}U_{lp}^{c})\Gamma_{mnop}(ij\,|\,kl)$$

$$-\sum_{im}\Bigg[\mathcal{S}_{im}^{abc}\Big(X_{im}^{[d]}-\sum_{k}U_{km}^{d}X_{ki}\Big)+\mathcal{S}_{im}^{bcd}\Big(X_{im}^{[a]}-\sum_{k}U_{km}^{a}X_{ki}\Big)$$

$$+\mathcal{S}_{im}^{cda}\Big(X_{im}^{[b]}-\sum_{k}U_{km}^{b}X_{ki}\Big)+\mathcal{S}_{im}^{dab}\Big(X_{im}^{[c]}-\sum_{k}U_{km}^{c}X_{ki}\Big)\Bigg]$$

$$
\begin{aligned}
&+2\sum_I C_I \sum_J \left(\frac{\partial C_J}{\partial a}\frac{\partial^3 H'_{IJ}}{\partial b\,\partial c\,\partial d}+\frac{\partial C_J}{\partial b}\frac{\partial^3 H'_{IJ}}{\partial c\,\partial d\,\partial a}+\frac{\partial C_J}{\partial c}\frac{\partial^3 H'_{IJ}}{\partial d\,\partial a\,\partial b}\right.\\
&\qquad\left.+\frac{\partial C_J}{\partial d}\frac{\partial^3 H'_{IJ}}{\partial a\,\partial b\,\partial c}\right)\\
&+2\sum_{IJ}\left[\frac{\partial C_I}{\partial a}\frac{\partial C_J}{\partial b}\left(\frac{\partial^2 H_{IJ}}{\partial c\,\partial d}-\delta_{IJ}\frac{\partial^2 E^{\mathrm{MC}}}{\partial c\,\partial d}\right)\right.\\
&\qquad+\frac{\partial C_I}{\partial a}\frac{\partial C_J}{\partial c}\left(\frac{\partial^2 H_{IJ}}{\partial b\,\partial d}-\delta_{IJ}\frac{\partial^2 E^{\mathrm{MC}}}{\partial b\,\partial d}\right)\\
&\qquad+\frac{\partial C_I}{\partial a}\frac{\partial C_J}{\partial d}\left(\frac{\partial^2 H_{IJ}}{\partial b\,\partial c}-\delta_{IJ}\frac{\partial^2 E^{\mathrm{MC}}}{\partial b\,\partial c}\right)\\
&\qquad+\frac{\partial C_I}{\partial b}\frac{\partial C_J}{\partial c}\left(\frac{\partial^2 H_{IJ}}{\partial a\,\partial d}-\delta_{IJ}\frac{\partial^2 E^{\mathrm{MC}}}{\partial a\,\partial d}\right)\\
&\qquad+\frac{\partial C_I}{\partial b}\frac{\partial C_J}{\partial d}\left(\frac{\partial^2 H_{IJ}}{\partial a\,\partial c}-\delta_{IJ}\frac{\partial^2 E^{\mathrm{MC}}}{\partial a\,\partial c}\right)\\
&\qquad\left.+\frac{\partial C_I}{\partial c}\frac{\partial C_J}{\partial d}\left(\frac{\partial^2 H_{IJ}}{\partial a\,\partial b}-\delta_{IJ}\frac{\partial^2 E^{\mathrm{MC}}}{\partial a\,\partial b}\right)\right]\\
&-2\sum_{IJ}\left(\frac{\partial^2 C_I}{\partial a\,\partial b}\frac{\partial^2 C_J}{\partial c\,\partial d}+\frac{\partial^2 C_I}{\partial a\,\partial c}\frac{\partial^2 C_J}{\partial b\,\partial d}+\frac{\partial^2 C_I}{\partial a\,\partial d}\frac{\partial^2 C_J}{\partial b\,\partial c}\right)(H_{IJ}-\delta_{IJ}E^{\mathrm{MC}}),
\end{aligned}
\tag{4.14}
$$

where

$$
\begin{aligned}
\frac{\partial^3 H'_{IJ}}{\partial a\,\partial b\,\partial c} &= H_{IJ}^{abc}-\sum_{im}\mathcal{S}_{im}^{abc}X_{im}^{IJ}\\
&+2\sum_{im}\left(U_{im}^{ab}X_{im}^{IJ^c}+U_{im}^{bc}X_{im}^{IJ^a}+U_{im}^{ca}X_{im}^{IJ^b}+U_{im}^{a}X_{im}^{IJ^{bc}}\right.\\
&\qquad\left.+U_{im}^{b}X_{im}^{IJ^{ca}}+U_{im}^{c}X_{im}^{IJ^{ab}}\right)\\
&+2\sum_{im}\sum_{jn}\{(U_{im}^{ab}U_{jn}^{c}+U_{im}^{bc}U_{jn}^{a}+U_{im}^{ca}U_{jn}^{b})Y_{imjn}^{IJ}\\
&\qquad+U_{im}^{a}U_{jn}^{b}Y_{imjn}^{IJ^c}+U_{im}^{b}U_{jn}^{c}Y_{imjn}^{IJ^a}+U_{im}^{c}U_{jn}^{a}Y_{imjn}^{IJ^b}\}\\
&+8\sum_{im}\sum_{jn}\sum_{ko}(U_{im}^{a}U_{jn}^{b}U_{ko}^{c}+U_{im}^{b}U_{jn}^{c}U_{ko}^{a}\\
&\qquad+U_{im}^{c}U_{jn}^{a}U_{ko}^{b})\sum_{l}\Gamma_{mnol}^{IJ}(ij|kl).
\end{aligned}
\tag{4.15}
$$

5. Energy derivatives for general RHF wavefunctions

When the SCF condition (4.2) is satisfied, one may evaluate up to the $(2n+1)$th energy derivatives by solving the nth order coupled perturbed Hartree–Fock equations, as we have shown in the previous section for the MCSCF wavefunction. This fact is known as the Wigner's $2n+1$ theorem [46, 48, 49]. Table 1 illustrates the derivatives of variational parameters necessary to calculate the derivatives of

Table 1. A classification of derivatives of variational parameters required to evaluate energy derivatives for CI, MCSCF and RHF wavefunctions.

		CI		MCSCF	RHF
		MO space	CI space	MO/CI Coupled space	MO space
Energy	E	C^i_μ			
First derivative	$\frac{\partial E}{\partial a}$	First-order CPHF U^a	C_I	C^i_μ, C_I	C^i_μ
Second derivative	$\frac{\partial^2 E}{\partial a\, \partial b}$	Second-order CPHF U^{ab}	First-order CPCI	First-order CPMCHF	First-order CPHF
Third derivative	$\frac{\partial^3 E}{\partial a\, \partial b\, \partial c}$	Third-order CPHF U^{abc}	$\frac{\partial C_I}{\partial a}$	$U^a, \frac{\partial C_I}{\partial a}$	U^a
Fourth derivative	$\frac{\partial^4 E}{\partial a\, \partial b\, \partial c\, \partial d}$	Fourth-order CPHF U^{abcde}	Second-order CPCI	Second-order CPMCHF	Second-order CPHF
Fifth derivative	$\frac{\partial^5 E}{\partial a\, \partial b\, \partial c\, \partial d\, \partial e}$	Fifth-order CPHF U^{abcde}	$\frac{\partial^2 C_I}{\partial a\, \partial b}$	$U^{ab}, \frac{\partial^2 C_I}{\partial a\, \partial b}$	U^{ab}

energy for various wavefunctions. The RHF wavefunction described by the one-configuration SCF method may be treated as a special case of the MCSCF wavefunction. In this section we present the energy derivative expressions for the general open-shell SCF wavefunction by reformulating the MCSCF derivative expressions.

5.1. *Electronic energy and variational condition for the general open-shell* SCF *wavefunction* [50]

The electronic energy for the general open-shell SCF wavefunction [51–53] is given by

$$E^{\mathrm{RHF}} = 2\sum_i f_i h_{ii} + \sum_{ij} \{\alpha_{ij}(ii\,|\,jj) + \beta_{ij}(ij\,|\,ij)\}. \tag{5.1}$$

This energy expression may be obtained from the MCSCF energy formula (4.1) by imposing the following relations on the one- and two-particle density matrix elements,

$$\gamma_{ij} = 2\delta_{ij} f_i \tag{5.2}$$

and

$$\Gamma_{ijkl} = \delta_{ij}\delta_{kl}\alpha_{ik} + \tfrac{1}{2}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\beta_{ij}. \tag{5.3}$$

By reference to the Lagrangian and generalized Lagrangian matrices [52, 53] for the general open-shell SCF wavefunction

$$\varepsilon_{ij}=f_i h_{ij}+\sum_k \{\alpha_{ik}(ij|kk)+\beta_{ik}(ik|jk)\} \tag{5.4}$$

and

$$\zeta^l_{ij}=f_l h_{ij}+\sum_k \{\alpha_{lk}(ij|kk)+\beta_{lk}(ik|jk)\}, \tag{5.5}$$

the following relationships with the Lagrangian and Y matrices for the MCSCF wavefunction are easily found,

$$X_{ij}=2\varepsilon_{ji}, \tag{5.6}$$

and

$$Y_{ijkl}=2\delta_{jl}\zeta^j_{ik}+2\mathscr{A}_{ijkl}, \tag{5.7}$$

where we define the $\mathscr{A}$ matrix as

$$\mathscr{A}_{ijkl}=2\alpha_{jl}(ij|kl)+\beta_{jl}\{(ik|jl)+(il|jk)\}. \tag{5.8}$$

It is convenient to note that

$$\zeta^l_{ij}=\zeta^l_{ji} \tag{5.9}$$

and

$$\varepsilon_{ij}=\zeta^i_{ij}. \tag{5.10}$$

Using the Lagrangian matrix defined in Eq. (5.4) the variational condition for the general RHF wavefunction is expressed as

$$\varepsilon_{ij}-\varepsilon_{ji}=0. \tag{5.11}$$

The energy derivative expressions for the general open-shell SCF wavefunction may be reformulated from the corresponding equations for the MCSCF wavefunction by appropriately imposing conditions (5.2)–(5.11). All terms involving the CI coefficients and their derivatives should of course be dropped.

5.2. *First derivatives* [35, 36]

The energy gradient is straightforwardly derived from Eq. (4.3) using the condition (5.11) as

$$\frac{\partial E^{\mathrm{RHF}}}{\partial a}=2\sum_i f_i h^a_{ii}+\sum_{ij}\{\alpha_{ij}(ii|jj)^a+\beta_{ij}(ij|ij)^a\}-2\sum_{ij}S^a_{ij}\varepsilon_{ij}. \tag{5.12}$$

5.3. *Second derivatives*

A symmetric formula for the second derivative of the general RHF energy [52, 53] may be easily obtained from Eq. (4.4)

$$\frac{\partial^2 E^{\mathrm{RHF}}}{\partial a\,\partial b}=2\sum_i f_i h_{ii}^{ab}+\sum_{ij}\{\alpha_{ij}(ii|jj)^{ab}+\beta_{ij}(ij|ij)^{ab}\}-2\sum_{ij}\mathcal{S}_{ij}^{ab}\varepsilon_{ij}$$
$$+4\sum_{ij}(U_{ij}^a\varepsilon_{ji}^b+U_{ij}^b\varepsilon_{ji}^a)+4\sum_{ij}\sum_{kl}U_{ij}^aU_{kl}^b(\delta_{jl}\zeta_{ik}^j+\mathcal{A}_{ijkl}) \tag{5.13}$$

where

$$\varepsilon_{ij}^a=f_ih_{ij}^a+\sum_k\{\alpha_{ik}(ij|kk)^a+\beta_{ik}(ik|jk)^a\}. \tag{5.14}$$

The U^a matrices in Eq. (5.13) may be obtained by solving the CPHF equations [28, 34, 52, 53] based on the general RHF method which may be derived from the relation (3.2) and the first derivative form of the variational condition,

$$\frac{\partial\varepsilon_{ij}}{\partial a}-\frac{\partial\varepsilon_{ji}}{\partial a}=0. \tag{5.15}$$

The first derivative of the Lagrangian matrix in Eq. (5.15) is given by

$$\frac{\partial\varepsilon_{ij}}{\partial a}=\varepsilon_{ij}^a+\sum_k(U_{ki}^a\zeta_{kj}^i+U_{kj}^a\varepsilon_{ik})+\sum_{kl}U_{kl}^a\mathcal{A}_{jikl} \tag{5.16}$$

and this equation corresponds to Eq. (4.6).

The direct differentiation of Eq. (5.12) with respect to a nuclear coordinate "b" also gives a second derivative expression. The result, however, does not turn out to be symmetric about "a" and "b" as presented in Refs. [52] and [53]. One has to use the CPHF Eq. (5.15) in order to prove that both expressions are equivalent.

5.4. *Third derivatives*

The third derivative of general open-shell RHF energy [54] may be obtained from the MCSCF third derivative expression (4.11),

$$\frac{\partial^3 E^{\mathrm{RHF}}}{\partial a\,\partial b\,\partial c}=2\sum_i f_ih_{ii}^{abc}+\sum_{ij}\{\alpha_{ij}(ii|jj)^{abc}+\beta_{ij}(ij|ij)^{abc}\}$$
$$-2\sum_{ij}\varepsilon_{ij}\Big[S_{ij}^{abc}-2\sum_k(S_{ik}^{ab}S_{jk}^c+S_{ik}^{bc}S_{jk}^a+S_{ik}^{ca}S_{jk}^b)$$
$$+2\sum_{kl}(S_{ik}^aS_{jl}^bS_{kl}^c+S_{ik}^bS_{jl}^cS_{kl}^a+S_{ik}^cS_{jl}^aS_{kl}^b)\Big]$$
$$+4\sum_{ij}(U_{ij}^a\varepsilon_{ji}^{bc}+U_{ij}^b\varepsilon_{ji}^{ca}+U_{ij}^c\varepsilon_{ji}^{ab})$$
$$+4\sum_{ij}\sum_k(U_{ik}^aU_{jk}^b\zeta_{ij}^{k^c}+U_{ik}^bU_{jk}^c\zeta_{ij}^{k^a}+U_{ik}^cU_{jk}^a\zeta_{ij}^{k^b})$$
$$+4\sum_{ij}\sum_{kl}(U_{ij}^aU_{kl}^b\mathcal{A}_{ijkl}^c+U_{ij}^bU_{kl}^c\mathcal{A}_{ijkl}^a+U_{ij}^cU_{kl}^a\mathcal{A}_{ijkl}^b)$$
$$+4\sum_{ij}\sum_{kl}\sum_m(U_{im}^aU_{jm}^bU_{kl}^c+U_{im}^bU_{jm}^cU_{kl}^a+U_{im}^cU_{jm}^aU_{kl}^b)$$
$$\times[2\alpha_{ml}(ij|kl)+\beta_{ml}\{(ik|jl)+(il|jk)\}]$$

$$-2\sum_{ij}\mathscr{S}_{ij}^{ab}\left[\varepsilon_{ij}^{c}+\sum_{k}(U_{ki}^{c}\zeta_{kj}^{i}-U_{kj}^{c}\varepsilon_{ik})+\sum_{kl}U_{kl}^{c}\mathscr{A}_{jikl}\right]$$

$$-2\sum_{ij}\mathscr{S}_{ij}^{bc}\left[\varepsilon_{ij}^{a}+\sum_{k}(U_{ki}^{a}\zeta_{kj}^{i}-U_{kj}^{a}\varepsilon_{ik})+\sum_{kl}U_{kl}^{a}\mathscr{A}_{jikl}\right]$$

$$-2\sum_{ij}\mathscr{S}_{ij}^{ca}\left[\varepsilon_{ij}^{b}+\sum_{k}(U_{ki}^{b}\zeta_{kj}^{i}-U_{kj}^{b}\varepsilon_{ik})+\sum_{kl}U_{kl}^{b}\mathscr{A}_{jikl}\right] \quad (5.17)$$

where

$$\varepsilon_{ij}^{ab}=f_i h_{ij}^{ab}+\sum_{k}\{\alpha_{ik}(ij|kk)^{ab}+\beta_{ik}(ik|jk)^{ab}\} \quad (5.18)$$

$$\zeta_{ij}^{l^a}=f_l h_{ij}^{a}+\sum_{k}\{\alpha_{lk}(ij|kk)^{a}+\beta_{lk}(ik|jk)^{a}\} \quad (5.19)$$

$$\mathscr{A}_{ijkl}^{a}=2\alpha_{jl}(ij|kl)^{a}+\beta_{jl}\{(ik|jl)^{a}+(il|jk)^{a}\}. \quad (5.20)$$

5.5. *Fourth derivatives*

The fourth energy derivative expression for the general RHF wavefunction may be derived from the MCSCF fourth derivative formula (4.14) by using the correspondence equations in subsection 5.1 and following relationships

$$X_{ij}^{[a]}=2\varepsilon_{ji}^{[a]}=2\left[\varepsilon_{ji}^{a}+\sum_{k}U_{kj}^{a}\zeta_{ik}^{j}+\sum_{kl}U_{kl}^{a}\mathscr{A}_{ijkl}\right], \quad (5.21)$$

$$X_{ij}^{[ab]}=2\varepsilon_{ji}^{[ab]}=2\left[\varepsilon_{ji}^{ab}+\sum_{k}(U_{kj}^{a}\zeta_{ik}^{j^b}+U_{kj}^{b}\zeta_{ik}^{j^a})+\sum_{kl}(U_{kl}^{a}\mathscr{A}_{ijkl}^{b}+U_{kl}^{b}\mathscr{A}_{ijkl}^{a})\right.$$

$$+\sum_{klm}U_{kj}^{a}U_{lm}^{b}[2\alpha_{jm}(ik|lm)+\beta_{jm}\{(il|km)+(im|kl)\}]$$

$$+\sum_{klm}U_{km}^{a}U_{lj}^{b}[2\alpha_{jm}(il|km)+\beta_{jm}\{(ik|lm)+(im|kl)\}]$$

$$\left.+\sum_{klm}U_{km}^{a}U_{lm}^{b}[2\alpha_{jm}(ij|kl)+\beta_{jm}\{(ik|jl)+(il|jk)\}]\right] \quad (5.22)$$

$$X_{ij}^{abc}=2\varepsilon_{ji}^{abc}, \quad (5.23)$$

$$Y_{ijkl}^{ab}=2\delta_{jl}\zeta_{ik}^{j^{ab}}+2\mathscr{A}_{ijkl}^{ab}, \quad (5.24)$$

$$2\sum_{im}\sum_{jn}\sum_{ko}U_{im}^{a}U_{jn}^{b}U_{ko}^{c}Z_{imjnko}^{d}$$

$$=4\sum_{ij}\sum_{kl}\sum_{m}(U_{im}^{a}U_{jm}^{b}U_{kl}^{c}+U_{im}^{b}U_{jm}^{c}U_{kl}^{a}+U_{im}^{c}U_{jm}^{a}U_{kl}^{b})$$

$$\times[2\alpha_{ml}(ij|kl)^{d}+\beta_{ml}\{(ik|jl)^{d}+(il|jk)^{d}\}], \quad (5.25)$$

$$8\sum_{im}\sum_{jn}\sum_{ko}\sum_{lp}(U_{im}^{a}U_{jn}^{b}U_{ko}^{c}U_{lp}^{d}+U_{im}^{a}U_{jn}^{c}U_{ko}^{b}U_{lp}^{d}+U_{im}^{a}U_{jn}^{d}U_{ko}^{b}U_{lp}^{c})\Gamma_{mnop}(ij|kl)$$

$$=4\sum_{ij}\sum_{kl}\sum_{mn}(U_{im}^{a}U_{jm}^{b}U_{kn}^{c}U_{ln}^{d}+U_{im}^{a}U_{jm}^{c}U_{kn}^{b}U_{ln}^{d}+U_{im}^{a}U_{jm}^{d}U_{kn}^{b}U_{ln}^{c})$$

$$\times[2\alpha_{mn}(ij|kl)+\beta_{mn}\{(ik|jl)+(il|jk)\}], \tag{5.26}$$

where

$$\varepsilon_{ij}^{abc}=f_i h_{ij}^{abc}+\sum_k \{\alpha_{ik}(ij|kk)^{abc}+\beta_{ik}(ik|jk)^{abc}\}, \tag{5.27}$$

$$\zeta_{ij}^{lab}=f_l h_{ij}^{ab}+\sum_k \{\alpha_{lk}(ij|kk)^{ab}+\beta_{lk}(ik|jk)^{ab}\}, \tag{5.28}$$

$$\mathscr{A}_{ijkl}^{ab}=2\alpha_{jl}(ij|kl)^{ab}+\beta_{jl}\{(ik|jl)^{ab}+(il|jk)^{ab}\}. \tag{5.29}$$

The final expression of the fourth derivative of the general RHF energy may be given as follows:

$$\begin{aligned}
\frac{\partial^4 E^{\mathrm{RHF}}}{\partial a\,\partial b\,\partial c\,\partial d} &= 2\sum_i f_i h_{ii}^{abcd}+\sum_{ij}\{\alpha_{ij}(ii|jj)^{abcd}+\beta_{ij}(ij|ij)^{abcd}\} \\
&\quad -2\sum_{ij}\varepsilon_{ij}\Bigg[S_{ij}^{abcd}-2\sum_k (S_{ik}^{abc}S_{jk}^{d}+S_{ik}^{bcd}S_{jk}^{a}+S_{ik}^{cda}S_{jk}^{b}+S_{ik}^{dab}S_{jk}^{c}) \\
&\quad -2\sum_k (S_{ik}^{ab}S_{jk}^{cd}+S_{ik}^{ac}S_{jk}^{bd}+S_{ik}^{ad}S_{jk}^{bc}) \\
&\quad +2\sum_k (U_{ik}^{ab}U_{jk}^{cd}+U_{ik}^{ac}U_{jk}^{bd}+U_{ik}^{ad}U_{jk}^{bc})+\mathscr{Q}_{ij}^{abcd}\Bigg] \\
&\quad +4\sum_{ij}\sum_k (U_{ik}^{ab}U_{jk}^{cd}+U_{ik}^{ac}U_{jk}^{bd}+U_{ik}^{ad}U_{jk}^{bc})\zeta_{ij}^{k} \\
&\quad +4\sum_{ij}\sum_{kl} (U_{ij}^{ab}U_{kl}^{cd}+U_{ij}^{ac}U_{kl}^{bd}+U_{ij}^{ad}U_{kl}^{bc})\mathscr{A}_{ijkl} \\
&\quad +4\sum_{ij} (U_{ij}^{ab}\varepsilon_{ji}^{[cd]}+U_{ij}^{ac}\varepsilon_{ji}^{[bd]}+U_{ij}^{ad}\varepsilon_{ji}^{[bc]}+U_{ij}^{bc}\varepsilon_{ji}^{[ad]} \\
&\qquad +U_{ij}^{bd}\varepsilon_{ji}^{[ac]}+U_{ij}^{cd}\varepsilon_{ji}^{[ab]}) \\
&\quad +4\sum_{ij} (U_{ij}^{a}\varepsilon_{ji}^{bcd}+U_{ij}^{b}\varepsilon_{ji}^{cda}+U_{ij}^{c}\varepsilon_{ji}^{dab}+U_{ij}^{d}\varepsilon_{ji}^{abc}) \\
&\quad +4\sum_{ij}\sum_k (U_{ik}^{a}U_{jk}^{b}\zeta_{ij}^{kcd}+U_{ik}^{a}U_{jk}^{c}\zeta_{ij}^{kbd}+U_{ik}^{a}U_{jk}^{d}\zeta_{ij}^{kbc} \\
&\qquad +U_{ik}^{b}U_{jk}^{c}\zeta_{ij}^{kad}+U_{ik}^{b}U_{jk}^{d}\zeta_{ij}^{kac}+U_{ik}^{c}U_{jk}^{d}\zeta_{ij}^{kab}) \\
&\quad +4\sum_{ij}\sum_{kl} (U_{ij}^{a}U_{kl}^{b}\mathscr{A}_{ijkl}^{cd}+U_{ij}^{a}U_{kl}^{c}\mathscr{A}_{ijkl}^{bd}+U_{ij}^{a}U_{kl}^{d}\mathscr{A}_{ijkl}^{bc} \\
&\qquad +U_{ij}^{b}U_{kl}^{c}\mathscr{A}_{ijkl}^{ad}+U_{ij}^{b}U_{kl}^{d}\mathscr{A}_{ijkl}^{ac}+U_{ij}^{c}U_{kl}^{d}\mathscr{A}_{ijkl}^{ab}) \\
&\quad +4\sum_{ij}\sum_{kl}\sum_m (U_{im}^{a}U_{jm}^{b}U_{kl}^{c}+U_{im}^{b}U_{jm}^{c}U_{kl}^{a}+U_{im}^{c}U_{jm}^{a}U_{kl}^{b}) \\
&\quad \times[2\alpha_{ml}(ij|kl)^{d}+\beta_{ml}\{(ik|jl)^{d}+(il|jk)^{d}\}] \\
&\quad +4\sum_{ij}\sum_{kl}\sum_m (U_{im}^{b}U_{jm}^{c}U_{kl}^{d}+U_{im}^{c}U_{jm}^{d}U_{kl}^{b}+U_{im}^{d}U_{jm}^{b}U_{kl}^{c}) \\
&\quad \times[2\alpha_{ml}(ij|kl)^{a}+\beta_{ml}\{(ik|jl)^{a}+(il|jk)^{a}\}] \\
&\quad +4\sum_{ij}\sum_{kl}\sum_m (U_{im}^{c}U_{jm}^{d}U_{kl}^{a}+U_{im}^{d}U_{jm}^{a}U_{kl}^{c}+U_{im}^{a}U_{jm}^{c}U_{kl}^{d})
\end{aligned}$$

$$
\begin{aligned}
&\times[2\alpha_{ml}(ij|kl)^b+\beta_{ml}\{(ik|jl)^b+(il|jk)^b\}]\\
&+4\sum_{ij}\sum_{kl}\sum_{m}(U^d_{im}U^a_{jm}U^b_{kl}+U^a_{im}U^b_{jm}U^d_{kl}+U^b_{im}U^d_{jm}U^a_{kl})\\
&\times[2\alpha_{ml}(ij|kl)^c+\beta_{ml}\{(ik|jl)^c+(il|jk)^c\}]\\
&+4\sum_{ij}\sum_{kl}\sum_{mn}(U^a_{im}U^b_{jm}U^c_{kn}U^d_{ln}+U^a_{im}U^c_{jm}U^b_{kn}U^d_{ln}\\
&+U^a_{im}U^d_{jm}U^b_{kn}U^c_{ln})\\
&\times[2\alpha_{mn}(ij|kl)+\beta_{mn}\{(ik|jl)+(il|jk)\}]\\
&-2\sum_{ij}\mathcal{S}^{abc}_{ij}\left[\varepsilon^d_{ij}+\sum_k(U^d_{ki}\zeta^i_{kj}-U^d_{kj}\varepsilon_{ik})+\sum_{kl}U^d_{kl}\mathcal{A}_{jikl}\right]\\
&-2\sum_{ij}\mathcal{S}^{bcd}_{ij}\left[\varepsilon^a_{ij}+\sum_k(U^a_{ki}\zeta^i_{kj}-U^a_{kj}\varepsilon_{ik})+\sum_{kl}U^a_{kl}\mathcal{A}_{jikl}\right]\\
&-2\sum_{ij}\mathcal{S}^{cda}_{ij}\left[\varepsilon^b_{ij}+\sum_k(U^b_{ki}\zeta^i_{kj}-U^b_{kj}\varepsilon_{ik})+\sum_{kl}U^b_{kl}\mathcal{A}_{jikl}\right]\\
&-2\sum_{ij}\mathcal{S}^{dab}_{ij}\left[\varepsilon^c_{ij}+\sum_k(U^c_{ki}\zeta^i_{kj}-U^c_{kj}\varepsilon_{ik})+\sum_{kl}U^c_{kl}\mathcal{A}_{jikl}\right].
\end{aligned}
\tag{5.30}
$$

Some obvious simplifications in Eqs. (5.17) and (5.30) may be made by incorporating the modified Lagrangian matrix $\varepsilon^{[a]}_{ij}$ as follows:

$$
\begin{aligned}
\varepsilon^{[a]}_{ij}-\sum_k U^a_{kj}\varepsilon_{ik}&=\varepsilon^a_{ij}+\sum_k(U^a_{ki}\zeta^i_{kj}-U^a_{kj}\varepsilon_{ik})+\sum_{kj}U^a_{kl}\mathcal{A}_{jikl}\\
&=\frac{\partial\varepsilon_{ij}}{\partial a}-2\sum_k U^a_{kj}\varepsilon_{ik}.
\end{aligned}
\tag{5.31}
$$

6. Energy derivatives for closed-shell SCF wavefunctions

In this section we demonstrate the effectiveness of the correspondence manipulation for the derivative expressions for the simplest and most frequently used case, the closed-shell SCF wavefunction. Since the closed-shell SCF method may be treated as a special case of the general open-shell SCF wavefunction, the closed-shell energy and its derivative expressions may be obtained from the formalism described in the previous section by setting the coupling constants f, α, and β to the following values;

$$
f_i=\begin{cases}1 & \text{for } i=\text{doubly occupied}\\ 0 & \text{for } i=\text{vacant}\end{cases}
\tag{6.1}
$$

$$
\alpha_{ij}=\begin{cases}2 & \text{for } i,j=\text{doubly occupied}\\ 0 & \text{otherwise}\end{cases}
\tag{6.2}
$$

$$
\beta_{ij}=\begin{cases}-1 & \text{for } i,j=\text{doubly occupied}\\ 0 & \text{otherwise.}\end{cases}
\tag{6.3}
$$

6.1. Electronic energy and variational condition for closed-shell SCF *wavefunctions* [55]

The electronic energy for the closed-shell SCF wavefunction is expressed as

$$E^{cl} = 2 \sum_{i}^{\text{d.o.}} h_{ii} + \sum_{ij}^{\text{d.o.}} \{2(ii|jj) - (ij|ij)\}, \tag{6.4}$$

where d.o. designates doubly occupied orbitals. The Lagrangian matrix (5.4) for the general open-shell RHF wavefunction is related to the Fock matrix for the closed-shell SCF wavefunction,

$$\varepsilon_{ij} = \begin{cases} F_{ji} & \text{for } i = \text{doubly occupied} \\ 0 & \text{otherwise,} \end{cases} \tag{6.5}$$

where

$$F_{ij} = F_{ji} = h_{ij} + \sum_{k}^{\text{d.o.}} \{2(ij|kk) - (ik|jk)\}. \tag{6.6}$$

The variational condition for the closed-shell SCF wavefunction becomes

$$F_{ij} = 0 \quad \text{for } i = \text{doubly occupied}, j = \text{virtual}. \tag{6.7}$$

Since the SCF energy is invariant under a unitary transformation within the occupied space, one normally uses the diagonality of the Fock matrix to define the canonical HF molecular orbitals. In order to maintain generality, we derive the energy derivatives for the closed-shell SCF energy without introducing the diagonality condition of the Fock matrix. If the canonical MO's are retained one may easily obtain these expressions by using the orbital energies instead of the Fock matrix elements, as we will discuss later.

6.2. Correspondence between closed-shell SCF *and* MCSCF *wavefunctions*

An alternative way to derive the closed-shell SCF energy derivatives is to exploit the MCSCF formalism described in Sect. 4 by neglecting the terms involving the derivatives of CI coefficients. Since the density matrices have non-vanishing values only for the occupied space, one can use this specificity to limit summations in the closed-shell energy derivative expressions. The correspondence for density matrices is given as

$$\gamma_{ij} = 2\delta_{ij} \tag{6.8}$$

and

$$\Gamma_{ijkl} = 2\delta_{ij}\delta_{kl} - \tfrac{1}{2}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \tag{6.9}$$

for i, j, k, l = doubly occupied.

The additional necessary relationships to derive the energy derivatives for the closed-shell SCF wavefunction from the MCSCF formalism are as follows:

$$X_{im} = 2F_{im} \quad \text{for } m = \text{doubly-occupied}, \ i = \text{all}, \tag{6.10}$$

$$Y_{imjn} = 2\delta_{mn}F_{ij} + 2A_{imjn} \quad \text{for } m, n = \text{doubly-occupied}, \ i, j = \text{all} \tag{6.11}$$

$$Z_{imjnko} = 2\delta_{mn}A_{ijko} + 2\delta_{mo}A_{ikjn} + 2\delta_{no}A_{imjk}$$
$$\text{for } m, n, o = \text{doubly-occupied}, \ i, j, k = \text{all}, \tag{6.12}$$

$$2\sum_{im}\sum_{jn}\sum_{ko} U^a_{im}U^b_{jn}U^c_{ko}Z_{imjnko}$$
$$= \sum_{ijk}^{\text{all}}\sum_{mn}^{\text{d.o.}} (U^a_{im}U^b_{jm}U^c_{kn} + U^b_{im}U^c_{jm}U^a_{kn} + U^c_{im}U^a_{jm}U^b_{kn})A_{ijkn}, \tag{6.13}$$

and

$$8\sum_{im}\sum_{jn}\sum_{ko}\sum_{lp} (U^a_{im}U^b_{jn}U^c_{ko}U^d_{lp} + U^a_{im}U^c_{jn}U^b_{ko}U^d_{lp} + U^a_{im}U^d_{jn}U^b_{ko}U^c_{lp})\Gamma_{mnop}(ij\,|\,kl)$$
$$= 4\sum_{ijkl}^{\text{all}}\sum_{mn}^{\text{d.o.}} (U^a_{im}U^b_{jm}U^c_{kn}U^d_{ln} + U^a_{im}U^c_{jm}U^b_{kn}U^d_{ln}$$
$$+ U^a_{im}U^d_{jm}U^b_{kn}U^c_{ln})A_{ijkl}, \tag{6.14}$$

where the A matrix [29, 56] is defined by

$$A_{ijkl} = 4(ij\,|\,kl) - (ik\,|\,jl) - (il\,|\,jk). \tag{6.15}$$

It should be noted that the SCF condition (6.7) for the closed-shell wavefunction is included in the variational condition for the MCSCF wavefunction.

$$X_{im} - X_{mi} = 0 \quad \text{for } m = \text{doubly-occupied}, \ i = \text{virtual}. \tag{6.16}$$

6.3. Energy derivatives for closed-shell SCF *wavefunctions*

Using correspondence equations defined in the preceding subsections, the first derivative of the closed-shell SCF energy [57–62] is reformulated from Eqs. (5.12) or (4.3),

$$\frac{\partial E^{cl}}{\partial a} = 2\sum_{i}^{\text{d.o.}} h^a_{ii} + \sum_{ij}^{\text{d.o.}} \{2(ii\,|\,jj)^a - (ij\,|\,ij)^a\} - 2\sum_{ij}^{\text{d.o.}} S^a_{ij}F_{ij}. \tag{6.17}$$

The second derivative [56, 63] expressions (5.13) or (4.4) may be reduced to

$$\frac{\partial^2 E^{cl}}{\partial a\,\partial b} = 2\sum_{i}^{\text{d.o.}} h^{ab}_{ii} + \sum_{ij}^{\text{d.o.}} \{2(ii\,|\,jj)^{ab} - (ij\,|\,ij)^{ab}\} - 2\sum_{ij}^{\text{d.o.}} \mathcal{S}^{ab}_{ij}F_{ij}$$
$$+ 4\sum_{i}^{\text{all}}\sum_{j}^{\text{d.o.}} (U^a_{ij}F^b_{ij} + U^b_{ij}F^a_{ij}) + 4\sum_{ij}^{\text{all}} F_{ij}\sum_{k}^{\text{d.o.}} U^a_{ik}U^b_{jk}$$

$$+4\sum_{i}^{\text{all}}\sum_{j}^{\text{d.o.}}\sum_{k}^{\text{all}}\sum_{l}^{\text{d.o.}} U_{ij}^{a}U_{kl}^{b}A_{ijkl}, \tag{6.18}$$

where

$$F_{ij}^{a}=h_{ij}^{a}+\sum_{k}^{\text{d.o.}}\{2(ij|kk)^{a}-(ik|jk)^{a}\}. \tag{6.19}$$

Similarly, the third derivative [46, 64-68] expressions (5.17) or (4.11) become

$$\begin{aligned}
\frac{\partial^3 E^{cl}}{\partial a\,\partial b\,\partial c} &= 2\sum_{i}^{\text{d.o.}} h_{ii}^{abc}+\sum_{ij}^{\text{d.o.}}\{2(ii|jj)^{abc}-(ij|ij)^{abc}\} \\
&\quad -2\sum_{ij}^{\text{d.o.}} F_{ij}\Bigg[S_{ij}^{abc}-2\sum_{k}^{\text{all}}(S_{ik}^{ab}S_{jk}^{c}+S_{ik}^{bc}S_{jk}^{a}+S_{ik}^{ca}S_{jk}^{b}) \\
&\quad +2\sum_{kl}^{\text{all}}(S_{ik}^{a}S_{jl}^{b}S_{kl}^{c}+S_{ik}^{b}S_{jl}^{c}S_{kl}^{a}+S_{ik}^{c}S_{jl}^{a}S_{kl}^{b})\Bigg] \\
&\quad +4\sum_{i}^{\text{all}}\sum_{j}^{\text{d.o.}}(U_{ij}^{a}F_{ij}^{bc}+U_{ij}^{b}F_{ij}^{ca}+U_{ij}^{c}F_{ij}^{ab}) \\
&\quad +4\sum_{i}^{\text{all}}\sum_{j}^{\text{all}}\sum_{k}^{\text{d.o.}}(U_{ik}^{a}U_{jk}^{b}F_{ij}^{c}+U_{ik}^{b}U_{jk}^{c}F_{ij}^{a}+U_{ik}^{c}U_{jk}^{a}F_{ij}^{b}) \\
&\quad +4\sum_{i}^{\text{all}}\sum_{j}^{\text{d.o.}}\sum_{k}^{\text{all}}\sum_{l}^{\text{d.o.}}(U_{ij}^{a}U_{kl}^{b}A_{ijkl}^{c}+U_{ij}^{b}U_{kl}^{c}A_{ijkl}^{a}+U_{ij}^{c}U_{kl}^{a}A_{ijkl}^{b}) \\
&\quad +4\sum_{i}^{\text{all}}\sum_{j}^{\text{d.o.}}\sum_{k}^{\text{all}}\sum_{l}^{\text{all}}\sum_{m}^{\text{d.o.}}(U_{ij}^{a}U_{km}^{b}U_{lm}^{c}+U_{ij}^{b}U_{km}^{c}U_{lm}^{a}+U_{ij}^{c}U_{km}^{a}U_{lm}^{b})A_{ijkl} \\
&\quad -2\sum_{i}^{\text{all}}\sum_{j}^{\text{d.o.}}\Bigg[\mathcal{S}_{ij}^{ab}\left(\frac{\partial F_{ij}}{\partial c}-2\sum_{k}^{\text{all}}U_{ki}^{c}F_{kj}\right)+\mathcal{S}_{ij}^{bc}\left(\frac{\partial F_{ij}}{\partial a}-2\sum_{k}^{\text{all}}U_{ki}^{a}F_{kj}\right) \\
&\qquad +\mathcal{S}_{ij}^{ac}\left(\frac{\partial F_{ij}}{\partial b}-2\sum_{k}^{\text{all}}U_{ki}^{b}F_{kj}\right)\Bigg]
\end{aligned} \tag{6.20}$$

where

$$F_{ij}^{ab}=h_{ij}^{ab}+\sum_{k}^{\text{d.o.}}\{2(ij|kk)^{ab}-(ik|jk)^{ab}\}, \tag{6.21}$$

$$A_{ijkl}^{a}=4(ij|kl)^{a}-(ik|jl)^{a}-(il|jk)^{a}, \tag{6.22}$$

$$\frac{\partial F_{ij}}{\partial a}=F_{ij}^{a}+\sum_{k}^{\text{all}}U_{ki}^{a}F_{kj}+\sum_{k}^{\text{all}}U_{kj}^{a}F_{ik}+\sum_{k}^{\text{all}}\sum_{l}^{\text{d.o.}}U_{kl}^{a}A_{ijkl}. \tag{6.23}$$

Finally, the fourth derivative Eq. (5.30) or (4.14) may be reduced to

$$\begin{aligned}
\frac{\partial^4 E^{cl}}{\partial a\,\partial b\,\partial c\,\partial d} &= 2\sum_{ij}^{\text{d.o.}} h_{ii}^{abcd}+\sum_{ij}^{\text{d.o.}}[2(ii|jj)^{abcd}-(ij|ij)^{abcd}] \\
&\quad -2\sum_{ij}^{\text{d.o.}} F_{ij}\Bigg[S_{ij}^{abcd}-2\sum_{k}^{\text{all}}(S_{ik}^{abc}S_{jk}^{d}+S_{ik}^{bcd}S_{jk}^{a}+S_{ik}^{cda}S_{jk}^{b}+S_{ik}^{dab}S_{jk}^{c}) \\
&\quad -2\sum_{k}^{\text{all}}(S_{ik}^{ab}S_{jk}^{cd}+S_{ik}^{ac}S_{jk}^{bd}+S_{ik}^{ad}S_{jk}^{bc}) \\
&\quad +2\sum_{k}^{\text{all}}(U_{ik}^{ab}U_{jk}^{cd}+U_{ik}^{ac}U_{jk}^{bd}+U_{ik}^{ad}U_{jk}^{bc})+\mathcal{Q}_{ij}^{abcd}\Bigg]
\end{aligned}$$

$$+4\sum_{ij}^{\text{all}}\sum_{k}^{\text{d.o.}}(U_{ik}^{ab}U_{jk}^{cd}+U_{ik}^{ac}U_{jk}^{bd}+U_{ik}^{ad}U_{jk}^{bc})F_{ij}$$

$$+4\sum_{i}^{\text{all}}\sum_{j}^{\text{d.o.}}\sum_{k}^{\text{all}}\sum_{l}^{\text{d.o.}}(U_{ij}^{ab}U_{kl}^{cd}+U_{ij}^{ac}U_{kl}^{bd}+U_{ij}^{ad}U_{kl}^{bc})A_{ijkl}$$

$$+4\sum_{i}^{\text{all}}\sum_{j}^{\text{d.o.}}(U_{ij}^{ab}F_{ij}^{[cd]}+U_{ij}^{ac}F_{ij}^{[bd]}+U_{ij}^{ad}F_{ij}^{[bc]}+U_{ij}^{bc}F_{ij}^{[ad]}$$

$$+U_{ij}^{bd}F_{ij}^{[ac]}+U_{ij}^{cd}F_{ij}^{[ab]})$$

$$+4\sum_{i}^{\text{all}}\sum_{j}^{\text{d.o.}}(U_{ij}^{a}F_{ij}^{bcd}+U_{ij}^{b}F_{ij}^{cda}+U_{ij}^{c}F_{ij}^{dab}+U_{ij}^{d}F_{ij}^{abc})$$

$$+4\sum_{ij}^{\text{all}}\sum_{k}^{\text{d.o.}}(U_{ik}^{a}U_{jk}^{b}F_{ij}^{cd}+U_{ik}^{a}U_{jk}^{c}F_{ij}^{bd}+U_{ik}^{a}U_{jk}^{d}F_{ij}^{bc}+U_{ik}^{b}U_{jk}^{c}F_{ij}^{ad}$$

$$+U_{ik}^{b}U_{jk}^{d}F_{ij}^{ac}+U_{ik}^{c}U_{jk}^{d}F_{ij}^{ab})$$

$$+4\sum_{ij}^{\text{all}}\sum_{kl}^{\text{d.o.}}(U_{ik}^{a}U_{jl}^{b}A_{ikjl}^{cd}+U_{ik}^{a}U_{jl}^{c}A_{ikjl}^{bd}+U_{ik}^{a}U_{jl}^{d}A_{ikjl}^{bc}+U_{ik}^{b}U_{jl}^{c}A_{ikjl}^{ad}$$

$$+U_{ik}^{b}U_{jl}^{d}A_{ikjl}^{ac}+U_{ik}^{c}U_{jl}^{d}A_{ikjl}^{ab})$$

$$+4\sum_{ijk}^{\text{all}}\sum_{lm}^{\text{d.o.}}[(U_{im}^{a}U_{jm}^{b}U_{kl}^{c}+U_{im}^{b}U_{jm}^{c}U_{kl}^{a}+U_{im}^{c}U_{jm}^{a}U_{kl}^{b})A_{ijkl}^{d}$$

$$+(U_{im}^{b}U_{jm}^{c}U_{kl}^{d}+U_{im}^{c}U_{jm}^{d}U_{kl}^{b}+U_{im}^{d}U_{jm}^{b}U_{kl}^{c})A_{ijkl}^{a}$$

$$+(U_{im}^{c}U_{jm}^{d}U_{kl}^{a}+U_{im}^{d}U_{jm}^{a}U_{kl}^{c}+U_{im}^{a}U_{jm}^{c}U_{kl}^{d})A_{ijkl}^{b}$$

$$+(U_{im}^{d}U_{jm}^{a}U_{kl}^{b}+U_{im}^{a}U_{jm}^{b}U_{kl}^{d}+U_{im}^{b}U_{jm}^{d}U_{kl}^{a})A_{ijkl}^{c}]$$

$$+4\sum_{ijkl}^{\text{all}}\sum_{mn}^{\text{d.o.}}(U_{im}^{a}U_{jm}^{b}U_{kn}^{c}U_{ln}^{d}+U_{im}^{a}U_{jm}^{c}U_{kn}^{b}U_{ln}^{d}$$

$$+U_{im}^{a}U_{jm}^{d}U_{kn}^{b}U_{ln}^{c})A_{ijkl}$$

$$-2\sum_{i}^{\text{all}}\sum_{j}^{\text{d.o.}}\left[\mathscr{S}_{ij}^{abc}\left(\frac{\partial F_{ij}}{\partial d}-2\sum_{k}^{\text{all}}U_{ki}^{d}F_{kj}\right)+\mathscr{S}_{ij}^{bcd}\left(\frac{\partial F_{ij}}{\partial a}-2\sum_{k}^{\text{all}}U_{ki}^{a}F_{kj}\right)\right.$$

$$+\mathscr{S}_{ij}^{cda}\left(\frac{\partial F_{ij}}{\partial b}-2\sum_{k}^{\text{all}}U_{ki}^{b}F_{kj}\right)$$

$$\left.+\mathscr{S}_{ij}^{dab}\left(\frac{\partial F_{ij}}{\partial c}-2\sum_{k}^{\text{all}}U_{ki}^{c}F_{kj}\right)\right] \tag{6.24}$$

where

$$F_{ij}^{abc}=h_{ij}^{abc}+\sum_{k}^{\text{d.o.}}\{2(ij|kk)^{abc}-(ik|jk)^{abc}\} \tag{6.25}$$

$$A_{ijkl}^{ab}=4(ij|kl)^{ab}-(ik|jl)^{ab}-(il|jk)^{ab} \tag{6.26}$$

$$F_{ij}^{[ab]}=F_{ij}^{ab}+\sum_{k}^{\text{all}}(U_{kj}^{a}F_{ik}^{b}+U_{kj}^{b}F_{ik}^{a})+\sum_{k}^{\text{all}}\sum_{l}^{\text{d.o.}}(U_{kl}^{a}A_{ijkl}^{b}+U_{kl}^{b}A_{ijkl}^{a})$$

$$+\sum_{kl}^{\text{all}}\sum_{m}^{\text{d.o.}}(U_{kj}^{a}U_{lm}^{b}A_{iklm}+U_{km}^{a}U_{lj}^{b}A_{ilkm}+U_{km}^{a}U_{lm}^{b}A_{ijkl}). \tag{6.27}$$

6.4. *Energy derivative expressions using orbital energies*

When the SCF MO's are determined so that the Fock matrix is diagonal, the SCF condition is given by

$$F_{ij} = \delta_{ij}\varepsilon_i, \tag{6.28}$$

where the quantity ε having a single suffix is specifically called an orbital energy. The Eq. (6.28) is one of the expressions for the variational condition for the closed-shell SCF wavefunction. It should be noted that Eq. (6.28) defines orbital energies for virtual orbitals as well as for doubly occupied orbitals.

If we use the condition (6.28), the formulae for the energy derivatives become a bit simpler. Since the double sum over the terms involving the overlap derivatives may be replaced to a single sum, the first derivative (6.17) becomes

$$\frac{\partial E^{\text{cl}}}{\partial a} = 2\sum_{i}^{\text{d.o.}} h_{ii}^{a} + \sum_{ij}^{\text{d.o.}} \{2(ii|jj)^a - (ij|ij)^a\} - 2\sum_{i}^{\text{d.o.}} S_{ii}^{a}\varepsilon_i. \tag{6.29}$$

Similarly, the second derivative (6.18) may be written as

$$\begin{aligned}\frac{\partial^2 E^{\text{cl}}}{\partial a\, \partial b} = {} & 2\sum_{i}^{\text{d.o.}} h_{ii}^{ab} + \sum_{ij}^{\text{d.o.}} \{2(ii|jj)^{ab} - (ij|ij)^{ab}\} - 2\sum_{i}^{\text{d.o.}} \mathcal{S}_{ii}^{ab}\varepsilon_i \\ & + 4\sum_{i}^{\text{all}} \varepsilon_i \sum_{k}^{\text{d.o.}} U_{ik}^{a} U_{ik}^{b} + 4\sum_{i}^{\text{all}}\sum_{j}^{\text{d.o.}} (U_{ij}^{a} F_{ij}^{b} + U_{ij}^{b} F_{ij}^{a}) \\ & + 4\sum_{i}^{\text{all}}\sum_{j}^{\text{d.o.}}\sum_{k}^{\text{all}}\sum_{l}^{\text{d.o.}} U_{ij}^{a} U_{kl}^{b} A_{ijkl}.\end{aligned} \tag{6.30}$$

Equation (6.30) is given in a symmetric form to aid in the evaluation of the analytic second derivatives of the closed-shell SCF energy. It should be realized that there are difficulties in deriving a symmetric expression by directly taking the derivative of Eq. (6.29). If we explicitly used the fact that the Lagrangian matrix is diagonal during the differentiation, one must remember that there are hidden terms involving the off-diagonal elements of the Fock matrix. In this respect, one must keep all the elements of the Fock matrix and use the condition for the closed-shell SCF wavefunction in the very last stage to get a final symmetric expression. In this derivation, therefore, we keep all elements of the derivative of the Fock matrix, although the following relation holds

$$\frac{\partial F_{ij}}{\partial a} = \delta_{ij}\frac{\partial \varepsilon_i}{\partial a}. \tag{6.31}$$

By the same token one should note that Eqs. (6.18) and (6.20) avoid the singularity problem [69] in the evaluation of derivatives of the closed-shell SCF energy even when the system has degenerate orbitals in the occupied space. This singularity problem does not appear if one uses the general open-shell formalism described in Sect. 5, since the diagonality of the Lagrangian and derivative Lagrangian matrices is never utilized.

The last term involving the derivatives of the Fock matrix elements in Eqs. (6.20) and (6.24) may be reexpressed by using the conditions (6.28) and (6.31) in the diagonal form,

$$-2\sum_{i}^{\text{all}}\sum_{j}^{\text{d.o.}}\mathcal{S}_{ij}^{ab}\left(\frac{\partial F_{ij}}{\partial c}-2\sum_{k}^{\text{all}}U_{ki}^{c}F_{kj}\right)=-2\sum_{i}^{\text{d.o.}}\mathcal{S}_{ii}^{ab}\frac{\partial\varepsilon_i}{\partial c}+4\sum_{i}^{\text{all}}\sum_{j}^{\text{d.o.}}\mathcal{S}_{ij}^{ab}U_{ji}^{c}\varepsilon_j. \tag{6.32}$$

Using the reduction (6.32), the third derivative for closed-shell SCF wavefunction (6.20) becomes

$$\begin{aligned}
\frac{\partial^3 E^{\text{cl}}}{\partial a\,\partial b\,\partial c} &= 2\sum_{i}^{\text{d.o.}} h_{ii}^{abc}+\sum_{ij}^{\text{d.o.}}\{2(ii\,|\,jj)^{abc}-(ij\,|\,ij)^{abc}\}\\
&-2\sum_{i}^{\text{d.o.}}\varepsilon_i\Bigg[S_{ii}^{abc}-2\sum_{k}^{\text{all}}(S_{ik}^{ab}S_{ik}^{c}+S_{ik}^{bc}S_{ik}^{a}+S_{ik}^{ca}S_{ik}^{b})\\
&+2\sum_{kl}^{\text{all}}(S_{ik}^{a}S_{il}^{b}S_{kl}^{c}+S_{ik}^{b}S_{il}^{c}S_{kl}^{a}+S_{ik}^{c}S_{il}^{a}S_{kl}^{b})\Bigg]\\
&+4\sum_{i}^{\text{all}}\sum_{j}^{\text{d.o.}}(U_{ij}^{a}F_{ij}^{bc}+U_{ij}^{b}F_{ij}^{ca}+U_{ij}^{c}F_{ij}^{ab})\\
&+4\sum_{i}^{\text{all}}\sum_{j}^{\text{all}}\sum_{k}^{\text{d.o.}}(U_{ik}^{a}U_{jk}^{b}F_{ij}^{c}+U_{ik}^{b}U_{jk}^{c}F_{ij}^{a}+U_{ik}^{c}U_{jk}^{a}F_{ij}^{b})\\
&+4\sum_{i}^{\text{all}}\sum_{j}^{\text{d.o.}}\sum_{k}^{\text{all}}\sum_{l}^{\text{d.o.}}(U_{ij}^{a}U_{kl}^{b}A_{ijkl}^{c}+U_{ij}^{b}U_{kl}^{c}A_{ijkl}^{a}+U_{ij}^{c}U_{kl}^{a}A_{ijkl}^{b})\\
&+4\sum_{i}^{\text{all}}\sum_{j}^{\text{d.o.}}\sum_{k}^{\text{all}}\sum_{l}^{\text{all}}\sum_{m}^{\text{d.o.}}(U_{ij}^{a}U_{km}^{b}U_{lm}^{c}+U_{ij}^{b}U_{km}^{c}U_{lm}^{a}+U_{ij}^{c}U_{km}^{a}U_{lm}^{b})A_{ijkl}\\
&-2\sum_{i}^{\text{d.o.}}\left(\mathcal{S}_{ii}^{ab}\frac{\partial\varepsilon_i}{\partial c}+\mathcal{S}_{ii}^{bc}\frac{\partial\varepsilon_i}{\partial a}+\mathcal{S}_{ii}^{ca}\frac{\partial\varepsilon_i}{\partial b}\right)\\
&+4\sum_{i}^{\text{d.o.}}\varepsilon_i\sum_{j}^{\text{all}}(\mathcal{S}_{ij}^{ab}U_{ij}^{c}+\mathcal{S}_{ij}^{bc}U_{ij}^{a}+\mathcal{S}_{ij}^{ca}U_{ij}^{b}),
\end{aligned} \tag{6.33}$$

where

$$\frac{\partial\varepsilon_i}{\partial a}=\varepsilon_i^{a}-S_{ii}^{a}\varepsilon_i+\sum_{k}^{\text{all}}\sum_{l}^{\text{d.o.}}U_{kl}^{a}A_{iikl}. \tag{6.34}$$

$$\varepsilon_i^{a}=h_{ii}^{a}+\sum_{k}^{\text{d.o.}}\{2(ii\,|\,kk)^{a}-(ik\,|\,ik)^{a}\}. \tag{6.35}$$

The fourth derivative expression may be reduced in a similar manner.

7. Conclusions

In this paper we have set out in systematic and explicit detail the relationships between the general expressions for configuration interaction (CI) energy derivatives and those necessarily simpler expressions for self-consistent-field (SCF) and multi-configuration (MC) SCF energy derivatives. The correspondences obtained provide insight into the general structure of the energy derivative formalism.

The present CI energy derivative expressions do not yet take advantage of the efficiencies arising from the Z-vector method of Handy and Schaefer [70]. The Z-vector method, of course, has been a critical ingredient in the development of the most efficient computational implementations to date for CI energy first and second derivatives [31, 33]. The most efficient CI third and fourth derivative methods will also use the Z-vector approach, unless some new insight is discovered prior to the first computational implementation. Nevertheless, the use in the present formal paper of the nth order CPHF equations for the nth CI energy derivative expressions simplifies the necessary mathematical manipulations. Furthermore, the present formalism provides the fundamental starting point for derivations incorporating the Z-vector approach.

It should be emphasized that analytic first and second derivative methods for CI, MCSCF, general open-shell and closed-shell SCF wavefunctions have already been implemented and are proving to be of great value in the study of molecular systems of chemical interest [71–75]. Although there exist formal expressions in operator form for third and fourth energy derivatives for correlated wavefunctions [76–79], and Hartree-Fock wavefunctions [80], the equations presented here are more explicit, and perhaps more useful for practical implementations.

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