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Configuration-interaction energy derivatives in a fully variational formulation

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A configuration-interaction energy function (Lagrange) which is variational in all variables, including the orbital rotational parameters, is constructed. When this Lagrangian is used for obtaining configuration-interaction derivatives, all the important simplifications which occur for derivatives of variational wave functions carry over in a straightforward way. In particular, the state and orbital rotational response parameters obey the $2n+1$ rule and the Lagrange multipliers obey the somewhat stronger $2n+2$ rule. The simplifications which are normally obtained by invoking the Handy-Schaefer technique are automatically incorporated to all orders. Simple expressions for energy derivatives up to third order are presented. The relationship between the numerical errors in the variational parameters and the errors in the calculated energy derivatives is discussed.

Key words: Energy derivatives — Variational formulation — Configuration interaction

1. Introduction

The advantages of fully variational methods over non-variational methods in calculations of energy derivatives have long been recognized. Indeed, the variational approaches such as self-consistent-field (SCF) and multi-configurational self-consistent-field (MCSCF) were the first to be considered both from a theoretical and a practical point of view [1-3]. Derivatives of the configuration-interaction (CI) energy appeared later [4-7] due to problems in handling the contributions from the non-variational molecular orbitals [8-9]. An important simplification in the calculation of CI derivatives was obtained in 1984, when Handy and Schaefer showed how the contributions from the high-order derivatives of the orbital rotational parameters could be rewritten in terms of the solution vectors of certain low-order equations [10]. The Handy–Schaefer technique has since been applied to the coupled-cluster (CC) [11–12] and Møller–Plesset (MP) [13] derivative expressions, yielding significant computational savings.

Notwithstanding the practical importance of the Handy-Schaefer technique, it is somewhat unsatisfactory that in each specific case it must be applied in a rather ad hoc manner. Although it is straightforward to apply the technique to lower-order derivatives such as the gradient, for higher derivatives the technique becomes rather cumbersome and tedious. It is no longer obvious how many sets of lower-order linear equations must be solved to take full advantage of the technique, or how one should proceed to derive the appropriate linear equations. Also, no satisfactory interpretation has been offered of the Handy-Schaefer technique except that it can be interpreted as a partial reoptimization of the MCSCF orbitals in the CI field [14].

In this paper we show how it is possible to construct a modified CI energy expression which is fully variational in both the state and the orbital rotational parameters, as well as in a set of Lagrange multipliers. The derivative expressions may then be obtained by using the standard techniques for variational wave functions. In particular, the state and orbital rotational parameters obey the $2n+1$ rule, and the Lagrange multipliers the stronger $2n+2$ rule. The Lagrange multipliers and their derivatives are determined from sets of linear equations identical to those obtained by applying the Handy-Schaefer technique in an optimal way. However, in our formulation these equations and the associated computational savings appear naturally and require no special attention.

Recently, Rice and Amos [15] and Shepard [16] have shown that CI gradients contain two distinct but similar contributions, one of which is constructed from CI densities and the other from modified MCSCF densities. Our approach generalizes this result to higher orders. For example, we show that the CI Hessian consists of two contributions, both of which are similar in structure to the expression for MCSCF Hessians. One of these contributions is calculated from CI densities and wave function responses, the other from modified MCSCF densities and MCSCF wave function responses.

The Lagrangian technique used in this paper has in a less complete form been applied to coupled-cluster wave functions [3]. Indeed it can be applied to any computational method whose electronic parameters are not variationally determined.

2. Derivatives of variational energies

We assume that the electronic energy function $\mathscr{E}(x, t)$ depends on two sets of parameters: the molecular geometry x and the variational parameters t. Expanding the energy at an arbitrary geometry x in the variational parameters $\Delta t = t - t^{(0)}$

we obtain

$$\mathscr{E}(x,t)=\mathscr{E}(x)+\mathscr{F}(x)\,\Delta t+\tfrac{1}{2}\mathscr{G}(x)\,\Delta t^2+\tfrac{1}{6}\mathscr{H}(x)\,\Delta t^3+\cdots \tag{1}$$

where $\mathscr{E}(x)$ and the electronic derivatives $\mathscr{F}(x)$, $\mathscr{G}(x)$, and $\mathscr{H}(x)$ are calculated at $t^{(0)}$. The total molecular electronic energy $\mathscr{W}(x)$ is obtained by imposing the condition

$$\frac{\partial\mathscr{E}(x,t)}{\partial t}=0 \tag{2}$$

at all geometries x. Eq. (2) determines Δt as a function of x, and the total electronic energy becomes

$$\mathscr{W}(x)=\mathscr{E}(x)+\mathscr{F}(x)\,\Delta t(x)+\tfrac{1}{2}\mathscr{G}(x)\,\Delta t^2(x)+\tfrac{1}{6}\mathscr{H}(x)\,\Delta t^3(x)+\cdots \tag{3}$$

where $t(x)$ fulfills the equation

$$\mathscr{F}(x)+\mathscr{G}(x)\,\Delta t(x)+\tfrac{1}{2}\mathscr{H}(x)\,\Delta t^2(x)+\cdots=0. \tag{4}$$

Differentiating Eqs. (3) and (4) with respect to x we obtain at x_0

$$\mathscr{W}^{(0)}=\mathscr{E}^{(0)} \tag{5}$$

$$\mathscr{W}^{(1)}=\mathscr{E}^{(1)} \tag{6}$$

$$\mathscr{W}^{(2)}=\mathscr{E}^{(2)}+2\mathscr{F}^{(1)}t^{(1)}+\mathscr{G}^{(0)}t^{(1)}t^{(1)} \tag{7}$$

$$\mathscr{W}^{(3)}=\mathscr{E}^{(3)}+3\mathscr{F}^{(2)}t^{(1)}+3\mathscr{G}^{(1)}t^{(1)}t^{(1)}+\mathscr{H}^{(0)}t^{(1)}t^{(1)}t^{(1)} \tag{8}$$

and

$$\mathscr{F}^{(0)}=0 \tag{9}$$

$$\mathscr{F}^{(1)}+\mathscr{G}^{(0)}t^{(1)}=0 \tag{10}$$

The zeroth-order condition of Eq. (9) determines $t^{(0)}$, since $\mathscr{F}^{(0)}$ is calculated at $t^{(0)}$, and the first -order condition of Eq. (10) determines $t^{(1)}=\Delta t^{(1)}$. In the above expressions Eqs. (6)–(8) we have used the zeroth-order condition Eq. (9) to eliminate $t^{(1)}$, $t^{(2)}$, and $t^{(3)}$ from $\mathscr{W}^{(1)}$, $\mathscr{W}^{(2)}$, and $\mathscr{W}^{(3)}$, respectively, and the first-order condition Eq. (10) to eliminate $t^{(2)}$ from $\mathscr{W}^{(3)}$. Note that the derivatives obey the $2n+1$ rule [17].

In practice the wave function and the wave function responses (the t parameters) are determined to some preset residual accuracy. The calculated derivatives Eqs. (5)–(8) then contain errors that depend on this residual accuracy. One can show that the error in $\mathscr{W}^{(0)}$ is quadratic in the error in the wave function and that the errors in $\mathscr{W}^{(1)}$, $\mathscr{W}^{(2)}$, and $\mathscr{W}^{(3)}$ are linear in the error in the wave function. Also the error in $\mathscr{W}^{(2)}$ is quadratic in the error in $t^{(1)}$, while the error in $\mathscr{W}^{(3)}$ is linear in the error in $t^{(1)}$. Hence, although odd-order derivatives have an edge over even-order derivatives in that a fewer number of linear equations must be solved, they are also more sensitive to errors in the highest-order wave function response. In many cases the Hessian is calculated from the expression

$$\mathscr{W}^{(2)}=\mathscr{E}^{(2)}+\mathscr{F}^{(1)}t^{(1)} \tag{11}$$

which is obtained from Eq. (7) by using the first-order condition Eq. (10). However, Sellers [18] pointed out that the symmetric expression Eq. (7) is to be preferred since the error in $\mathscr{W}^{(2)}$ is linear rather than quadratic in the error in $t^{(1)}$ when Eq. (11) rather than Eq. (7) is used. The computational expenses are identical for the two expressions. More general discussions of errors occurring as a result of using wave functions and wave function responses that are determined to a preset tolerance can be found in [19].

3. CI energy function

CI energies and wave functions are usually obtained in the following way. First an MCSCF calculation is carried out to determine a set of molecular orbitals. This is achieved by optimizing the MCSCF energy function $e(x, \lambda)$ with respect to all variational parameters λ:

$$\frac{\partial e(x, \lambda)}{\partial \lambda} = 0 \tag{12}$$

where

$$\lambda = \begin{bmatrix} \kappa \\ p \end{bmatrix} \tag{13}$$

is the collection of independent MCSCF orbital rotational parameters κ and MCSCF state transfer parameters p. Next the CI energy is optimized with respect to the configuration expansion coefficients, keeping the MCSCF orbitals fixed. The CI energy function $E(x, \Lambda)$ thus depends on the CI state transfer parameters P and the MCSCF orbital rotation parameters κ

$$\Lambda = \begin{bmatrix} P \\ \kappa \end{bmatrix} \tag{14}$$

where the orbital part of Λ (i.e. κ) satisfies Eq. (12) and the CI state transfer parameters satisfy the CI variational condition

$$\frac{\partial E(x, \Lambda)}{\partial P} = 0. \tag{15}$$

The calculation of the CI energy and wave function may be viewed in a slightly different way: we wish to optimize $E(x, \Lambda)$ with respect to Λ subject to the constraint that $e(x, \lambda)$ is optimal with respect to λ. A standard technique for constrained optimization is to introduce a set of undetermined Lagrange multipliers ζ, one for each constraint. This gives us the CI Lagrangian

$$\mathscr{E}(x, t) = E(x, \Lambda) + \zeta \frac{\partial e(x, \lambda)}{\partial \lambda} \tag{16}$$

where t is the collection of Lagrange multipliers, CI state transfer parameters, MCSCF orbital rotation parameters, and MCSCF state transfer parameters:

$$t = \begin{bmatrix} \zeta \\ P \\ \kappa \\ p \end{bmatrix}. \tag{17}$$

The CI energy and wave function may now be determined by an unconstrained optimization of $\mathscr{E}(x, t)$ with respect to t. The CI energy is variational in all parameters.

The CI Lagrange $\mathscr{E}(x, t)$ is not especially useful for energy optimizations since the constraints are easily handled by first determining a set of orbitals using Eq. (12) and then keeping the orbitals fixed during the optimization of the configuration coefficients. The only advantage of $\mathscr{E}(x, t)$ over $E(x, \Lambda)$ in that the error in the CI energy in quadratic in the error in the orbitals when $\mathscr{E}(x, t)$ is used, but linear in the error in the orbitals when $E(x, \Lambda)$ is used. However, this does not justify using a larger variational space. In contrast, $\mathscr{E}(x, t)$ is very useful for calculating derivatives since the variational property ensures that we can take full advantage of the simplifications that occur for fully variational wave functions, in particular the $2n+1$ rule. Epstein has previously shown that energy Lagrangians satisfy a $2n+1$ rule. In Sect. 4.2 we demonstrate that Lagrange multipliers even satisfy a $2n+2$ rule.

Let us conclude this section by stating the CI variational condition in terms of the Lagrangian function $\mathscr{E}(x, t)$:

$$\frac{\partial \mathscr{E}}{\partial \zeta} = \frac{\partial e}{\partial \lambda} = 0 \tag{18}$$

$$\frac{\partial \mathscr{E}}{\partial P} = \frac{\partial E}{\partial P} = 0 \tag{19}$$

$$\frac{\partial \mathscr{E}}{\partial \lambda} = \frac{\partial E}{\partial \lambda} + \zeta \frac{\partial^2 e}{\partial \lambda^2} = 0. \tag{20}$$

Eqs. (18) and (19) are, respectively, the usual MCSCF and CI variational conditions while the linear set of equations, Eq. (20), determines the Lagrange multipliers and ensures that the energy is fully variational.

4. CI energy derivatives

In the following we denote the electronic derivatives (i.e., the derivatives with respect to the variational parameters) of the CI energy expectation value by capital letters

$$E(x, \Lambda) = E(x) + F(x)\Lambda + \tfrac{1}{2}G(x)\Lambda^2 + \tfrac{1}{6}K(x)\Lambda^3 + \cdots \tag{21}$$

and the electronic derivatives of the MCSCF energy by small letters

$$e(x, \lambda) = e(x) + f(x)\lambda + \tfrac{1}{2}g(x)\lambda^2 + \tfrac{1}{6}k(x)\lambda^3 + \tfrac{1}{24}l(x)\lambda^4 + \cdots. \tag{22}$$

In Eqs. (21) and (22) we have assumed that the wave functions are parametrized such that $\Lambda^{(0)}$ and $\lambda^{(0)}$ are zero. The electronic derivatives of the CI Lagrangian are denoted as in Eq. (1). By straightforward differentiation of Eq. (16) we obtain

$$\mathcal{E}(x) = E(x) + \zeta^{(0)} f(x) \tag{23}$$

$$\mathcal{F}(x) = \begin{bmatrix} 0 \\ F(x) \\ 0 \end{bmatrix} + \begin{bmatrix} f(x) \\ 0 \\ \zeta^{(0)} g(x) \end{bmatrix} \tag{24}$$

$$\mathcal{G}(x) = \begin{bmatrix} 0 & 0 & 0 \\ 0 & G(x) & 0 \\ 0 & 0 & 0 \end{bmatrix} + \begin{bmatrix} 0 & 0 & g(x) \\ 0 & 0 & 0 \\ g(x) & 0 & \zeta^{(0)} k(x) \end{bmatrix} \tag{25}$$

$$\mathcal{K}(x)\,\Delta t^3 \doteq K(x)\Lambda^3 + \zeta^{(0)} l(x)\lambda^3 + 3k(x)\lambda^2\,\Delta\zeta \tag{26}$$

where for both Eqs. (24) and (25) the dimensions of the sub-blocks in the two terms are not the same. Note that $\mathcal{G}(x)$ is not positive definite, hence the optimized energy does not represent a minimum. Also note that $\zeta^{(0)}$ is not zero.

4.1. Response equations

The variational CI response equations are obtained by inserting the electronic derivatives of the CI Lagrangian Eqs. (24) and (25) into the general expressions Eqs. (9) and (10). We obtain to zeroth order

$$f^{(0)} = 0 \tag{27}$$

$$^{c}F^{(0)} = 0 \tag{28}$$

$$-g^{(0)}\zeta^{(0)} = \begin{bmatrix} {}^{o}F^{(0)} \\ 0 \end{bmatrix} \tag{29}$$

and to first order

$$-g^{(0)}\lambda^{(1)} = f^{(1)} \tag{30}$$

$$-{}^{cc}G^{(0)}P^{(1)} = {}^{c}F^{(1)} + {}^{co}G^{(0)}\kappa^{(1)} \tag{31}$$

$$-g^{(0)}\zeta^{(1)} = \begin{bmatrix} {}^{o}F^{(1)} + {}^{oc}G^{(0)}P^{(1)} + {}^{oo}G^{(0)}\kappa^{(1)} \\ 0 \end{bmatrix} + g^{(1)}\zeta^{(0)} + k^{(0)}\zeta^{(0)}\lambda^{(1)} \tag{32}$$

where left superscripts c and o on the CI electronic derivatives denote the configuration and orbital blocks, respectively.

The above sets of equations are coupled and must be solved in the order indicated. For example, $\zeta^{(0)}$ cannot be determined from Eq. (29) until Eqs. (27) and (28) (the MCSCF and CI variational conditions) are satisfied. Similarly the first-order responses must be solved in the order $\lambda^{(1)}$, $P^{(1)}$, and $\zeta^{(1)}$.

The zeroth-order equations Eqs. (27) and (28) and the first-order equations Eqs. (30) and (31) are the usual MCSCF and CI equations discussed many places [6, 8, 21, 22]. The equations Eqs. (29) and (32) determine $\zeta^{(0)}$ and $\zeta^{(1)}$, and occur since we insist on a variational formulation of the CI energy. The linear sets of equations which determine $\zeta^{(0)}$ and $\zeta^{(1)}$ have the same structure as the equations which determine $\lambda^{(1)}$, and they are identical to the equations that appear when the Handy–Schaefer technique is invoked in an optimal way to simplify the calculation of CI derivatives in a standard (non-variational) formulation.

4.2. Derivative expressions

The CI derivative expressions are obtained by substituting the electronic derivatives of the CI Lagrangian Eqs. (23)–(26) into the general expressions Eqs. (5)–(8). We obtain, to third order

$$W^{(0)} = E^{(0)} + \zeta^{(0)} f^{(0)} \tag{33}$$

$$W^{(1)} = E^{(1)} + \zeta^{(0)} f^{(1)} \tag{34}$$

$$\begin{aligned} W^{(2)} = {} & E^{(2)} + 2F^{(1)}\Lambda^{(1)} + G^{(0)}\Lambda^{(1)}\Lambda^{(1)} + \zeta^{(0)}(f^{(2)} + 2g^{(1)}\lambda^{(1)} \\ & + k^{(0)}\lambda^{(1)}\lambda^{(1)}) + 2\zeta^{(1)}(f^{(1)} + g^{(0)}\lambda^{(1)}) \end{aligned} \tag{35}$$

$$\begin{aligned} W^{(3)} = {} & E^{(3)} + 3F^{(2)}\Lambda^{(1)} + 3G^{(1)}\Lambda^{(1)}\Lambda^{(1)} + K^{(0)}\Lambda^{(1)}\Lambda^{(1)}\Lambda^{(1)} \\ & + \zeta^{(0)}(f^{(3)} + 3g^{(2)}\lambda^{(1)} + 3k^{(1)}\lambda^{(1)}\lambda^{(1)} + l^{(0)}\lambda^{(1)}\lambda^{(1)}\lambda^{(1)}) \\ & + 3\zeta^{(1)}(f^{(2)} + 2g^{(1)}\lambda^{(1)} + k^{(0)}\lambda^{(1)}\lambda^{(1)}). \end{aligned} \tag{36}$$

The last terms in the expressions for $W^{(0)}$ and $W^{(2)}$ vanish since the zeroth- and first-order MCSCF conditions, Eqs. (27) and (30), are satisfied. In general, in even-order derivatives $W^{(2n)}$ the terms containing $\zeta^{(n)}$ vanish since the nth-order MCSCF condition is satisfied. Hence ζ obeys a $2n+2$ rule.

If we introduce the notation

$$e^{(m,n)} = \zeta^{(n)} f^{(m)} \tag{37}$$

$$f^{(m,n)} = \zeta^{(n)} g^{(m)} \tag{38}$$

$$g^{(m,n)} = \zeta^{(n)} k^{(m)} \tag{39}$$

$$k^{(m,n)} = \zeta^{(n)} l^{(m)} \tag{40}$$

the CI derivatives may be written as

$$W^{(0)} = E^{(0)} \tag{41}$$

$$W^{(1)} = E^{(1)} + e^{(1,0)} \tag{42}$$

$$\begin{aligned} W^{(2)} = {} & E^{(2)} + 2F^{(1)}\Lambda^{(1)} + G^{(0)}\Lambda^{(1)}\Lambda^{(1)} \\ & + e^{(2,0)} + 2f^{(1,0)}\lambda^{(1)} + g^{(0,0)}\lambda^{(1)}\lambda^{(1)} \end{aligned} \tag{43}$$

$$\begin{aligned} W^{(3)} = {} & E^{(3)} + 3F^{(2)}\Lambda^{(1)} + 3G^{(1)}\Lambda^{(1)}\Lambda^{(1)} + K^{(0)}\Lambda^{(1)}\Lambda^{(1)}\Lambda^{(1)} \\ & + e^{(3,0)} + 3f^{(2,0)}\lambda^{(1)} + 3g^{(1,0)}\lambda^{(1)}\lambda^{(1)} + k^{(0,0)}\lambda^{(1)}\lambda^{(1)}\lambda^{(1)} \\ & + 3(e^{(2,1)} + 2f^{(1,1)}\lambda^{(1)} + g^{(0,1)}\lambda^{(1)}\lambda^{(1)}) \end{aligned} \tag{44}$$

It is instructive to compare these expressions with the MCSCF energy derivatives $w^{(n)}$:

$$w^{(1)} = e^{(1)} \tag{45}$$

$$w^{(2)} = e^{(2)} + 2f^{(1)}\lambda^{(1)} + g^{(0)}\lambda^{(1)}\lambda^{(1)} \tag{46}$$

$$w^{(3)} = e^{(3)} + 3f^{(2)}\lambda^{(1)} + 3g^{(1)}\lambda^{(1)}\lambda^{(1)} + k^{(0)}\lambda^{(1)}\lambda^{(1)}\lambda^{(1)}. \tag{47}$$

In Sect. 5.3 we show that the quantities $a^{(m,n)}$ ($a = e, f, g, k$) which appear in the CI derivatives (42–44) are identical to the electronic derivatives $a^{(m)}$ which appear in the MCSCF derivatives (45–47), except that $a^{(m,n)}$ are calculated from a set of modified MCSCF densities. Note that $e^{(0,n)}$ is zero, which implies that the modified MCSCF densities give energy zero.

Comparing the MCSCF and CI energy derivative expressions we note their structural similarities. Each CI derivative contains a contribution (capital letters) which is identical in structure to the MCSCF energy derivative expression, in other words, identical to the expression one would obtain by treating the parameters of the CI expectation value [Eq. (21)] as variational. The non-variational character of the CI expectation value is corrected for by adding one or more MCSCF derivatives (small letters) calculated from modified densities. This generalizes the result of Rice and Amos [15] and Shepard [16], namely that the CI gradient can be calculated in the same way as the MCSCF gradient by constructing a set of modified densities.

In general the numerical error in variational Hessians is quadratic in the error in the first-order response of the wave function. This is also true for the CI Hessian calculated from Eq. (35). However, if the Hessian is calculated from the simpler expression Eq. (43), the error becomes linear in the error in the MCSCF first-order response $\lambda^{(1)}$ since we have used the first-order condition, Eq. (30), to eliminate the terms containing $\zeta^{(1)}$. Nevertheless, this is a small price to pay for such a significant saving. Note that Eq. (43) still gives errors which are quadratic in the error in $P^{(1)}$.

5. Parametrization of wave functions and electronic derivatives

5.1. *The CI wave function and electronic derivatives*

The CI state is parametrized as

$$|\Lambda\rangle = \exp(-\kappa)\exp(-P)|\mathrm{CI}\rangle \tag{48}$$

where $|\mathrm{CI}\rangle$ is the optimized state at the reference geometry (the reference state) [23]. The operators κ and P are given by

$$P = \sum_{K \neq \mathrm{CI}} P_K R_K \tag{49}$$

$$\kappa = \sum_{p>q} \kappa_{pq} Q_{pq} \tag{50}$$

in terms of the state transfer and orbital rotation operators

$$R_K = |K\rangle\langle \mathrm{CI}| - |\mathrm{CI}\rangle\langle K| \tag{51}$$

$$Q_{pq} = E_{pq} - E_{qp}. \tag{52}$$

The orthonormal set of states $\{|K\rangle\}$ constitutes a basis for the orthogonal complement to $|\mathrm{CI}\rangle$, and $\{E_{pq}\}$ are the usual orbital-excitation operators (generators of the unitary group).

The CI expectation energy

$$E(x, \Lambda) = \langle \Lambda | H(x) | \Lambda \rangle \tag{53}$$

is calculated from the Hamiltonian

$$H(x) = \sum_{pq} h_{pq}(x) E_{pq} + \tfrac{1}{2} \sum_{pqrs} g_{pqrs}(x)(E_{pq}E_{rs} - \delta_{rq}E_{ps}) \tag{54}$$

where the summations are over symmetrically orthonormalized molecular orbitals [3, 8, 24], and $h_{pq}(x)$ and $g_{pqrs}(x)$ are the usual one- and two-electron integrals. Substituting Eq. (54) into Eq. (53) and setting $\Lambda = 0$, we obtain

$$E(x) = \sum_{pq} D^{\mathrm{CI}}_{pq} h_{pq}(x) + \tfrac{1}{2} \sum_{pqrs} d^{\mathrm{CI}}_{pqrs} g_{pqrs}(x) \tag{55}$$

where the CI density elements are given by

$$D^{\mathrm{CI}}_{pq} = \langle \mathrm{CI} | E_{pq} | \mathrm{CI} \rangle \tag{56}$$

$$d^{\mathrm{CI}}_{pqrs} = \langle \mathrm{CI} | E_{pq}E_{rs} - \delta_{rq}E_{ps} | \mathrm{CI} \rangle. \tag{57}$$

By expanding the CI energy

$$E(x, \Lambda) = \langle \mathrm{CI} | \exp(P) \exp(\kappa) H(x) \exp(-\kappa) \exp(-P) | \mathrm{CI} \rangle \tag{58}$$

in a Baker-Campbell-Hausdorff (BCH) series around x_0 we obtain explicit expressions for the CI electronic derivatives of Eq. (21). Using the notation T_i for R_K or Q_{pq}, these derivatives may be written

$$E^{(n)} = \langle \mathrm{CI} | H^{(n)} | \mathrm{CI} \rangle \tag{59}$$

$$F^{(n)}_i = \langle \mathrm{CI} | [T_i, H^{(n)}] | \mathrm{CI} \rangle \tag{60}$$

$$G^{(n)}_{ij} = \langle \mathrm{CI} | [T_i, T_j, H^{(n)}] | \mathrm{CI} \rangle \tag{61}$$

$$K^{(n)}_{ijk} = \langle \mathrm{CI} | [T_i, T_j, T_k, H^{(n)}] | \mathrm{CI} \rangle \tag{62}$$

where the symmetric commutators [25] should be interpreted as follows. First rearrange the operators T_i so that all state transfer operators R_K appear to the left of the orbital rotation operators Q_{pq}. Then symmetrize over the state transfer operators and the orbital rotation operators separately. The following example illustrates the notation:

$$\begin{aligned}\langle \mathrm{CI} | [Q_{pq}, R_K, R_L, H^{(n)}] | \mathrm{CI} \rangle &= \langle \mathrm{CI} | [R_K, R_L, [Q_{pq}, H^{(n)}]] | \mathrm{CI} \rangle \\ &= \tfrac{1}{2} \langle \mathrm{CI} | [R_K, [R_L, [Q_{pq}, H^{(n)}]]] | \mathrm{CI} \rangle \\ &\quad + \tfrac{1}{2} \langle \mathrm{CI} | [R_L, [R_K, [Q_{pq}, H^{(n)}]]] | \mathrm{CI} \rangle. \end{aligned} \tag{63}$$

The evaluation of these electronic derivatives, in particular the multiplication of vectors on the derivatives, has been discussed elsewhere [3, 25, 26]. In Eqs. (59–62) $H^{(n)}$ denotes the nth-order derivatives of the Hamiltonian with respect to geometrical distortions. Explicit expressions for these derivatives can be found in [3, 9].

5.2. The MCSCF wave function and electronic derivatives

The MCSCF wave function is parametrized in the same way as the CI wave function [23]:

$$|\lambda\rangle = \exp(-\kappa)\exp(-p)|\mathrm{MC}\rangle \tag{64}$$

Here $|\mathrm{MC}\rangle$ is the optimized state at the reference geometry (the reference state), the orbital rotation operator κ is the same as in the CI case [Eq. (50)], and the state rotation operator p is defined in terms of an orthonormal basis $\{|k\rangle\}$ for the orthogonal complement to $|\mathrm{MC}\rangle$:

$$p = \sum_{k\neq \mathrm{MC}} p_k R_k \tag{65}$$

$$R_k = |k\rangle\langle \mathrm{MC}| - |\mathrm{MC}\rangle\langle k|. \tag{66}$$

Keeping with the notation for CI operators we shall use t_i to refer to either the orbital rotation operators Q_{pq} [Eq. (52)] or the state transfer operators R_k [Eq. (66)].

We may expand the MCSCF expectation value $\langle\lambda|H(x)|\lambda\rangle$ in exactly the same way as we expand the CI energy. The resulting electronic derivatives are identical to the CI derivatives Eqs. (59)-(62) except that $|\mathrm{MC}\rangle$ replaces $|\mathrm{CI}\rangle$ and t_i replaces T_i. This procedure is convenient for calculating MCSCF energy derivatives Eqs. (45)-(47) [26] and may also be used for calculating CI derivatives. However, when CI derivatives are calculated, the MCSCF electronic derivatives are always multiplied by a single set of Lagrange multipliers $\zeta^{(n)}$ and possibly by one or several additional sets of MCSCF response vectors $\lambda^{(1)}$. To avoid the explicit construction of the MCSCF electronic derivatives these multiplications should be carried out in a direct fashion. However, the presence of the symmetrized commutators in the electronic derivatives [as in Eqs. (61) and (62)] then makes it more difficult to treat $\zeta^{(n)}$ and $\lambda^{(1)}$ separately. In the following we describe how the multiplication of $\zeta^{(n)}$ can be carried out such that this multiplication is avoided.

We determined $\lambda(x)$ above by requiring the MCSCF gradient $f(x, \lambda)$ to vanish at all geometries:

$$f_i = \frac{\partial\langle\lambda|H(x)|\lambda\rangle}{\partial\lambda_i} = 0. \tag{67}$$

It can be shown that [25]

$$\frac{\partial\langle\lambda|H(x)|\lambda\rangle}{\partial\lambda_i} = \sum_j A_{ij}\langle\lambda|[t_j, H(x)]|\lambda\rangle \tag{68}$$

where A_{ij} is non-singular. [$\langle\lambda|[t_i, H(x)]|\lambda\rangle$ is often referred to as the generalized Brillouin theorem (GBT) matrix element. It is identical to the gradient only when $\lambda = 0$.] Hence the requirement that the MCSCF gradient vanishes is equivalent to the requirement that the MCSCF GBT vector vanishes. We may therefore construct the CI Lagrangian in terms of the MCSCF GBT vector rather than the

MCSCF gradient, and determine $\lambda(x)$ by requiring that the MCSCF GBT matrix elements vanish at all geometries. We adopt this procedure for reasons that will become apparent below. To avoid new notation we will denote the GBT matrix elements by f_i and its electronic derivatives by g_{ij}, k_{ijk}, and l_{ijkl}. However, it should be kept in mind that these quantities are strictly speaking not the same as those previously referred to by the same notation. For example, in g_{ij}, k_{ijk}, and l_{ijkl} the first index denotes the GBT matrix element and not differentiation. These quantities are therefore symmetric with respect to permutations involving all indices except the first.

To determine the electronic derivatives of the GBT matrix elements we BCH expand the expressions

$$f_{pq}(x,\lambda)=\langle \mathrm{MC}|\exp(p)[Q_{pq},\exp(\kappa)H(x)\exp(-\kappa)]\exp(-p)|\mathrm{MC}\rangle \tag{69}$$

$$f_{k}(x,\lambda)=\langle \mathrm{MC}|[R_k,\exp(p)\exp(\kappa)H(x)\exp(-\kappa)\exp(-p)]|\mathrm{MC}\rangle \tag{70}$$

for all $p>q$ and all $k\neq \mathrm{MC}$. At x_0 we obtain

$$f_i^{(n)}=\langle \mathrm{MC}|[t_i,H^{(n)}]|\mathrm{MC}\rangle \tag{71}$$

$$g_{ij}^{(n)}=\langle \mathrm{MC}|[t_i,[t_j,H^{(n)}]]|\mathrm{MC}\rangle \tag{72}$$

$$k_{ijk}^{(n)}=\langle \mathrm{MC}|[t_i,[t_j,t_k,H^{(n)}]]|\mathrm{MC}\rangle \tag{73}$$

$$l_{ijkl}^{(n)}=\langle \mathrm{MC}|[t_i,[t_j,t_k,t_l,H^{(n)}]]|\mathrm{MC}\rangle \tag{74}$$

where the commutators are to be interpreted in the following way. First rearrange the operators such that all state transfer operators appear to the left of the orbital rotation operators, and such that within each group the operator defining the GBT matrix element (if present) appears before the operators corresponding to differentiation. Then symmetrize the state transfer operators and the orbital rotation operators separately, excluding the operator defining the GBT matrix element from the symmetrization. The following examples illustrate the notation:

$$\begin{aligned}l_{pq,rs,k,l}^{(n)}&=\langle \mathrm{MC}|[Q_{pq},[Q_{rs},R_k,R_l,H^{(n)}]]|\mathrm{MC}\rangle\\&=\langle \mathrm{MC}|[R_k,R_l,[Q_{pq},[Q_{rs},H^{(n)}]]]|\mathrm{MC}\rangle\end{aligned} \tag{75}$$

$$\begin{aligned}l_{k,l,pq,rs}^{(n)}&=\langle \mathrm{MC}|[R_k,[R_l,Q_{pq},Q_{rs},H^{(n)}]]|\mathrm{MC}\rangle\\&=\langle \mathrm{MC}|[R_k,[R_l,[Q_{pq},Q_{rs},H^{(n)}]]]|\mathrm{MC}\rangle.\end{aligned} \tag{76}$$

Note that the expressions are only symmetric in the second and higher indices.

5.3. Calculation of terms containing electronic derivatives $a^{(n,m)}$

In this section we discuss the calculation of the quantities $a^{(n,m)}$ [Eqs. (37)-(40)] in greater detail. In particular we illustrate how CI derivative terms containing $a^{(n,0)}$ may be calculated in a way which closely parallels the calculation of MCSCF derivative terms containing $a^{(n)}$.

We start by comparing the calculation of $e^{(n,0)}$ and $e^{(n)}$. The term $e^{(n)}$ is simply the expectation value of the nth derivative of the Hamiltonian:

$$e^{(n)}=\sum_{pq} D_{pq}^{\mathrm{MC}}h_{pq}^{(n)}+\tfrac{1}{2}\sum_{pqrs} d_{pqrs}^{\mathrm{MC}}g_{pqrs}^{(n)} \tag{77}$$

where the densities are defined as in Eqs. (56)-(57) but in terms of the MCSCF reference state. In a similar way

$$e^{(n,0)} = \sum_i \zeta_i^{(0)} \langle \mathrm{MC}|[t_i, H^{(n)}]|\mathrm{MC}\rangle \tag{78}$$

may be written as the expectation value of a set of effective density elements:

$$e^{(n,0)} = \sum_{pq} D^{E1}_{pq} h^{(n)}_{pq} + \tfrac{1}{2} \sum_{pqrs} d^{E1}_{pqrs} g^{(n)}_{pqrs}. \tag{79}$$

The one-electron effective density is given by [15, 16]

$$D^{E1}_{pq} = -\{\zeta^{(0)}, D^{\mathrm{MC}}\}_{pq} - 2D^{\mathrm{MC}\zeta}_{pq} \tag{80}$$

where the first term is a one-index transformed MCSCF density

$$\{\zeta^{(0)}, D^{\mathrm{MC}}\}_{pq} = \sum_\alpha (\zeta^{(0)}_{p\alpha} D^{\mathrm{MC}}_{\alpha q} + \zeta^{(0)}_{q\alpha} D^{\mathrm{MC}}_{p\alpha}) \tag{81}$$

and the second term is a transition density

$$D^{\mathrm{MC}\zeta}_{pq} = \sum_{k \neq \mathrm{MC}} \zeta^{(0)}_k \langle \mathrm{MC}|E_{pq}|k\rangle. \tag{82}$$

The two-electron densities d^{E1}_{pqrs} are obtained in a similar way. Once the effective densities have been constructed, $e^{(n)}$ and $e^{(n,0)}$ may be calculated in the same way.

We now turn to the CI derivative terms $f^{(n,0)}\lambda^{(1)}$ and compare these with the terms $f^{(n)}\lambda^{(1)}$ which appear in the calculation of MCSCF derivatives:

$$f^{(n)}\lambda^{(1)} = {}^{o}f^{(n)}\kappa^{(1)} + {}^{c}f^{(n)}p^{(1)}. \tag{83}$$

The orbital part may be calculated as

$${}^{o}f^{(n)}\kappa^{(1)} = 2\,Tr\kappa^{(1)}\Phi^{(n)} \tag{84}$$

where $\Phi^{(n)}$ is the Fock matrix [27]

$$\Phi^{(n)}_{pq} = \sum_\beta D^{\mathrm{MC}}_{p\beta} h^{(n)}_{q\beta} + \sum_{\beta\gamma\delta} d^{\mathrm{MC}}_{p\beta\gamma\delta} g^{(n)}_{q\beta\gamma\delta}. \tag{85}$$

The configuration part is calculated according to

$${}^{c}f^{(n)}p^{(1)} = -2\sum_{pq} D^{\mathrm{MC}p}_{pq} h^{(n)}_{pq} - \sum_{pqrs} d^{\mathrm{MC}p}_{pqrs} g^{(n)}_{pqrs} \tag{86}$$

where the transition densities are given by

$$D^{\mathrm{MC}p}_{pq} = \sum_{k \neq \mathrm{MC}} p^{(1)}_k \langle \mathrm{MC}|E_{pq}|k\rangle \tag{87}$$

and similarly for two-electron densities.

The CI derivative terms $f^{(n,0)}\lambda^{(1)}$ may be partitioned in the same way

$$f^{(n,0)}\lambda^{(1)} = {}^{o}f^{(n,0)}\kappa^{(1)} + {}^{c}f^{(n,0)}p^{(1)} \tag{88}$$

where both parts may be calculated as above [Eqs. (84) and (86)], but in terms of a set of modified densities. The orbital part becomes

$${}^{o}f^{(n,0)}\kappa^{(1)} = 2\,Tr\kappa^{(1)}\Phi^{(n,0)} \tag{89}$$

where $\Phi^{(n,0)}$ is defined as in Eq. (85) but calculated from the effective densities of Eq. (80) that are used in the calculation of $e^{(n,0)}$. The configuration part is calculated as

$$ {}^{c}f^{(n,0)}p^{(1)} = -2\sum_{pq} D^{E2}_{pq} h^{(n)}_{pq} - \sum_{pqrs} d^{E2}_{pqrs} g^{(n)}_{pqrs} - 2e^{(n)} \sum_{k\neq \mathrm{MC}} \zeta^{(0)}_{k} p^{(1)}_{k} \tag{90} $$

where we have introduced a new set of effective densities

$$ D^{E2}_{pq} = -\{\zeta^{(0)}, D^{\mathrm{MC}p}\}_{pq} - \sum_{kl} \zeta^{(0)}_{k} p^{(1)}_{l} \langle k|E_{pq}|l\rangle \tag{91} $$

and similarly for the two-electron case. Note the similarity between the two sets of effective densities in Eqs. (80) and (91). We conclude that $f^{(n,0)}\lambda^{(1)}$ may be calculated in the same way as $f^{(n)}\lambda^{(1)}$ once the effective densities of Eqs. (80) and (91) have been constructed.

We have shown how $e^{(n,0)}$ and $f^{(n,0)}\lambda^{(1)}$ may be calculated in a way which closely resembles the calculation of $e^{(n)}$ and $f^{(n)}\lambda^{(1)}$. Exactly the same techniques may be used to calculate $e^{(n,1)}$ and $f^{(n,1)}\lambda^{(1)}$ [which appear in the CI first anharmonicity expression Eq. (44)], but in this case we must construct one effective density for each perturbation (using $\zeta^{(1)}$ rather than $\zeta^{(0)}$). Similar techniques may also be used to calculate the terms containing $g^{(n,m)}$ and $k^{(n,m)}$, although the explicit expressions become more complicated. We will therefore not describe the calculation of these terms in detail. However, for the important special case of single-reference CI a simple and general prescription can be given for the calculation of $a^{(n,m)}$.

The expressions for SCF Hessians and first anharmonicities contain terms such as

$$ f^{(n)}\kappa^{(1)} = 2\,Tr\kappa^{(1)}\Phi^{(n)} \tag{92} $$

$$ g^{(n)}\kappa^{(1)}\kappa^{(1)} = 2\,Tr\kappa^{(1)}(\kappa^{(1)}, \Phi^{(n)}) \tag{93} $$

$$ k^{(n)}\kappa^{(1)}\kappa^{(1)}\kappa^{(1)} = 2\,Tr\kappa^{(1)}(\kappa^{(1)}, \kappa^{(1)}, \Phi^{(n)}) \tag{94} $$

where

$$ (\kappa^{(1)}, \Phi^{(n)})_{pq} = \sum_{\beta} D^{\mathrm{SCF}}_{p\beta}\{\kappa^{(1)}, h^{(n)}\}_{q\beta} + \sum_{\beta\gamma\delta} d^{\mathrm{SCF}}_{p\beta\gamma\delta}\{\kappa^{(1)}, g^{(n)}\}_{q\beta\gamma\delta} \tag{95} $$

is the Fock matrix calculated from one-index transformed integrals, and $(\kappa^{(1)}, \kappa^{(1)}, \Phi^{(n)})$ is the Fock matrix calculated from doubly one-index transformed integrals. In the SCF case these matrices may be calculated in the atomic orbital (AO) basis [3, 26].

The corresponding contributions to the single-reference CI derivatives are

$$ f^{(n,m)}\kappa^{(1)} = 2\,Tr\kappa^{(1)}\Phi^{(n,m)} \tag{96} $$

$$ g^{(n,m)}\kappa^{(1)}\kappa^{(1)} = 2\,Tr\kappa^{(1)}(\kappa^{(1)}, \Phi^{(n,m)}) \tag{97} $$

$$ k^{(n,m)}\kappa^{(1)}\kappa^{(1)}\kappa^{(1)} = 2\,Tr\kappa^{(1)}(\kappa^{(1)}, \kappa^{(1)}, \Phi^{(n,m)}) \tag{98} $$

where $\Phi^{(n,m)}$ is the Fock matrix calculated from one-index transformed densities

$$ D^{(n)}_{pq} = \{\zeta^{(n)}, D^{\mathrm{SCF}}\}_{pq} \tag{99} $$

and similarly for the two-electron case. The same set of effective densities are used in all three terms Eqs. (96)-(98) as well as in the term $e^{(n,m)}$.

When the electronic derivatives f, g, and k are obtained by differentiating the GBT condition, the linear transformations of $\zeta^{(n)}$ can be transferred completely to the densities as discussed above. When the derivatives are obtained by differentiating the SCF electronic energy, additional terms appear because of the symmetrization of the commutators. The two procedures give the same final results, and are therefore equivalent, but they differ in the complexity with which the results are obtained.

6. Practical considerations

In this section we discuss the practical implementation of the above expressions. We concentrate on the structure and the general features of the calculations and refer to [3] for more details.

6.1. *The CI gradient*

The calculation of the CI gradient is preceded by the optimization of the MCSCF and CI wave functions, and the determination of the zeroth-order Lagrange multipliers $\zeta^{(0)}$ [Eqs. (27)-(29)]. The requirements on the numerical accuracy of the wave functions and on the multipliers $\zeta^{(0)}$ are quite stringent since the error in the gradient is linear in the errors in the wave function and the multipliers. The multipliers $\zeta^{(0)}$ are determined using the techniques developed for second-order MCSCF optimization and for the solution of the first-order MCSCF response equations.

The subsequent evaluation of the gradient $W^{(1)}$ according to Eq. (42) is straightforward once the effective densities D_{pq}^{E1} and d_{pqrs}^{E1} have been constructed. By adding these to the CI densities

$$D_{pq}^{E3} = D_{pq}^{\mathrm{CI}} + D_{pq}^{E1} \tag{100}$$

and transforming these to the AO basis, the CI gradient can be calculated in a way which closely resembles the calculation of, for example, SCF gradients [15, 16]. This allows for a very efficient calculation of CI gradients.

6.2. *The CI Hessian*

The calculation of the CI Hessian requires the solution of the first-order MCSCF and CI response equations Eqs. (30) and (31) (in that order). No calculation of $\zeta^{(1)}$ is needed since the Hessian is an even-order derivative of the CI Lagrangian ($2n+2$ rule). If the threshold on the numerical error in the Hessian is ε, we must calculate $\lambda^{(1)}$ to an error ε, and $P^{(1)}$ to an error $\sqrt{\varepsilon}$. The strict requirements on the error in $\lambda^{(1)}$ occurs since we have eliminated $\zeta^{(1)}$ from the CI Hessian expression (43).

The solution of the first-order response equations Eqs. (30)-(31) has been discussed before [6, 8]. We only note that in order to construct $f^{(1)}$ and ${}^{c}F^{(1)}$ the first derivatives of the integrals are needed in the molecular orbital (MO) basis.

The CI Hessian $W^{(2)}$ of Eq. (43) consists of three pairs of terms, containing second-derivative, first-derivative, and undifferentiated integrals, respectively. (Note that these integrals are calculated from symmetrically orthonormalized orbitals, and that their derivatives therefore also contain contributions from the overlap matrix. Detailed expressions are given in [3]). The terms containing second-derivative integrals $E^{(2)}$ and $e^{(2,0)}$ may be calculated in parallel, using the densities D_{pq}^{E3} and d_{pqrs}^{E3} [Eq. (100)] which were constructed and transformed to the AO basis when calculating the gradient $W^{(1)}$. No transformation of second-derivative integrals to the MO basis is therefore required.

The terms in Eq. (43) containing the first-derivative integrals may be calculated as

$$F^{(1)}\Lambda^{(1)}+f^{(1,0)}\lambda^{(1)}=2Tr\kappa^{(1)}A^{(1)}-2\sum_{pq} D_{pq}^{E4}h_{pq}^{(1)}-\sum_{pqrs} d_{pqrs}^{E4}g_{pqrs}^{(1)}$$
$$-2e^{(n)}\sum_{k\neq \mathrm{MC}} \zeta_k^{(0)}p_k^{(1)}. \tag{101}$$

Here $A^{(1)}$ is the Fock matrix calculated from the first-derivative integrals and the $E3$ densities [Eq. (100)], and the $E4$ densities are given by

$$D_{pq}^{E4}=D_{pq}^{E2}+\sum_{K\neq \mathrm{CI}} \langle \mathrm{CI}|E_{pq}|K\rangle P_K^{(1)} \tag{102}$$

and similarly for the two-electron densities. We note that the ${}^cF^{(1)}P^{(1)}$ contribution to Eq. (101) could have been calculated directly from ${}^cF^{(1)}$, since this is needed anyway for solving the CI response equations (31). However, the $E4$ densities of Eq. (102) are useful for calculating contributions to the CI first anharmonicities (44).

The contributions to the CI Hessian containing undifferentiated integrals are best calculated in the MO basis using direct MCSCF techniques. Again a set of modified densities may be constructed to simplify the calculations, although we do not give any details here.

6.3. The CI first anharmonicities

To calculate CI first anharmonicities we need the first-order responses of all the variational parameters $\lambda^{(1)}$, $P^{(1)}$, and $\zeta^{(1)}$. The MCSCF responses $\lambda^{(1)}$ are already available to the required accuracy (error less than ε) from the calculation of the CI Hessian. The CI responses $P^{(1)}$ are also available but the accuracy (error less than $\sqrt{\varepsilon}$) may not be sufficient since the numerical error in CI anharmonicities is linear in the error in $P^{(1)}$. Finally the first derivatives of the Lagrange multipliers $\zeta^{(1)}$ are not available from lower derivatives and must be obtained by solving the linear equations Eq. (32) to error smaller than ε.

The CI first anharmonicities Eq. (44) contain three distinct sets of terms: the first four terms are calculated from CI densities and responses, the next four terms have a similar structure but are calculated from $\zeta^{(0)}$ and the MCSCF densities and responses. Finally the three last terms have a structure similar to MCSCF Hessians, and are calculated from $\zeta^{(1)}$ and from the MCSCF densities and responses.

The Hessian-like terms are calculated in the same way as the MCSCF contribution to the CI Hessian, the only difference being that the modified densities are calculated from $\zeta^{(1)}$ rather than $\zeta^{(0)}$. Hence one set of modified densities must be constructed for each perturbation. Once these densities have been constructed, these contributions to $W^{(3)}$ may be evaluated simultaneously with the calculation of the CI Hessian.

The remaining eight contributions to $W^{(3)}$ may be calculated pairwise as discussed above for the CI Hessian. For example, $E^{(3)}+e^{(3,0)}$ may be calculated simultaneously with $E^{(2)}+e^{(2,0)}$ and $E^{(1)}+e^{(1,0)}$, using the same densities $E3$ [Eq. (100)] transformed to the AO basis. Also, the second-derivative terms $F^{(2)}\Lambda^{(1)}$ and $f^{(2,0)}\lambda^{(1)}$ may be evaluated simultaneously with the CI Hessian terms $F^{(1)}\Lambda^{(1)}$ and $f^{(1,0)}\lambda^{(1)}$, using the modified densities $E3$ [Eq. (100)] and $E4$ [Eq. (102)]. These calculations may be carried out in the AO basis, completely avoiding the transformation of second-derivative integrals to the MO basis.

The remaining four contributions to $W^{(3)}$ are best calculated in the MO basis, using standard direct CI and MCSCF techniques. Again we may simplify the calculations by constructing a set of effective densities.

7. Conclusions

We have constructed a CI energy Lagrangian which is variational in all parameters, including the orbital rotational parameters. By applying standard techniques for variational wave functions to this Lagrangian, we have directly obtained a convenient set of expressions for the CI response equations and derivatives. The state and orbital rotational parameters obey the $2n+1$ rule, and the Lagrange multipliers obey the somewhat stronger $2n+2$ rule. The simplifications which are usually obtained by invoking the Handy-Schaefer technique are automatically incorporated to all orders and require no special attention.

We have derived and discussed CI derivative expressions up to third order, with emphasis on the overall structure. The expressions derived reveal a structure in the CI derivatives which has previously not been fully apparent. For example, the CI Hessian contains two distinct contributions, both of which are similar to the expression for MCSCF Hessians. One of these contributions is calculated from CI densities and responses, the other is calculated from MCSCF modified densities and responses. By fully exploring this structure one may significantly reduce the cost of CI derivative calculations, as has already been recognized by Rice and Amos [15] and Shepard [16] for the calculation of CI gradients.

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