Generalization of analytic energy derivatives for configuration interaction wave functions

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This paper takes the form of a review including some original contributions. A fresh derivation of analytic energy derivative expressions for configuration interaction (CI) wave functions is presented. In this method the CI energy is described by $\sum_{IJ} C_I C_J (H_{IJ} - \delta_{IJ} E)$ so that the orthonormality condition is explicitly included therein. In the sequence of differentiations up to fourth order it will be demonstrated that each derivative may be expressed in terms of $(H_{IJ} - \delta_{IJ} E)$ and its derivatives in a symmetric way with respect to the interchange of differential variables. In a similar manner, the CI variational condition may be described in an equation which explicitly includes the normalization condition. It is shown that the differentiation of the modified variational condition produces the coupled perturbed configuration interaction (CPCI) equations in directly soluble and compact forms. The necessary formulae for the energy derivatives up to fourth order and the CPCI equations up to second order are explicitly given.

Key words: Analytic CI derivatives — CPCI equations

1. Introduction

Since 1970, much theoretical effort in quantum chemistry has been expended to obtain detailed information concerning potential energy surfaces, as the computation of accurate wave functions has become practical for many chemical systems [1]. The analytical evaluation of the first and second derivatives with respect to

nuclear coordinates has widely opened the theoretical window toward molecular structure and chemical reactions in the framework of *ab initio* quantum mechanical methods [2].

The analytical evaluation of derivative atomic orbital (AO) integrals using Gaussian basis functions was first applied successfully to the energy gradient using self-consistent-field (SCF) wave functions [3]. Following the pioneering work by Pople and coworkers [4] on analytic second derivatives of the closed shell SCF energy, subsequent studies have seen the development of methods for the evaluation of analytic first derivatives of correlated energies using configuration interaction (CI) wave functions [5], Møller–Plesset perturbation theory [4, 6] and the coupled-cluster [7] methods as well as analytic second derivatives for general SCF wave functions [8]. The analytic evaluation of second derivatives using CI [9] and multi-configuration (MC) SCF [10] wave functions has also been achieved by several groups. Most recently the first analytic *third* derivative methods for SCF wave functions have appeared, involving Raman intensities [11] as well as energy third derivatives [12].

Although one obtains much more information concerning potential energy hypersurfaces by going to higher orders of derivatives, the degree of difficulty in formulation and implementation also increases significantly, especially when one uses correlated wave functions [5–10]. The orthodox way to solve the Schrödinger equation in terms of one-electron basis functions is to construct a CI wave function, where the electron configurations are based on Hartree–Fock molecular orbitals described as linear combinations of atomic orbitals [13]. While the full CI wave function is the ultimate point to be reached, various approximations have to be made for realistic applications to the majority of chemical systems.

It is evident that typical variationally determined correlated wave functions, such as MCSCF and CI, invoke the orthonormality condition both in the MO and CI spaces, as well as the variational condition for each space. In this study we are mainly concerned with two (orthonormality and variational) conditions on the CI space. It is desirable to have general expressions for analytic energy derivatives of the CI wave function, since the corresponding derivative expressions of other variationally determined wave functions, such as MCSCF and SCF, may be derived as limiting cases of the general CI formulae by imposing two additional conditions on the MO space.

The format for this paper is primarily that of a review, but also presenting a new perspective on the derivation of analytic derivative expressions. In the following section an energy expression which explicitly includes the normalization condition for the CI wave function is first proposed. Then it is shown that sequential differentiation of the new energy expression straightforwardly produces higher energy derivative formulae in a manner symmetric with respect to the interchange of differential variables.

In Sect. 3, the CI variational condition is introduced in an equation that explicitly includes the normalization condition. Then it will be demonstrated that the

differentiation of the modified variational condition generates the coupled perturbed configuration interaction (CPCI) equations in directly soluble and compact forms.

After briefly describing the derivatives of the MO coefficients in Sect. 4, all necessary formulae for the CI energy derivatives up to fourth order and the derivatives of the Hamiltonian matrix elements up to second order will be explicitly given in Sect. 5.

In light of the complexity of the formalism described in the Sects. 3-5, we detail possible computational procedures to obtain the analytic first and second derivatives for CI wave functions and discuss the various problems involved in a practical implementation in Sect. 6.

It is to be emphasized that the primary goal of this paper is to present a fresh approach to the *derivation* of higher CI energy derivatives. In that sense, the present work is most closely related to earlier research by Helgaker et al. [2d] and by Almlöf and Taylor [14]. In this context the more recent paper by King and Komornicki [15] should also be cited. The most efficient computational method available at this time for analytic CI derivatives is that of Rice et al. (RAHLS) [5g]. Similarly, the fastest currently available CI second derivative method is that of Lee et al. (LHRSS) [9b]. The CI first and second derivative formalism presented here will not be competitive with RAHLS and LHRSS until it is modified to incorporate the Z-vector method of Handy and Schaefer [16].

2. General theory of energy derivative formula using CI wave functions

The CI wave function Ψ is described as a linear combination of electronic configurations Φ_I which are constructed from various electron occupations of the molecular orbitals

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

Here, we assume that we are focusing on a single electronic state described by Ψ, i.e. $\{C_I\}$ is one of the sets obtained by solving the eigenvalue problem

$$H |\Psi\rangle = E |\Psi\rangle. \tag{2.2}$$

Definining the CI Hamiltonian matrix

$$H_{IJ} = \langle \Phi_I |H|\Phi_J\rangle = \sum_{ij} \gamma_{ij}^{IJ} h_{ij} + \sum_{ijkl} \Gamma_{ijkl}^{IJ} (ij \,|\, kl), \tag{2.3}$$

the eigenvalue problem (secular equation) may be expressed by

$$\sum_J C_J (H_{IJ} - \delta_{IJ} E) = 0 \tag{2.4}$$

which is the variational condition for the determination of the wave function (2.1), where h_{ij} and $(ij \,|\, kl)$ are one- and two-electron molecular orbital (MO) integrals, and γ_{ij}^{IJ} and Γ_{ijkl}^{IJ} are the one- and two-electron coupling constants between electronic configurations and molecular orbitals.

Since the wave function is normalized, we have the condition

$$\sum_I C_I^2 = 1. \tag{2.5}$$

While the electronic energy is usually described by

$$E = \sum_{IJ} C_I C_J H_{IJ}, \tag{2.6}$$

the energy expression in the following form will be used in this paper

$$\sum_{IJ} C_I C_J (H_{IJ} - \delta_{IJ} E) = 0 \tag{2.7}$$

so that the equation explicitly includes the normalization condition (2.5).

2.1. First derivatives

The differentiation of Eq. (2.7) with respect to a nuclear coordinate a gives the expression for the CI gradient,

$$\sum_{IJ} C_I C_J \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E}{\partial a} \right) + 2 \sum_I \frac{\partial C_I}{\partial a} \sum_J C_J (H_{IJ} - \delta_{IJ} E) = 0. \tag{2.8}$$

The second term of Eq. (2.8) has zero value due to the variational condition (2.4), and therefore

$$\sum_{IJ} C_I C_J \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E}{\partial a} \right) = 0 \tag{2.9}$$

leading to a familiar expression for the CI gradient

$$\frac{\partial E}{\partial a} = \sum_{IJ} C_I C_J \frac{\partial H_{IJ}}{\partial a}. \tag{2.10}$$

Note that two conditions are included in deriving Eq. (2.10), although only the variational condition (2.4) appears to be used. This is because Eq. (2.7) itself includes the orthonormality condition (2.5).

2.2. Second derivatives

The CI second derivative may be obtained by further differentiation of Eq. (2.8) with respect to a second nuclear coordinate b

$$\frac{\partial^2}{\partial a \, \partial b} \left[\sum_{IJ} C_I C_J (H_{IJ} - \delta_{IJ} E) \right]$$

$$= \sum_{IJ} C_I C_J \left(\frac{\partial^2 H_{IJ}}{\partial a \, \partial b} - \delta_{IJ} \frac{\partial^2 E}{\partial a \, \partial b} \right) + 2 \sum_I \frac{\partial C_I}{\partial a} \sum_J C_J \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E}{\partial b} \right)$$

$$+ 2 \sum_I \frac{\partial C_I}{\partial b} \sum_J C_J \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E}{\partial a} \right) + 2 \sum_{IJ} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} (H_{IJ} - \delta_{IJ} E)$$

$$+ 2 \sum_I \frac{\partial^2 C_I}{\partial a \, \partial b} \sum_J C_J (H_{IJ} - \delta_{IJ} E) = 0. \tag{2.11}$$

One should note that the last term of Eq. (2.11) which includes the second derivatives of the CI coefficients vanishes due to the variational condition (2.4).

The differentiation of the variational condition (2.4) gives the relationship between the derivatives of CI coefficients and those of Hamiltonian matrix elements

$$\sum_J \frac{\partial C_J}{\partial a}(H_{IJ} - \delta_{IJ}E) + \sum_J C_J \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ}\frac{\partial E}{\partial a}\right) = 0 \tag{2.12}$$

which is equivalent to the so-called coupled perturbed configuration interaction (CPCI) equation.

Substituting Eq. (2.12) into the second and third terms in Eq. (2.11), one may obtain the compact formula

$$\sum_{IJ} C_I C_J \left(\frac{\partial^2 H_{IJ}}{\partial a\,\partial b} - \delta_{IJ}\frac{\partial^2 E}{\partial a\,\partial b}\right) - 2\sum_{IJ} \frac{\partial C_I}{\partial a}\frac{\partial C_J}{\partial b}(H_{IJ} - \delta_{IJ}E) = 0. \tag{2.13}$$

Alternatively, one may differentiate Eq. (2.9) instead of the entire Eq. (2.8) in order to get the second derivative of CI energy. This leads to

$$\frac{\partial^2 E}{\partial a\,\partial b} = \sum_{IJ} C_I C_J \frac{\partial^2 H_{IJ}}{\partial a\,\partial b} + 2\sum_I \frac{\partial C_I}{\partial b}\sum_J C_J \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ}\frac{\partial E}{\partial a}\right). \tag{2.14}$$

Although this equation does not seem to be symmetric with respect to the interchange of variables a and b, it may be proved to be identical to the symmetric form of Eq. (2.13) using the following relationship (for related discussion see [15])

$$\sum_I \frac{\partial C_I}{\partial a}\sum_J C_J \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ}\frac{\partial E}{\partial b}\right) = \sum_I \frac{\partial C_I}{\partial b}\sum_J C_J \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ}\frac{\partial E}{\partial a}\right)$$

$$= -\sum_{IJ} \frac{\partial C_I}{\partial a}\frac{\partial C_J}{\partial b}(H_{IJ} - \delta_{IJ}E) \tag{2.15}$$

which is derived from the CPCI equation (2.12).

2.3. Third derivatives

Similarly, the further differentiation of Eq. (2.13) with respect to a third variable c gives the third derivative formula

$$\frac{\partial^3}{\partial a\,\partial b\,\partial c}\left[\sum_{IJ} C_I C_J (H_{IJ} - \delta_{IJ}E)\right]$$

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

$$- 2\sum_{IJ} \frac{\partial C_I}{\partial a}\frac{\partial C_J}{\partial b}\left(\frac{\partial H_{IJ}}{\partial c} - \delta_{IJ}\frac{\partial E}{\partial c}\right) - 2\sum_I \frac{\partial C_I}{\partial a}\sum_J \frac{\partial^2 C_J}{\partial b\,\partial c}(H_{IJ} - \delta_{IJ}E)$$

$$- 2\sum_I \frac{\partial C_I}{\partial b}\sum_J \frac{\partial^2 C_J}{\partial c\,\partial a}(H_{IJ} - \delta_{IJ}E) = 0. \tag{2.16}$$

Using the second derivative of the variational condition Eq. (2.4),

$$
\sum_J \frac{\partial^2 C_J}{\partial a \, \partial b}(H_{IJ} - \delta_{IJ}E) + \sum_J \left[\frac{\partial C_J}{\partial a}\left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ}\frac{\partial E}{\partial b} \right) + \frac{\partial C_J}{\partial b}\left(\frac{H_{IJ}}{\partial a} - \delta_{IJ}\frac{\partial E}{\partial a} \right) \right.
$$
$$
\left. + C_J \left(\frac{\partial^2 H_{IJ}}{\partial a \, \partial b} - \delta_{IJ}\frac{\partial^2 E}{\partial a \, \partial b} \right) \right] = 0, \tag{2.17}
$$

the last two terms in Eq. (2.16) may be rewritten without including the second derivatives of CI coefficients. The fact that the third-order energy only requires the first-order CI coefficients is called the Wigner's $2n + 1$ rule [17], and has been demonstrated for an analytical third derivative expression for MCSCF wave functions by Pulay [18].

Finally, one can get the third-order expression for the CI energy,

$$
\sum_{IJ} C_I C_J \left(\frac{\partial^3 H_{IJ}}{\partial a \, \partial b \, \partial c} - \delta_{IJ}\frac{\partial^3 E}{\partial a \, \partial b \, \partial c} \right)
$$
$$
+ 2 \sum_I C_I \sum_J \left[\frac{\partial C_J}{\partial a}\left(\frac{\partial^2 H_{IJ}}{\partial b \, \partial c} - \delta_{IJ}\frac{\partial^2 E}{\partial b \, \partial c} \right) + \frac{\partial C_J}{\partial b}\left(\frac{\partial^2 H_{IJ}}{\partial c \, \partial a} - \delta_{IJ}\frac{\partial^2 E}{\partial c \, \partial a} \right) \right.
$$
$$
\left. + \frac{\partial C_J}{\partial c}\left(\frac{\partial^2 H_{IJ}}{\partial a \, \partial b} - \delta_{IJ}\frac{\partial^2 E}{\partial a \, \partial b} \right) \right]
$$
$$
+ 2 \sum_{IJ} \left[\frac{\partial C_I}{\partial a}\frac{\partial C_J}{\partial b}\left(\frac{\partial H_{IJ}}{\partial c} - \delta_{IJ}\frac{\partial E}{\partial c} \right) + \frac{\partial C_I}{\partial b}\frac{\partial C_J}{\partial c}\left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ}\frac{\partial E}{\partial a} \right) \right.
$$
$$
\left. + \frac{\partial C_I}{\partial c}\frac{\partial C_J}{\partial a}\left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ}\frac{\partial E}{\partial b} \right) \right] = 0. \tag{2.18}
$$

In this equation, the terms including the second derivatives of CI energy, such as $\delta_{IJ}\,\partial^2 E/\partial a \, \partial b$, may be eliminated using the condition derived from the derivative of the normalization condition (2.5),

$$
\sum_I C_I \frac{\partial C_I}{\partial a} = 0. \tag{2.19}
$$

These terms, however, are included for further differentiation so that one may obtain higher-order derivatives in symmetric forms.

2.4. Fourth derivatives

The fourth derivative relation may be obtained by differentiating Eq. (2.18) with respect to a fourth nuclear coordinate d,

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

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

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

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

$$-2\sum_{IJ}\left(\frac{\partial^2 C_I}{\partial a\,\partial b}\frac{\partial^2 C_J}{\partial c\,\partial d}+\frac{\partial^2 C_I}{\partial a\,\partial c}\frac{\partial^2 C_J}{\partial b\,\partial d}+\frac{\partial^2 C_I}{\partial a\,\partial d}\frac{\partial^2 C_J}{\partial b\,\partial c}\right)(H_{IJ}-\delta_{IJ}E)=0 \qquad (2.20)$$

where we used the relation (2.17) which is the second-order CPCI equation. In the fourth derivative expression (2.20), the third derivatives of CI energy may be eliminated using the condition (2.19) as well as in the case of the third derivative (2.18).

It is noticeable that, in the sequence of differentiation, each term always carries the Hamiltonian matrix and the energy in the form of $(H_{IJ}-\delta_{IJ}E)$ and its derivatives. This fact is one of the advantages of getting the higher derivatives by differentiating Eq. (2.7). In the present derivation the CPCI equations may be effectively introduced to express the results in terms of lower order derivatives of the CI coefficients. Moreover, one can avoid missing the derivatives of "hidden terms" due to the conditions used in the determination of the wave function.

3. Coupled perturbed configuration interaction (CPCI) equations

The CPCI equations already introduced as Eqs. (2.12) and (2.17) are the simultaneous equations which provide the derivatives of the CI coefficients. While coupled perturbed equations are generally obtained by collecting the same order terms of the Taylor expansion about an infinitesimal nuclear displacement, we have derived them straightforwardly by differentiating the variational condition (2.4) as shown in the previous section. Equations (2.12) and (2.17), however, cannot be solved directly, because these equations have a singularity due to the constraint (2.5). In order to solve CPCI equations practically, Eq. (2.4) can be modified by adding the zero term $\theta(1-\sum_I C_I^2)$, an approach which is similar to the Lagrange multiplier method. Since the factor θ may be arbitrarily chosen, we use $\theta=1$ in the following derivation

$$\sum_J C_J\left\{H_{IJ}-\delta_{IJ}\left(E+1-\sum_K C_K^2\right)\right\}=0. \qquad (3.1)$$

The differentiation of Eq. (3.1) with respect to a variable a gives a practically soluble first-order CPCI equation

$$\sum_J (H_{IJ}-\delta_{IJ}E+2C_IC_J)\frac{\partial C_J}{\partial a}=-\sum_J\left(\frac{\partial H_{IJ}}{\partial a}-\delta_{IJ}\frac{\partial E}{\partial a}\right)C_J. \qquad (3.2)$$

It should be realized that the determinant of the left-hand side $|H_{IJ}-\delta_{IJ}E+2C_IC_J|$ is no longer zero when one explicitly includes the derivative form (2.19) of the normalization condition (2.5). This technique is mathematically equivalent

to the projection operator method from electronic states to configuration space in the quadratically convergent (Newton–Raphson) MCSCF procedure by Lengsfield and Liu [19].

The second-order CPCI equation may be obtained by the further differentiation of Eq. (3.2),

$$\sum_J (H_{IJ} - \delta_{IJ}E + 2C_I C_J) \frac{\partial^2 C_J}{\partial a\, \partial b} = -\sum_J \left(\frac{\partial^2 H_{IJ}}{\partial a\, \partial b} - \delta_{IJ} \frac{\partial^2 E}{\partial a\, \partial b} \right) C_J$$

$$-\sum_J \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E}{\partial a} + C_I \frac{\partial C_J}{\partial a} \right) \frac{\partial C_J}{\partial b}$$

$$-\sum_J \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E}{\partial b} + C_I \frac{\partial C_J}{\partial b} \right) \frac{\partial C_J}{\partial a}. \qquad (3.3)$$

Comparing this equation with (2.17), it is seen that the second-order CPCI equation naturally includes the relation from the second derivative of the normalization condition (2.5),

$$\sum_I \left(C_I \frac{\partial^2 C_I}{\partial a\, \partial b} + \frac{\partial C_I}{\partial a} \frac{\partial C_I}{\partial b} \right) = 0. \qquad (3.4)$$

The explicit formula for the derivatives of the Hamiltonian matrix appearing in the CPCI equations will be given in the Sect. 5.

4. Derivatives of molecular orbital coefficients

Before writing down the practical formulae for the derivatives of the CI energy, we shall discuss the derivatives of the MO coefficients which appear in the expression for the derivatives of Hamiltonian matrix elements H_{IJ}.

Since the CI Hamiltonian matrix is constructed from MO integrals, the derivatives with respect to nuclear coordinates include both the derivatives of AO integrals, $h_{\mu\nu}$ and $(\mu\nu | \rho\sigma)$, and the derivatives of MO coefficients. The latter may usually be expressed by the U matrices. The derivatives of the μth coefficient of the ith molecular orbital, C_μ^i, define U matrices as follows.

$$\frac{\partial C_\mu^i}{\partial a} = \sum_m U_{mi}^a C_\mu^m \qquad (4.1)$$

$$\frac{\partial^2 C_\mu^i}{\partial a\, \partial b} = \sum_m U_{mi}^{ab} C_\mu^m \qquad (4.2)$$

$$\frac{\partial^3 C_\mu^i}{\partial a\, \partial b\, \partial c} = \sum_m U_{mi}^{abc} C_\mu^m \qquad (4.3)$$

$$\frac{\partial^4 C_\mu^i}{\partial a\, \partial b\, \partial c\, \partial d} = \sum_m U_{mi}^{abcd} C_\mu^m. \qquad (4.4)$$

In carrying out the differentiation of the MO coefficients, it is convenient to have following relations

$$\frac{\partial U_{ij}^a}{\partial b} = U_{ij}^{ab} - \sum_k U_{ik}^b U_{kj}^a \qquad (4.5)$$

$$\frac{\partial U_{ij}^{ab}}{\partial c} = U_{ij}^{abc} - \sum_k U_{ik}^c U_{kj}^{ab} \tag{4.6}$$

$$\frac{\partial U_{ij}^{abc}}{\partial d} = U_{ij}^{abcd} - \sum_k U_{ik}^d U_{kj}^{abc}. \tag{4.7}$$

The U matrices may be obtained by solving the coupled equations based on the particular procedure by which the molecular orbitals are determined. The coupled perturbed Hartree–Fock (CPHF) equations for the nuclear displacement based on the closed-shell SCF method were presented by Gerratt and Mills in 1968 [20]. Pople's group and the Berkeley group have utilized the closed-shell CPHF equation to evaluate *ab initio* SCF second derivatives [4] and CI gradients [5]. More recently, CPHF equations have been extended to general open-shell [8], two-configuration SCF [10f], and multi-configuration (MC) SCF wave functions [10].

5. Derivatives of the CI energy

5.1. First derivatives

Using the U^a matrices described in the previous section, the first derivative of the CI Hamiltonian matrix elements may be given as follows.

$$\frac{\partial H_{IJ}}{\partial a} = \sum_{ij} \gamma_{ij}^{IJ} \frac{\partial h_{ij}}{\partial a} + \sum_{ijkl} \Gamma_{ijkl}^{IJ} \frac{\partial (ij|kl)}{\partial a} \tag{5.1}$$

$$= H_{IJ}^a + 2 \sum_{im} U_{im}^a X_{im}^{IJ} \tag{5.2}$$

where

$$H_{IJ}^a = \sum_{ij} \gamma_{ij}^{IJ} h_{ij}^a + \sum_{ijkl} \Gamma_{ijkl}^{IJ} (ij|kl)^a \tag{5.3}$$

$$X_{im}^{IJ} = \sum_j \gamma_{mj}^{IJ} h_{ij} + 2 \sum_{jkl} \Gamma_{mjkl}^{IJ} (ij|kl) \tag{5.4}$$

$$h_{ij}^a = \sum_{\mu\nu} C_\mu^i C_\nu^j \frac{\partial h_{\mu\nu}}{\partial a} \tag{5.5}$$

and

$$(ij|kl)^a = \sum_{\mu\nu\rho\sigma} C_\mu^i C_\nu^j C_\rho^k C_\sigma^l \frac{\partial (\mu\nu|\rho\sigma)}{\partial a}. \tag{5.6}$$

Defining the density matrices

$$\gamma_{ij} = \sum_{IJ} C_I C_J \gamma_{ij}^{IJ}, \tag{5.7}$$

and

$$\Gamma_{ijkl} = \sum_{IJ} C_I C_J \Gamma_{ijkl}^{IJ}, \tag{5.8}$$

the alternative energy expression of Eq. (2.6) is given in the integral form

$$E = \sum_{ij} \gamma_{ij} h_{ij} + \sum_{ijkl} \Gamma_{ijkl} (ij|kl). \tag{5.9}$$

The first derivative of the CI energy, i.e. CI gradient, is obtained by

$$\frac{\partial E}{\partial a} = \sum_{ij} \gamma_{ij} h_{ij}^a + \sum_{ijkl} \Gamma_{ijkl} (ij|kl)^a + 2 \sum_{im} U_{im}^a X_{im}, \tag{5.10}$$

where X is the Lagrangian matrix defined as

$$X_{im} = \sum_{j} \gamma_{mj} h_{ij} + 2 \sum_{jkl} \Gamma_{mjkl} (ij|kl). \tag{5.11}$$

Note that the matrix X is not in general symmetric with respect to the interchange of the indices i and m.

5.2. Second derivatives

An expression for the second derivative of the electronic energy of CI wave functions may be obtained from Eq. (2.13),

$$\frac{\partial^2 E}{\partial a\, \partial b} = \sum_{IJ} C_I C_J \frac{\partial^2 H_{IJ}}{\partial a\, \partial b} - 2 \sum_{IJ} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} (H_{IJ} - \delta_{IJ} E). \tag{5.12}$$

The second derivative of the Hamiltonian matrix element H_{IJ} in the first term of Eq. (5.12) is explicitly written as

$$\frac{\partial^2 H_{IJ}}{\partial a\, \partial b} = \sum_{ij} \gamma_{ij}^{IJ} \frac{\partial^2 h_{ij}}{\partial a\, \partial b} + \sum_{ijkl} \Gamma_{ijkl}^{IJ} \frac{\partial^2 (ij|kl)}{\partial a\, \partial b} \tag{5.13}$$

$$= H_{IJ}^{ab} + 2 \sum_{im} (U_{im}^{ab} X_{im}^{IJ} + U_{im}^a X_{im}^{IJb} + U_{im}^b X_{im}^{IJa})$$

$$+ 2 \sum_{im} \sum_{jn} U_{im}^a U_{jn}^b Y_{imjn}^{IJ} \tag{5.14}$$

where

$$H_{IJ}^{ab} = \sum_{ij} \gamma_{ij}^{IJ} h_{ij}^{ab} + \sum_{ijkl} \Gamma_{ijkl}^{IJ} (ij|kl)^{ab} \tag{5.15}$$

$$X_{im}^{IJa} = \sum_{j} \gamma_{mj}^{IJ} h_{ij}^a + 2 \sum_{jkl} \Gamma_{mjkl}^{IJ} (ij|kl)^a \tag{5.16}$$

$$Y_{imjn}^{IJ} = \gamma_{mn}^{IJ} h_{ij} + 2 \sum_{kl} \{ \Gamma_{mnkl}^{IJ} (ij|kl) + 2\Gamma_{mknl}^{IJ} (ik|jl) \} \tag{5.17}$$

$$h_{ij}^{ab} = \sum_{\mu\nu} C_\mu^i C_\nu^j \frac{\partial^2 h_{\mu\nu}}{\partial a\, \partial b} \tag{5.18}$$

and

$$(ij|kl)^{ab} = \sum_{\mu\nu\rho\sigma} C_\mu^i C_\nu^j C_\rho^k C_\sigma^l \frac{\partial^2 (\mu\nu|\rho\sigma)}{\partial a\, \partial b}. \tag{5.19}$$

The CI second derivative may now be explicitly given by combining Eqs. (5.12)–(5.19).

$$\frac{\partial^2 E}{\partial a\, \partial b} = \sum_{ij} \gamma_{ij} h_{ij}^{ab} + \sum_{ijkl} \Gamma_{ijkl} (ij|kl)^{ab} + 2 \sum_{im} U_{im}^{ab} X_{im}$$

$$+ 2 \sum_{im} (U_{im}^a X_{im}^b + U_{im}^b X_{im}^a) + 2 \sum_{im} \sum_{jn} U_{im}^a U_{jn}^b Y_{imjn}$$

$$- 2 \sum_{IJ} \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b} (H_{IJ} - \delta_{IJ} E) \tag{5.20}$$

where

$$X_{im}^a = \sum_j \gamma_{mj} h_{ij}^a + 2 \sum_{jkl} \Gamma_{mjkl} (ij|kl)^a \tag{5.21}$$

and

$$Y_{imjn} = \gamma_{mn} h_{ij} + 2 \sum_{kl} \{\Gamma_{mnkl} (ij|kl) + 2\Gamma_{mknl} (ik|jl)\}. \tag{5.22}$$

While $X_{im} \neq X_{mi}$ and $X_{im}^a \neq X_{mi}^a$, the Y matrix has the following symmetry properties

$$Y_{imjn} = Y_{jnim} \neq Y_{mijn} = Y_{jnmi} \neq Y_{imnj} = Y_{njim} \neq Y_{minj} = Y_{njmi}. \tag{5.23}$$

The derivative of the CI coefficients $\partial C_I / \partial a$ may be determined by solving the first-order CPCI Eq. (3.2). The U^{ab} matrices which are related to the second derivative of MO coefficients may be evaluated by solving the second-order CPHF equations [21].

5.3. Third derivatives

The third derivative expression for the CI energy is given from Eq. (2.18)

$$\frac{\partial^3 E}{\partial a \, \partial b \, \partial c} = \sum_{IJ} C_I C_J \frac{\partial^3 H_{IJ}}{\partial a \, \partial b \, \partial c}$$

$$+ 2 \sum_I C_I \sum_J \left(\frac{\partial C_J}{\partial a} \frac{\partial^2 H_{IJ}}{\partial b \, \partial c} + \frac{\partial C_J}{\partial b} \frac{\partial^2 H_{IJ}}{\partial c \, \partial a} + \frac{\partial C_J}{\partial c} \frac{\partial^2 H_{IJ}}{\partial a \, \partial b} \right)$$

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

$$\left. + \frac{\partial C_I}{\partial c} \frac{\partial C_J}{\partial a} \left(\frac{\partial H_{IJ}}{\partial b} - \delta_{IJ} \frac{\partial E}{\partial b} \right) \right]. \tag{5.24}$$

The terms involving the second derivatives of the energy in Eq. (2.18) are eliminated by the condition (2.19). The first term in Eq. (5.24) may be expressed as follows

$$\sum_{IJ} C_I C_J \frac{\partial^3 H_{IJ}}{\partial a \, \partial b \, \partial c} = \sum_{ij} \gamma_{ij} h_{ij}^{abc} + \sum_{ijkl} \Gamma_{ijkl} (ij|kl)^{abc} + 2 \sum_{im} U_{im}^{abc} X_{im}$$

$$+ 2 \sum_{im} (U_{im}^{ab} X_{im}^c + U_{im}^{bc} X_{im}^a + U_{im}^{ca} X_{im}^b)$$

$$+ 2 \sum_{im} \sum_{jn} (U_{im}^{ab} U_{jn}^c + U_{im}^{bc} U_{jn}^a + U_{im}^{ca} U_{jn}^b) Y_{imjn}$$

$$+ 2 \sum_{im} (U_{im}^a X_{im}^{bc} + U_{im}^b X_{im}^{ca} + U_{im}^c X_{im}^{ab})$$

$$+ 2 \sum_{im} \sum_{jn} (U_{im}^a U_{jn}^b Y_{imjn}^c + U_{im}^b U_{jn}^c Y_{imjn}^a + U_{im}^c U_{jn}^a Y_{imjn}^b)$$

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

$$+ U_{im}^c U_{jn}^a U_{ko}^b) \sum_l \Gamma_{mnol} (ij|kl) \tag{5.25}$$

where

$$h_{ij}^{abc} = \sum_{\mu\nu} C_\mu^i C_\nu^j \frac{\partial^3 h_{\mu\nu}}{\partial a\, \partial b\, \partial c} \tag{5.26}$$

$$(ij\,|\,kl)^{abc} = \sum_{\mu\nu\rho\sigma} C_\mu^i C_\nu^j C_\rho^k C_\sigma^l \frac{\partial^3 (\mu\nu\,|\,\rho\sigma)}{\partial a\, \partial b\, \partial c} \tag{5.27}$$

$$X_{im}^{ab} = \sum_j \gamma_{mj} h_{ij}^{ab} + 2 \sum_{jkl} \Gamma_{mjkl} (ij\,|\,kl)^{ab} \tag{5.28}$$

and

$$Y_{imjn}^{a} = \gamma_{mn} h_{ij}^{a} + 2 \sum_{kl} \{ \Gamma_{mnkl} (ij\,|\,kl)^{a} + 2\Gamma_{mknl} (ik\,|\,jl)^{a} \}. \tag{5.29}$$

The first and second derivatives of the Hamiltonian matrix appearing in Eq. (5.24) have been already defined in Eqs. (5.2) and (5.14).

5.4. Fourth derivatives

In a manner analogous to that employed in the previous section, the terms involving $\delta_{IJ}\, \partial^3 E/\partial a\, \partial b\, \partial c$ in Eq. (2.20) may be removed to give an expression for the fourth derivatives of the electronic energy, namely

$$
\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} \right. \\
&\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}{\partial c\, \partial d} \right) \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) \\
&+ \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) \\
&\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] \\
&- 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).
\end{aligned}
\tag{5.30}
$$

The first term of Eq. (5.30) may be expressed as follows

$$\sum_{IJ} C_I C_J \frac{\partial^4 H_{IJ}}{\partial a\, \partial b\, \partial c\, \partial d}$$

$$= \sum_{ij} \gamma_{ij} h_{ij}^{abcd} + \sum_{ijkl} \Gamma_{ijkl} (ij|kl)^{abcd} + 2 \sum_{im} U_{im}^{abcd} X_{im}$$

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

$$+ 2 \sum_{im} \sum_{jn} (U_{im}^{abc} U_{jn}^d + U_{im}^{abd} U_{jn}^c + U_{im}^{acd} U_{jn}^b + U_{im}^{bcd} U_{jn}^a) Y_{imjn}$$

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

$$+ 2 \sum_{im} \sum_{jn} \{ (U_{im}^{ab} U_{jn}^c + U_{im}^{ac} U_{jn}^b + U_{im}^{bc} U_{jn}^a) Y_{imjn}^d$$

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

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

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

$$+ 2 \sum_{im} \sum_{jn} \sum_{ko} (U_{im}^{ab} U_{jn}^c U_{ko}^d + U_{im}^{ac} U_{jn}^b U_{ko}^d + U_{im}^{ad} U_{jn}^b U_{ko}^c$$

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

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

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

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

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

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

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

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

$$\Gamma_{mnop} (ij|kl) \tag{5.31}$$

where

$$h_{ij}^{abcd} = \sum_{\mu\nu} C_\mu^i C_\nu^j \frac{\partial^4 h_{\mu\nu}}{\partial a\, \partial b\, \partial c\, \partial d} \tag{5.32}$$

$$(ij|kl)^{abcd} = \sum_{\mu\nu\rho\sigma} C_\mu^i C_\nu^j C_\rho^k C_\sigma^l \frac{\partial^4 (\mu\nu|\rho\sigma)}{\partial a\, \partial b\, \partial c\, \partial d} \tag{5.33}$$

$$X_{im}^{abc} = \sum_j \gamma_{mj} h_{ij}^{abc} + 2 \sum_{jkl} \Gamma_{mjkl} (ij|kl)^{abc} \tag{5.34}$$

$$Y_{imjn}^{ab} = \gamma_{mn} h_{ij}^{ab} + 2 \sum_{kl} \{ \Gamma_{mnkl} (ij|kl)^{ab} + 2\Gamma_{mknl} (ik|jl)^{ab} \} \tag{5.35}$$

$$Z_{imjnko} = 4 \sum_{l} \{ \Gamma_{mnol} (ij|kl) + \Gamma_{monl} (ik|jl) + \Gamma_{mlno} (il|jk) \} \tag{5.36}$$

and

$$Z_{imjnko}^{a} = 4 \sum_{l} \{ \Gamma_{mnol} (ij|kl)^{a} + \Gamma_{monl} (ik|jl)^{a} + \Gamma_{mlno} (il|jk)^{a} \}. \tag{5.37}$$

The term involving the third derivative of Hamiltonian matrix may be written as

$$\sum_{IJ} C_I \frac{\partial C_J}{\partial a} \frac{\partial^3 H_{IJ}}{\partial b \, \partial c \, \partial d}$$

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

$$+ 2 \sum_{im} (U_{im}^{bc} X_{im}^{(a)d} + U_{im}^{cd} X_{im}^{(a)b} + U_{im}^{bd} X_{im}^{(a)c})$$

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

$$+ 2 \sum_{im} (U_{im}^{b} X_{im}^{(a)cd} + U_{im}^{c} X_{im}^{(a)bd} + U_{im}^{d} X_{im}^{(a)bc})$$

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

$$+ 8 \sum_{im} \sum_{jn} \sum_{ko} U_{im}^{b} U_{jn}^{c} U_{ko}^{d} \sum_{l} \{ \Gamma_{mnol}^{(a)} (ij|kl) + \Gamma_{monl}^{(a)} (ik|jl) + \Gamma_{mlno}^{(a)} (il|jk) \} \tag{5.38}$$

where

$$\gamma_{ij}^{(a)} = \sum_{IJ} C_I \frac{\partial C_J}{\partial a} \gamma_{ij}^{IJ} \tag{5.39}$$

$$\Gamma_{ijkl}^{(a)} = \sum_{IJ} C_I \frac{\partial C_J}{\partial a} \Gamma_{ijkl}^{IJ} \tag{5.40}$$

$$X_{im}^{(a)} = \sum_{j} \gamma_{mj}^{(a)} h_{ij} + 2 \sum_{jkl} \Gamma_{mjkl}^{(a)} (ij|kl) \tag{5.41}$$

$$X_{im}^{(a)b} = \sum_{j} \gamma_{mj}^{(a)} h_{ij}^{b} + 2 \sum_{jkl} \Gamma_{mjkl}^{(a)} (ij|kl)^{b} \tag{5.42}$$

$$X_{im}^{(a)bc} = \sum_{j} \gamma_{mj}^{(a)} h_{ij}^{bc} + 2 \sum_{jkl} \Gamma_{mjkl}^{(a)} (ij|kl)^{bc} \tag{5.43}$$

$$Y_{imjn}^{(a)} = \gamma_{mn}^{(a)} h_{ij} + 2 \sum_{kl} \{ \Gamma_{mnkl}^{(a)} (ij|kl) + 2\Gamma_{mknl}^{(a)} (ik|jl) \} \tag{5.44}$$

and

$$Y_{imjn}^{(a)b} = \gamma_{mn}^{(a)} h_{ij}^{b} + 2 \sum_{kl} \{ \Gamma_{mnkl}^{(a)} (ij|kl)^{b} + 2\Gamma_{mknl}^{(a)} (ik|jl)^{b} \}. \tag{5.45}$$

Equation (5.30) clearly reflects Wigner's $2n+1$ rule [17] such that the fourth derivative of the CI energy requires only the first and second derivatives of the

CI coefficients, which may be determined via the first and second-order CPCI equations (3.2) and (3.3).

6. Computational implementation of the first and second derivatives

The analytic evaluation of energy derivatives using correlated wave functions has already been implemented for the first and second derivatives of CI [4, 5, 9] and MCSCF [10] energies. When one employs the MCSCF wave function, it is possible to skip the steps to evaluate the second derivatives of the MO coefficients. However, there still remain computational difficulties in solving the coupled perturbed MCSCF equations routinely. Similar problem comes with the CPCI equations, which must be solved to obtain the CI second derivatives. In the present formulation, the other major problem in the evaluation of CI second derivatives is to solve the second-order CPHF equations for the second derivatives of the MO coefficients. This problem has already been successfully resolved for closed-shell and general open-shell RHF wave functions [21]. Moreover, the solution of the $(3N)(3N+1)/2$ second-order CPHF equations may be avoided by solving one CPHF-like equation using the Z-vector method of Handy and Schaefer [16].

In this section, we present an overview of the computational procedure for the CI first and second derivative methods, and discuss the various problems to be solved. Figure 1 illustrates the present algorithm for the evaluation of energy gradients and the second derivatives using CI wave function based on the following description.

6.1. First derivatives

The energy gradient for CI wave function (5.10) may be divided into two terms [5a]

$$\frac{\partial E}{\partial a} = E^a_{(1)} + E^a_{(2)} \tag{6.1}$$

where

$$E^a_{(1)} = \sum_{ij} \gamma_{ij} h^a_{ij} + \sum_{ijkl} \Gamma_{ijkl} (ij \mid kl)^a \tag{6.2}$$

$$= \sum_{\mu\nu} \gamma_{\mu\nu} \frac{\partial h_{\mu\nu}}{\partial a} + \sum_{\mu\nu\rho\sigma} \Gamma_{\mu\nu\rho\sigma} \frac{\partial(\mu\nu \mid \rho\sigma)}{\partial a} \tag{6.3}$$

and

$$E^a_{(2)} = 2 \sum_{im} U^a_{im} X_{im}. \tag{6.4}$$

The first term of Eq. (6.1) may be evaluated in the AO basis using the back transformed density matrices $\gamma_{\mu\nu}$ and $\Gamma_{\mu\nu\rho\sigma}$ as shown in Eq. (6.3). The one- and
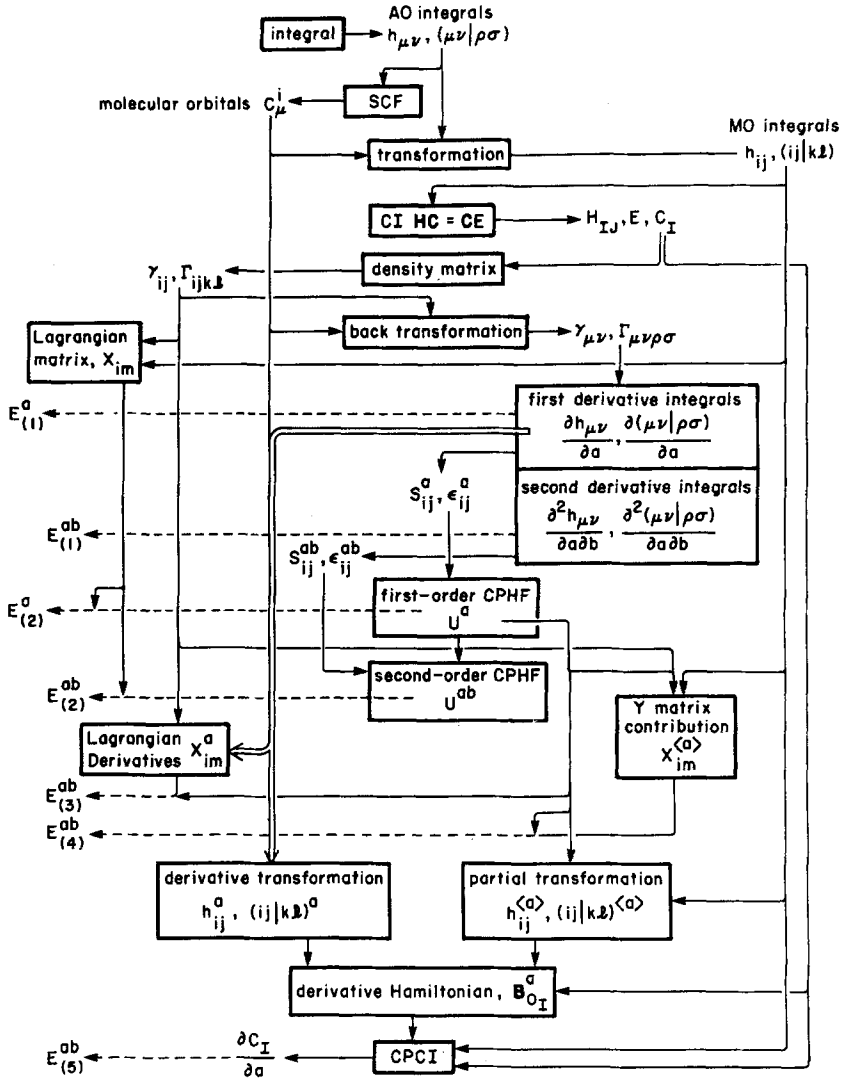
Fig. 1. Computational procedures for the analytic evaluation of energy first and second derivatives for configuration interaction wave functions. Note that the solution of the $3N(3N+1)/2$ second-order CPHF equations may be avoided by solving one CPHF-like equation using the Z-vector method of Handy and Schaefer [16]

two-electron density matrices in the AO basis are obtained via

$$\gamma_{\mu\nu} = \sum_{ij} C^i_\mu C^j_\nu \gamma_{ij}, \tag{6.5}$$

and

$$\Gamma_{\mu\nu\rho\sigma} = \sum_{ijkl} C^i_\mu C^j_\nu C^k_\rho C^l_\sigma \Gamma_{ijkl}. \tag{6.6}$$

The second term, $E^a_{(2)}$, is evaluated from the Lagrangian matrix (5.11) and the U^a matrix.

6.2. Second derivatives

The CI energy second derivative formula (5.20) may be divided into the following five terms

$$\frac{\partial^2 E}{\partial a\,\partial b} = E^{ab}_{(1)} + E^{ab}_{(2)} + E^{ab}_{(3)} + E^{ab}_{(4)} + E^{ab}_{(5)} \tag{6.7}$$

where

$$E^{ab}_{(1)} = \sum_{ij} \gamma_{ij} h^{ab}_{ij} + \sum_{ijkl} \Gamma_{ijkl} (ij\,|\,kl)^{ab} \tag{6.8}$$

$$= \sum_{\mu\nu} \gamma_{\mu\nu} \frac{\partial^2 h_{\mu\nu}}{\partial a\,\partial b} + \sum_{\mu\nu\rho\sigma} \Gamma_{\mu\nu\rho\sigma} \frac{\partial^2 (\mu\nu\,|\,\rho\sigma)}{\partial a\,\partial b} \tag{6.9}$$

$$E^{ab}_{(2)} = 2 \sum_{im} U^{ab}_{im} X_{im} \tag{6.10}$$

$$E^{ab}_{(3)} = 2 \sum_{im} (U^a_{im} X^b_{im} + U^b_{im} X^a_{im}) \tag{6.11}$$

$$E^{ab}_{(4)} = 2 \sum_{im} \sum_{jn} U^a_{im} U^b_{jn} Y_{imjn} \tag{6.12}$$

and

$$E^{ab}_{(5)} = -2 \sum_{IJ} (H_{IJ} - \delta_{IJ} E) \frac{\partial C_I}{\partial a} \frac{\partial C_J}{\partial b}. \tag{6.13}$$

The first term $E^{ab}_{(1)}$ involves second derivatives of AO integrals, and the second term $E^{ab}_{(2)}$ requires the solution of the second-order CPHF equations, the U^{ab} matrices. The Lagrangian derivative matrices X^a appearing in the third term, $E^{ab}_{(3)}$, may be evaluated either by using the transformed first derivative integrals in the MO basis, h^a_{ij} and $(ij\,|\,kl)^a$, (see Eq. (5.21)) or by using the partially transformed derivative Lagrangian and density matrices, $X^a_{\mu m}$, $\gamma_{m\nu}$ and $\Gamma_{m\nu\rho\sigma}$,

$$X^a_{im} = \sum_\mu C^i_\mu X^a_{\mu m} \tag{6.14}$$

where

$$X^a_{\mu m} = \sum_\nu \gamma_{m\nu} \frac{\partial h_{\mu\nu}}{\partial a} + 2 \sum_{\nu\rho\sigma} \Gamma_{m\nu\rho\sigma} \frac{\partial(\mu\nu\,|\,\rho\sigma)}{\partial a} \tag{6.15}$$

and

$$\gamma_{m\nu} = \sum_j \gamma_{mj} C^j_\nu \tag{6.16}$$

$$\Gamma_{m\nu\rho\sigma} = \sum_{jkl} \Gamma_{mjkl} C^j_\nu C^k_\rho C^l_\sigma. \tag{6.17}$$

The direct evaluation of the Y matrix appearing in $E_{(4)}^{ab}$ requires a major computational effort. Page et al. [10d] and Lee et al. [9b] developed a method to calculate the term $E_{(4)}^{ab}$ without forming the Y matrix. There are two ways to evaluate $E_{(4)}^{ab}$; using either partially transformed derivative MO integrals or derivative density matrices,

$$E_{(4)}^{ab} = 2 \sum_{im} \sum_{jn} U_{im}^a U_{jn}^b \left[\gamma_{mn} h_{ij} + 2 \sum_{kl} \{ \Gamma_{mnkl} (ij \,|\, kl) + 2\Gamma_{mknl} (ik \,|\, jl) \} \right] \tag{6.18}$$

$$= 2 \sum_{im} U_{im}^a \chi_{im}^{\langle b \rangle} \tag{6.19}$$

where

$$\chi_{im}^{\langle b \rangle} = \sum_{n} \gamma_{mn} h_{i\bar{n}}^{\langle b \rangle} + 2 \sum_{nkl} \Gamma_{mnkl} \{ (i\bar{n} \,|\, kl)^{\langle b \rangle} + (in \,|\, \bar{k}l)^{\langle b \rangle} + (in \,|\, k\bar{l})^{\langle b \rangle} \} \tag{6.20}$$

$$= \sum_{j} \gamma_{m\bar{j}}^{\langle b \rangle} h_{ij} + 2 \sum_{jkl} \{ \Gamma_{m\bar{j}kl}^{\langle b \rangle} + \Gamma_{mj\bar{k}l}^{\langle b \rangle} + \Gamma_{mjk\bar{l}}^{\langle b \rangle} \} (ij \,|\, kl). \tag{6.21}$$

The partially transformed derivative integrals and derivative density matrices are defined as follows

$$h_{i\bar{n}}^{\langle b \rangle} = \sum_{j} U_{jn}^b h_{ij} \tag{6.22}$$

$$(i\bar{n} \,|\, kl)^{\langle b \rangle} = \sum_{j} U_{jn}^b (ij \,|\, kl) \tag{6.23}$$

$$\gamma_{m\bar{j}}^{\langle b \rangle} = \sum_{n} U_{jn}^b \gamma_{mn} \tag{6.24}$$

$$\Gamma_{m\bar{j}kl}^{\langle b \rangle} = \sum_{n} U_{jn}^b \Gamma_{mnkl}. \tag{6.25}$$

The last term of the CI second derivative expression, $E_{(5)}^{ab}$, requires the derivatives of the CI coefficients which may be obtained by solving the CPCI equations (3.2).

6.3. First-order CPCI equations

The first-order CPCI equation (3.2) is the linear equation which may be written in a simple matrix form;

$$A \cdot \frac{\partial C}{\partial a} = B_0^a. \tag{6.26}$$

The matrix elements of Eq. (6.26) are given by

$$A_{IJ} = H_{IJ} - \delta_{IJ} E + 2 C_I C_J \tag{6.27}$$

and

$$B_{0_I}^a = -\sum_{J} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} \frac{\partial E}{\partial a} \right) C_J. \tag{6.28}$$

The first derivative of the Hamiltonian matrix element involved in (6.28) may be evaluated using the transformed derivative integrals in the MO basis [(5.5), (5.6)] and partially transformed derivative MO integrals [(6.22) and (6.23)]

$$\frac{\partial H_{IJ}}{\partial a} = \sum_{ij} \gamma_{ij}^{IJ} (h_{ij}^{a} + h_{ij}^{\langle a \rangle}) + \sum_{ijkl} \Gamma_{ijkl}^{IJ} \{(ij|kl)^{a} + (ij|kl)^{\langle a \rangle}\} \tag{6.29}$$

where

$$h_{ij}^{\langle a \rangle} = h_{\bar{i}j}^{\langle a \rangle} + h_{i\bar{j}}^{\langle a \rangle} \tag{6.30}$$

and

$$(ij|kl)^{\langle a \rangle} = (\bar{i}j|kl)^{\langle a \rangle} + (i\bar{j}|kl)^{\langle a \rangle} + (ij|\bar{k}l)^{\langle a \rangle} + (ij|k\bar{l})^{\langle a \rangle}. \tag{6.31}$$

One of the most time consuming steps in the CPCI procedure is the evaluation of the derivative integrals in the MO basis, $(ij|kl)^{a}$ to form the derivative Hamiltonian matrix $\partial H_{IJ}/\partial a$. When the derivative Hamiltonian matrix element is evaluated, one may directly form B_{0I}^{a} by multiplying with the CI coefficients so that one can avoid storing the huge derivative Hamiltonian matrix. After the B_{0}^{a} matrix is calculated for all nuclear coordinates a, the linear equation (6.26) may be solved iteratively by using Pople's method [4]. One may use an alternative procedure to evaluate $E_{(5)}^{ab}$ with the direct inversion of $(H_{IJ} - \delta_{IJ}E + 2C_{I}C_{J})$.

6.4. Computational problems and the future

The practical problem in solving the CPCI equations is the large requirement of memory storage, not to mention computation time. This fact may be appreciated by noting that the CPCI procedure involves roughly $3N$ times the computation of the CI energy in order to get $(3N)^{2}$ force constants, where N is the number of atoms.

Although the CI energy and wave function are usually determined by employing only configurations that contribute to the electronic state, one must expand the configuration space in order to solve the CPCI equation. This is due to the fact that the derivatives of the Hamiltonian matrix are not necessarily zero even if the corresponding matrix elements of the (zeroth order) Hamiltonian are zero by molecular symmetry. If the CPCI equation is solved by exploiting the molecular symmetry, the linear equations (6.26) should take a block-diagonal form determined by symmetry of both the electronic configurations and nuclear displacements.

In order to make the CI second derivative more tractable, one obviously needs to develop an efficient CI code. The analytic derivative procedure is also enhanced if one can easily vectorize or parallelize the programming code. In this regard the progress of appropriate computer software and hardware is also strongly looked for. Fig. 2 shows a qualitative sketch of the computation time requirements for analytic derivative methods.
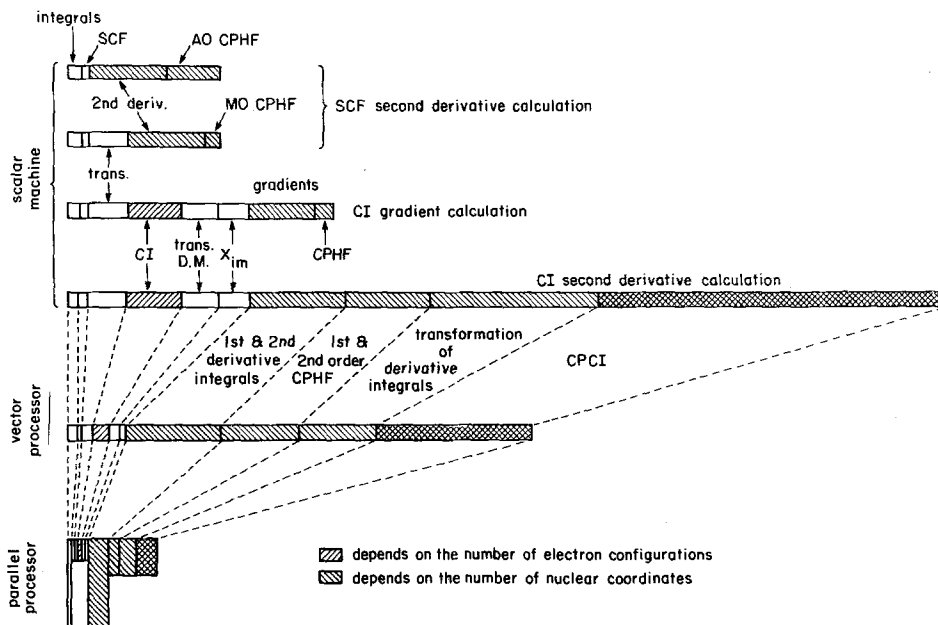
Fig. 2. Rough estimation of computation times for analytic energy derivative methods. Note that the estimates do not refer to any particular example and the relative amounts of computation will vary significantly from case to case. As discussed in the text, the solution of the $3N$ CPHF equations for the CI gradient, and the solution of the $3N(3N+1)/2$ second-order CPHF equations for the CI second derivatives, may be avoided by solving one CPHF-like equation using the Z-vector method of Handy and Schaefer [16]

7. Concluding remarks

In modern molecular electronic structure theory the development of analytic energy derivative techniques is essential in order to obtain reliable information concerning potential energy hypersurfaces in an efficient and precise manner. In this review a straightforward way of deriving explicit analytic higher energy derivative expressions for the CI wave function is presented. Also shown is a new route to the formulation of the CPCI equations in directly soluble forms. In this paper we have concentrated on the two (orthogonality and variational) conditions on the CI space. It should be noted that in his important monograph contribution Pulay [22] anticipated some aspects of the present approach, by using a related form of the energy expression and making use of Lagrange multipliers in the CI part of the MCSCF energy. In a forthcoming paper we plan to pursue the correspondence among higher energy derivatives of the CI, MCSCF, and SCF wave functions by imposing additional two conditions on the MO space and considering the uniqueness of the coupling constants.

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