Chemical Physics 86 (1984) 413-432 North-Holland, Amsterdam

HIGHER MOLECULAR-DEFORMATION DERIVATIVES OF THE CONFIGURATION-INTERACTION ENERGY

Jack SIMONS

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, USA

Poul JØRGENSEN

Department of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

and

Trygve U. HELGAKER

Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

Received 26 October 1983

We derive expressions for the first through fourth derivatives of the configuration-interaction (CI) electronic energy with respect to molecular deformation. By using unitary exponential parameterizations of the wavefunction's orbital and configuration amplitude response together with a power-series expansion of the geometry dependence of the hamiltonian, a computationally attractive expression for the CI energy derivatives is obtained. The use of so-called direct methods in evaluating the CI derivatives is discussed as are the relative efforts involved in using our CI-based energy-derivative expressions and those which we obtained earlier for derivatives of the multiconfigurational self-consistent-field energy. The power-series expansion of the geometry dependence of the hamiltonian that we have derived may be used for evaluating molecular-deformation derivatives for any approximate wavefunction constructed from a set of orthonormal orbitals.

1. Introduction

The analytical evaluation of derivatives of the ab initio Born-Oppenheimer electronic energy with respect to molecular deformation has blossomed in recent years [1-9]. First (gradient) and second (hessian) derivatives are now computationally feasible to calculate for at least Hartree-Fock (HF), configuration-in-teraction (CI), and multiconfigurational self-consistent-field (MC SCF) wavefunctions. Knowledge of such energy derivatives promises to be of great benefit in locating and characterizing (via force constants) local minima and transition states on potential-energy surfaces. It is also likely to be used in classical dynamical studies of molecular motion on such surfaces.

Higher (e.g., third and fourth) derivatives of the electronic energy with respect to molecular deformation contain information about the local anharmonicities of the energy surface. Such knowledge is important to spectroscopists [10] who are interested in characterizing molecular potential-energy surfaces based upon spectral and ab initio quantum-mechanical data. Recent semiclassical dynamics [11] work indicates that such anharmonicities also play central roles in determining both rates of intramolecular energy transfer and under what conditions quasiperiodic vibrational motion will become chaotic.

Until quite recently, the ab initio analytical evaluation of third and higher derivatives has not been possible. However, very recently Pulay [12] has given an expression for the third derivative of the MC SCF energy and Simons and Jørgensen [13] have shown how to compute the third and fourth MC SCF-energy

0301-0104/84/\$03.00 © Elsevier Science Publishers B.V. (North-Holland Physics Publishing Division)

J. Simons et al. / Molecular - deformation derivatives of the CI energy

derivatives. In our opinion, it is the introduction of new theoretical tools, including the use of explicitly unitary orbital- and configuration-space transformation operators [9,14,15] as well as representations of the electronic hamiltonian in an orthonormal and differentiable basis set, which made these recent developments tractable. The most recent development of Helgaker and Almlöf [16], where the hamiltonian is expanded in an orthogonal basis which reduces to the molecular-orbital basis as derivatives are taken, has made this development even more tractable. It is the purpose of the present paper to derive and analyze for computational feasibility the expressions for CI-based energy derivatives through fourth order. The first and second derivatives have been given earlier by us [9]. In the present paper we cast the results of this derivation in a computationally even more tractable form and we also address how to go about the actual calculation of the third and fourth energy derivatives for CI wavefunctions which may contain as many as 10⁶ configurations. Although the present state of the art in computer and disk hardware may not yet allow one to perform third- and fourth-derivative calculations for larger molecules using reasonable basis sets and configuration expansion lengths, it is only a matter of time before such will be possible.

In section 2 we derive expressions for higher-order derivatives of one- and two-electron integrals constructed from a set of symmetrically orthonormalized molecular orbitals. The derivatives are expressed in an especially compact form involving atomic-orbital integral derivatives transformed to the molecular-orbital basis followed by a series of one-index transformations of the undifferentiated molecular-orbital integrals using derivatives of the overlap matrix as transformation matrices.

In section 3 we determine the first four geometrical derivatives of the CI total energy. To do this we first determine the response of the orthonormal MC SCF orbitals used to form the configurations of the CI wavefunction. These orbital responses (corresponding to orbital reoptimization) together with the response of the hamiltonian described in section 2 (corresponding to orbital reorthonormalization) are then used to construct an effective hamiltonian operator. The effective hamiltonian is set up in terms of a sequence of one-index transformations involving the derivatives of the overlap matrix, and a sequence of transformations involving the MC SCF orbital response parameters. Using this effective hamiltonian the CI response is determined and the CI energy derivatives then identified. In section 4 we discuss how to solve, using so-called "direct methods", the large set of linear equations which determine the MC SCF orbital responses. Finally, section 5 contains a summary of how our results can be computationally implemented as well as a comparison of the relative efforts involved in computing CI- and MC SCF-based energy derivatives through fourth order.

2. The effect of geometrical deformation on the electronic hamiltonian

In this section we will study the effect of a geometrical deformation on the electronic hamiltonian. The power-series expansion of the hamiltonian which will be derived is general in the sense that it can be used for any approximate wavefunction constructed from a set of orthonormal orbitals.

Let us assume that the electronic hamiltonian H_0 at the undisplaced geometry denoted by R^0 is expressed in terms of a set of orthonormal molecular orbitals $\{\phi_r\}$ (e.g., a set of SCF or MC SCF orbitals)

$$H_0 = \sum_{pq} h_{pq} a_p^+ a_q + \frac{1}{2} \sum_{pqts} g_{ptqs} a_p^+ a_q^+ a_s a_t,$$
(1)

where the two-electron integrals are defined as

$$g_{p_{1}q_{s}} = \int \phi_{p}^{*}(1) \ \phi_{q}^{*}(2) r_{12}^{-1} \phi_{r}(1) \ \phi_{s}(2) \ \mathrm{d}\tau_{1} \ \mathrm{d}\tau_{2} \tag{2}$$

and the one-electron integrals are

$$h_{pq} = \langle \phi_p | h_1 | \phi_q \rangle. \tag{3}$$

The operator h_1 is given by

$$h_{1} = -\frac{1}{2} \nabla_{r}^{2} - \sum_{A} \frac{Z_{A}}{|r - R_{A}|} + \frac{1}{2} \sum_{A \neq B} \frac{Z_{A} Z_{B}}{|R_{A} - R_{B}|},$$
(4)

where Z_A denotes the charge and R_A the position of nucleus A. At a displaced molecular geometry $R^0 + \mu$, where μ is a row vector

$$\mu = \left\{ \mu_x^{\mathsf{A}} \mu_y^{\mathsf{A}} \mu_z^{\mathsf{A}} \mu_z^{\mathsf{B}} \mu_y^{\mathsf{B}} \dots \right\},\tag{5}$$

containing the small displacements in the x, y and z components of all nuclei A, B,..., the hamiltonian may be expressed in a power-series expansion in μ :

$$H(R^{0} + \mu) = H_{0} + \mu H_{1} + \frac{1}{2}\mu\mu H_{2} + \frac{1}{6}\mu\mu\mu H_{3} + \frac{1}{24}\mu\mu\mu\mu H_{4} + \dots$$
(6)

We will, in the remainder of this section, describe how to evaluate H_1 , H_2 , H_3 and H_4 .

The nuclear displacement dependence appears in the hamiltonian in the atomic-orbital basis in which the molecular orbitals are expanded, as well as in the electron-nuclear and nuclear-nuclear interaction terms. The nuclear displacement dependence of the nuclear-nuclear interaction term will not be considered further as it may be straightforwardly evaluated. The nuclear displacement dependence of the electron-nuclear interaction may be determined by carrying out a Taylor-series expansion around $\mu = 0$:

$$|r - R_{A}|^{-1} = |r - R_{A}^{0} - \mu_{A}|^{-1}$$

= $|r - R_{A}^{0}|^{-1} + \mu_{A} (\nabla_{A} |r - R_{A}^{0}|^{-1}) + \frac{1}{2} \mu_{A} \mu_{A} (\nabla_{A} \nabla_{A} |r - R_{A}^{0}|^{-1})$
+ $\frac{1}{6} \mu_{A} \mu_{A} \mu_{A} (\nabla_{A} \nabla_{A} \nabla_{A} |r - R_{A}^{0}|^{-1}) + \frac{1}{24} \mu_{A} \mu_{A} \mu_{A} \mu_{A} (\nabla_{A} \nabla_{A} \nabla_{A} \nabla_{A} |r - R_{A}^{0}|^{-1}) + \dots$ (7)

The displacement dependence which occurs through the atomic basis functions presents further challenges. To treat this dependence in a relatively simple fashion requires: (1) that the orthonormality of the orbitals $\{\phi_r\}$ used to express H is preserved at all geometries; (2) that the orbitals $\{\phi_r\}$ can be differentiated analytically and conveniently and (3) that the power-series expansion of the hamiltonian generated by taking such orbital derivatives be expressed directly in the molecular-orbital basis. Condition (1) is desirable because the geometry dependence of the annihilation and creation operators then need not explicitly be considered since the usual anticommutation relations $\{a_p^+, a_q\} = \delta_{pq}$ are satisfied at any geometry. Condition (2) is necessary to derive analytical expressions for the power-series expansion of the hamiltonian. Condition (3) is computationally useful even though it is not a necessary condition. If this condition is fulfilled it immediately gives the hamiltonian expansion in the molecular-orbital basis [16] in which the calculation is actually carried out; it allows one to avoid [9,17] carrying out unnecessary transformations of the integrals (see later).

2.1. Dependence of the orthonormal orbital basis on deformation

In a recent publication [9], we expressed the nuclear displacement dependence of the atomic orbitals in terms of a set of symmetrically orthogonalized atomic orbitals. These orbitals satisfy conditions (1) and (2) but not condition (3), as a result of which integrals and integral derivatives have to be transformed from the symmetrically orthogonalized atomic-orbital basis to the molecular-orbital basis. Such a transformation is, of course, unappealing because it has to be carried out for each component of the nuclear displacement. Helgaker and Almlöf [16] have described how this transformation may be avoided by setting up the hamiltonian in a basis of orthogonalized molecular orbitals in which the atomic-to-molecular orbital

J. Simons et al. / Molecular-deformation derivatives of the CI energy

expansion coefficients are fixed at the values they have at the undisplaced geometry. At the geometry R^0 the orthonormal basis orbitals $\{\phi_i^0\}$ become the actual Hartree-Fock or MC SCF molecular orbitals

$$\phi_i^0 = \sum_{\alpha} C_{i\alpha}^0 \chi_{\alpha},\tag{8}$$

and at a displaced geometry $R^0 + \mu$ the orthonormal basis orbitals $\{\phi_i\}$ are defined as

$$\phi_i = \sum_{j\alpha} S_{ij}^{-1/2} C_{j\alpha}^0 \chi_{\alpha}, \tag{9}$$

where (we assume that all atomic orbitals χ_{α} and expansion coefficients $C_{i\alpha}^0$ are real)

$$S_{ij} = \sum_{\alpha\beta} C^0_{i\alpha} C^0_{j\beta} \langle \chi_{\alpha} | \chi_{\beta} \rangle.$$
(10)

If the hamiltonian at $\mathbb{R}^0 + \mu$ is expressed in terms of the orbitals appearing in eq. (9), conditions (1) and (2) are straightforwardly satisfied. Furthermore, the power-series expansion of the hamiltonian is expressed directly in terms of the HF or MC SCF molecular orbitals at \mathbb{R}^0 , and condition (3) is therefore satisfied. In the following derivation, we use the orbitals of eq. (9) to derive our results because these orbitals offer a conceptually simpler way to derive our CI derivative expressions than the symmetrically orthogonalized atomic orbitals.

The hamiltonian at a displaced geometry may be expressed in terms of the symmetrically orthogonalized basis in eq. (9) as

$$H(R^{0} + \mu) = \sum_{pq} \tilde{h}_{pq} a_{p}^{+} a_{q} + \frac{1}{2} \sum_{pqls} \tilde{g}_{plqs} a_{p}^{+} a_{q}^{+} a_{s} a_{l}, \qquad (11)$$

where a tilde is used to denote that the integrals are evaluated in the symmetrically orthogonalized basis. In order to determine the power-series expansion of $H(R^0 + \mu)$ it is necessary to determine the derivatives of the one- and two-electron integrals in eq. (11) and we therefore initially consider how to differentiate the symmetrically orthogonalized orbitals of eq. (9). The derivative of ϕ_i in eq. (9) is conveniently taken by dividing S into a diagonal part consisting of the unit matrix and a residual part denoted Δ . The derivative of

$$\phi_i = \sum_{j\alpha} (1+\Delta)_{ij}^{-1/2} C_{j\alpha}^0 \chi_{\alpha},$$
(12)

with respect to the *a*th component of the displacement μ , can then be obtained by differentiating the AO basis function χ_{α} and the term $(1 + \Delta)_{ij}^{-1/2}$. Following Helgaker and Almlöf [16], we Taylor-series expand $(1 + \Delta)^{-1/2}$

$$(1+\Delta)^{-1/2} = 1 - \frac{1}{2}\Delta + \frac{3}{8}\Delta\Delta - \frac{5}{16}\Delta\Delta\Delta + \frac{35}{128}\Delta\Delta\Delta\Delta + \dots,$$
(13)

and find that the first four derivatives of

$$T = (1 + \Delta)^{-1/2} \tag{14}$$

evaluated at $\mu = 0$ (where $\Delta = 0$) are as follows:

$$(1+\Delta)_{a}^{-1/2} = -\frac{1}{2}S(a) \equiv T^{(1)}.$$
(15)

$$(1+\Delta)_{ab}^{-1/2} = -\frac{1}{2}S(ab) + \frac{3}{8}SS(ab) \equiv T^{(2)},$$
(16)

$$(1+\Delta)_{abc}^{-1/2} = -\frac{1}{2}S(abc) + \frac{3}{8}SS(abc) - \frac{5}{16}SSS(abc) \equiv T^{(3)},$$
(17)

$$(1+\Delta)_{abcd}^{-1/2} = -\frac{1}{2}S(abcd) + \frac{3}{8}SS(abcd) - \frac{5}{16}SSS(abcd) + \frac{35}{128}SSSS(abcd) \equiv T^{(4)}.$$
 (18)

$$SS(abc) = S(a)S(bc) + S(bc)S(a) + S(b)S(ac) + S(ac)S(b) + S(c)S(ab) + S(ab)S(c)$$
(19)

and

$$SS(ab) = S(a)S(b) + S(b)S(a).$$
 (20)

Note that in, for example, eq. (19) S(a) S(cb) is not included because it is identical to S(a) S(bc) and therefore is not unique. Recall that the above overlap matrix S is given in terms of the primitive atomic-orbital (AO) overlap $\langle \chi_{\nu} | \chi_{\nu} \rangle$ as

$$S_{ij} = \sum_{\nu\gamma} C^0_{i\nu} \langle \chi_{\nu} | \chi_{\gamma} \rangle C^0_{j\gamma}.$$
⁽²¹⁾

Hence the above derivatives of S are evaluated in terms of derivatives of $\langle \chi_{\mu} | \chi_{\gamma} \rangle$ by transforming (with C_{μ}^{0}) to the orthonormal basis. For example

$$S_{ij}(a) = \sum_{\nu\gamma} C_{i\nu}^0 \langle \chi_{\nu} | \chi_{\gamma} \rangle(a) C_{j\gamma}^0, \qquad (22)$$

where $\langle \chi_{\nu} | \chi_{\gamma} \rangle(a)$ is the derivative of $\langle \chi_{\nu} | \chi_{\gamma} \rangle$ with respect to a nuclear deformation *a*. In eqs. (15)–(18) we have also introduced the notation $T^{(i)}$ where the superscript (*i*) indicates differentiation with respect to a given set of *i* coordinates.

2.2. Dependence of one- and two-electron integrals on displacement

The matrices $T^{(1)}$, $T^{(2)}$, $T^{(3)}$ and $T^{(4)}$ are straightforward to compute and can be stored if the number (N) of geometrical degrees of freedom is not extremely large. Once computed, these matrices can be used to evaluate derivatives of the one- and two-electron integrals appearing in H. For example, the first derivative of \tilde{h}_{ag} is given by

$$\tilde{h}_{pq}^{(1)} = h_{pq}^{(1)} + \sum_{i} \left(h_{iq} T_{ip}^{(1)} + h_{pi} T_{iq}^{(1)} \right), \tag{23}$$

where

$$h_{\rho q}^{(1)} = \sum_{\alpha,\beta} C_{\rho\alpha}^{0} C_{q\beta}^{0} \left(\chi_{\alpha} |h| \chi_{\beta} \right)^{(1)}, \tag{24}$$

is nothing but the AO-level integral derivatives transformed to the orthonormal molecular-orbital basis. In eq. (24) the differentiation acts on the atomic orbitals and on the electron-nuclear interactions. The second contribution of eq. (23) involves a one-index transformation of the one-electron integrals in the orthonormal molecular orbital basis [16], and has its origin in differentiating $(1 + \Delta)^{-1/2}$ of eq. (12). The first derivative of the two-electron integrals can be written in an analogous way

$$\tilde{g}_{pqrs}^{(1)} = g_{pqrs}^{(1)} + \sum_{i} \left(g_{iqrs} T_{ip}^{(1)} + g_{pirs} T_{iq}^{(1)} + g_{pqis} T_{ir}^{(1)} + g_{pqri} T_{is}^{(1)} \right),$$
(25)

where

$$g_{\rho q r s}^{(1)} = \sum_{\alpha \beta \gamma \delta} C_{\rho \alpha}^{0} C_{q \beta}^{0} C_{r \gamma}^{0} C_{s \delta}^{0} \left(\chi_{\alpha} \chi_{\beta} | \chi_{\gamma} \chi_{\delta} \right)^{(1)}, \tag{26}$$

and the last four terms represent a one-index transformation of the two-electron integrals in the molecular-orbital basis. When the modified one- and two-electron integrals of eqs. (23) and (25), respectively, are multiplied by the appropriate creation and annihilation operators and summed over orbital indices, the above integral derivatives provide an expression for the first derivative $H^{(1)}$ of H:

$$H^{(1)} = \sum_{pq} \tilde{h}^{(1)}_{pq} a^+_p a^-_q + \frac{1}{2} \sum_{pqrs} \tilde{g}^{(1)}_{pqrs} a^+_p a^+_r a^-_s a^-_q.$$
(27)

We will now show that expressions for the higher integral derivatives may be obtained by a generalization of the above procedure, i.e. by writing the derivatives in terms of AO-level integral derivatives transformed to the molecular-orbital basis [see eqs. (24) and (26)] followed by a series of one-index transformations using $T^{(1)}$, $T^{(2)}$, $T^{(3)}$, and $T^{(4)}$ as transformation matrices. The one-index transformations are introduced because terms originating from differentiation of the T matrix are then grouped together in a very convenient way for carrying out the differentiation. We will for simplicity treat the one-electron case first.

Using matrix notation the set of transformed integrals may be written

$$\tilde{h} = ThT, \tag{28}$$

where

$$T = 1 + \delta. \tag{29}$$

From eq. (14) it is clear that the matrix δ vanishes for the unperturbed system and that the derivatives of δ are equal to the derivatives of T given by eqs. (15)–(18). In this matrix notation a one-index transformation is given by an anticommutator, e.g. eq. (23) may be written as

$$\tilde{h}^{(1)} = h^{(1)} + \{T^{(1)}, h\}.$$
(30)

The explicit use of anticommutators is convenient as it avoids any reference to individual orbital indices, treating the integral as a whole. To introduce the same simplifications for higher derivatives we first write eq. (28) as a sequence of anticommutators and then differentiate this sequence to obtain the integral derivatives $\tilde{h}^{(i)}$. This may be accomplished by introducing a Baker-Campbell-Hausdorf (BCH) expansion of the exponential matrices when the identity

$$T \equiv \exp(\ln T), \tag{31}$$

is introduced into eq. (28):

$$\tilde{h} = ThT = \exp(\ln T)h\exp(\ln T) = h + \{\ln T, h\} + \frac{1}{2}\{\ln T, \ln T, h\} + \dots$$
(32)

In the last equation we have introduced the *n*-tuple symmetric anticommutator defined as

$$\{A_1, A_2, \dots, A_n, h\} = (1/n!) P(1, 2, \dots, n) \{A_1, \{A_2, \dots, \{A_n, h\} \dots\}\},$$
(33)

where P(1, 2, ..., n) is a permutation operator which contains the n! permutations of the indices 1, 2,...n. From eq. (32) it is evident that the derivatives of \tilde{h} may be determined once the derivatives of the matrix ln T are known. To obtain those we expand ln T in a power series in δ

$$U = \ln T = \ln(1+\delta) = \delta - \frac{1}{2}\delta^2 + \frac{1}{3}\delta^3 - \frac{1}{4}\delta^4 + \dots,$$
(34)

and find that the first four derivatives may be written as

$$U^{(1)} = T^{(1)},$$

$$U^{(2)} = T^{(2)} - \frac{1}{2}T^{(1)}T^{(1)},$$

$$U^{(3)} = T^{(3)} - \frac{1}{2}T^{(1)}T^{(2)} - \frac{1}{2}T^{(2)}T^{(1)} + \frac{1}{3}T^{(1)}T^{(1)}T^{(1)},$$

$$U^{(4)} = T^{(4)} - \frac{1}{2}T^{(1)}T^{(3)} - \frac{1}{2}T^{(2)}T^{(2)} - \frac{1}{2}T^{(3)}T^{(1)} + \frac{1}{3}T^{(1)}T^{(1)}T^{(1)} + \frac{1}{3}T^{(1)}T^{(1)}T^{(1)} + \frac{1}{3}T^{(2)}T^{(1)} + \frac{1}{3}T^{(2)}T^{(1)} - \frac{1}{4}T^{(1)}T^{(1)}T^{(1)}T^{(1)}.$$

(35)

In these expressions the derivatives are symmetrized, e.g. the second term of $U^{(3)}$ becomes for the deformation coordinates a, b, and c

$$-\frac{1}{2}T^{(1)}T^{(2)} = -\frac{1}{2}T^{(1)}(a)T^{(2)}(bc) - \frac{1}{2}T^{(1)}(b)T^{(2)}(ac) - \frac{1}{2}T^{(1)}(c)T^{(2)}(ab).$$
(36)

Finally, by differentiating eq. (32) we obtain the MO integral derivatives in terms of the AO-level integral derivatives transformed to the molecular basis and a sequence of one-index transformations involving the matrices $U^{(i)}$. The first four derivatives become:

$$\begin{split} \tilde{h}^{(1)} &= h^{(1)} + \{U^{(1)}, h\}, \\ \tilde{h}^{(2)} &= h^{(2)} + \{U^{(1)}, h^{(1)}\} + \{U^{(2)}, h\} + \frac{1}{2}\{U^{(1)}, U^{(1)}, h\}, \\ \tilde{h}^{(3)} &= h^{(3)} + \{U^{(1)}, h^{(2)}\} + \{U^{(2)}, h^{(1)}\} + \frac{1}{2}\{U^{(1)}, U^{(1)}, h^{(1)}\} + \{U^{(3)}, h\} + \{U^{(1)}, U^{(2)}, h\} \\ &+ \frac{1}{6}\{U^{(1)}, U^{(1)}, U^{(1)}, h\}, \\ \tilde{h}^{(4)} &= h^{(4)} + \{U^{(1)}, h^{(3)}\} + \{U^{(2)}, h^{(2)}\} + \frac{1}{2}\{U^{(1)}, U^{(1)}, h^{(2)}\} + \{U^{(3)}, h^{(1)}\} + \{U^{(1)}, U^{(2)}, h^{(1)}\} \\ &+ \frac{1}{6}\{U^{(1)}, U^{(1)}, U^{(1)}, h^{(1)}\} + \{U^{(4)}, h\} + \frac{1}{2}\{U^{(2)}, U^{(2)}, h\} + \{U^{(1)}, U^{(3)}, h\} \\ &+ \frac{1}{2}\{U^{(1)}, U^{(1)}, U^{(2)}, h\} + \frac{1}{24}\{U^{(1)}, U^{(1)}, U^{(1)}, h\}. \end{split}$$
(37)

Certain simplifications may be introduced in the expressions for the third and higher derivatives for the one-electron integral case in eq. (37) due to the fact that h is a two-index quantity. To see this we recognize that \tilde{h} using eq. (29) may be written as

$$\tilde{h} = (1+\delta)h(1+\delta) = h + \{\delta - \frac{1}{2}\delta^2, h\} + \frac{1}{2}\{\delta, \{\delta, h\}\},$$
(38)

where the last equality sign can easily be checked by explicitly writing the anticommutators as matrix products. By comparing eq. (32) and eq. (38) we see that eq. (38) expresses in a direct fashion the fact that in the BCH expansion in eq. (32) all terms containing products of more than two $T^{(i)}$ matrices cancel exactly to any order. This cancellation simplifies the expressions for $\tilde{h}^{(3)}$ and $\tilde{h}^{(4)}$, e.g. the third derivative becomes:

$$\tilde{h}^{(3)} = h^{(3)} + \{T^{(1)}, h^{(2)}\} + \{T^{(2)} - \frac{1}{2}T^{(1)}T^{(1)}, h^{(1)}\} + \frac{1}{2}\{T^{(1)}, T^{(1)}, h^{(1)}\} + \{T^{(3)} - \frac{1}{2}T^{(1)}T^{(2)} - \frac{1}{2}T^{(2)}T^{(1)}, h\} + \{T^{(1)}, T^{(2)}, h\}.$$
(39)

Later in this section we show that the two-electron integral derivatives may be expressed in a form identical to eq. (37) with *h* replaced by *g*. In practical applications it may therefore be more convenient also to use eq. (37) to determine the one-electron integral derivatives since the simplifications obtained by using for example eq. (39) are not computationally significant.

We will now derive expressions for the two-electron integral derivatives. This derivation turns out to be

very similar to the one treated above for the one-electron case. The two-electron integrals contain four indices and a one-index transformation of the two-electron integrals may therefore be written as

$$\{g, T\}_{pqrs} = \sum_{i} (g_{iqrs}T_{ip} + g_{pirs}T_{iq} + g_{pqis}T_{ir} + g_{pqri}T_{is}).$$
(40)

Our aim therefore becomes to express a four-index transformation

$$\tilde{g}_{pqrs} = \sum_{ijkl} g_{ijkl} T_{ip} T_{jq} T_{kr} T_{ls}$$
⁽⁴¹⁾

as a series of anticommutators. Introducing the identity in eq. (31) into eq. (41) allows us to write eq. (41) as

$$\tilde{g}_{pqrs} = \sum_{ijkl} g_{ijkl} \left[\exp(\ln T) \right]_{ip} \left[\exp(\ln T) \right]_{jq} \left[\exp(\ln T) \right]_{kr} \left[\exp(\ln T) \right]_{ls}.$$
(42)

Eq. (42) is a generalized matrix product involving four exponential matrices and it therefore becomes convenient to derive a generalization of the BCH expansion which is valid for this case. To do so we introduce the function

$$f(x) = \sum_{ijkl} g_{ijkl} [\exp(x \ln T)]_{ip} [\exp(x \ln T)]_{jq} [\exp(x \ln T)]_{kr} [\exp(x \ln T)]_{ls},$$
(43)

and determine the Taylor-expansion coefficients of f(x) around x = 0:

$$f(0) = \sum_{ijkl} g_{ijkl} \delta_{ip} \delta_{jq} \delta_{kr} \delta_{ls} = g_{pqrs},$$

$$f'(0) = \sum_{ijkl} g_{ijkl} \left\{ \left[\ln T \exp(0) \right]_{ip} \delta_{jq} \delta_{kr} \delta_{ls} + \dots + \delta_{ip} \delta_{jq} \delta_{kr} \left[\ln T \exp(0) \right]_{ls} \right\}$$

$$= \sum_{i} \left[g_{iqrs} (\ln T)_{ip} + \dots + g_{pqri} (\ln T)_{is} \right] = \left\{ g, \ln T \right\}_{pqrs},$$

$$f''(0) = \left\{ \left\{ g, \ln T \right\}, \ln T \right\}_{pqrs}$$
(44)

and likewise for higher-order terms. The general BCH-formula is now obtained by setting x = 1 in the expansion of f(x):

$$\tilde{g} = g + \{\ln T, g\} + \frac{1}{2}\{\ln T, \ln T, g\} + \dots$$
(45)

Eq. (45) is formally identical to the conventional BCH expansion of eq. (32). The two-electron integral derivatives may now be determined by differentiating eq. (45) and using eq. (35). The resulting formulas obviously become identical to eq. (37) except that g now replaces h.

In the one-electron case we saw that all terms containing more than two matrices $T^{(i)}$ as factors cancel exactly. The corresponding simplification in the two-electron case occurs for all terms containing more than four matrices $T^{(i)}$, as is easily seen by substituting $T = 1 + \delta$ in eq. (41). This implies that no simplification occurs in the derivative expressions up to fourth order given in eq. (37).

Due to the use of one-index transformations (anticommutators) the derivatives as given by eq. (37) involve relatively few distinct contributions to each order. In contrast, a straightforward differentiation of eqs. (28) and (41) would lead to more complicated expressions for higher-order derivatives involving a greater number of distinct contributions. The use of one-index transformations also simplifies the construction of higher-order derivatives as most of the terms contributing to the higher-order derivatives may be constructed from contributions to lower-order derivatives. For example, all four individual

J. Simons et al. / Molecular - deformation derivatives of the CI energy

contributions to the second-order derivatives enter as entities in the calculation of third-order derivatives. The third-order contributions are obtained by simply performing further one-index transformations on the individual contributions to the second-order derivatives.

The analysis presented above provides us with practical expressions for the integral derivative arrays which enter into $H^{(1)}$, $H^{(2)}$, $H^{(3)}$, and $H^{(4)}$ and are used to form H_1 , H_2 , H_3 , and H_4 , respectively, of eq. (6). These hamiltonian derivatives have components along each of the 3N directions which describe the molecular displacements μ . As a result, H_1 has 3N components, H_2 has $(3N)^2$, H_3 has $(3N)^3$ and H_4 has $(3N)^4$ components.

3. Analysis of the CI energy

In the present section we evaluate geometrical derivatives of the total energy for the approximate electronic wavefunction case where a configuration-interaction (CI) calculation is carried out with a set of multiconfiguration self-consistent-field (MC SCF) orbitals. The calculation we describe can thus be considered to consist of two separate steps. In the first step, a MC SCF calculation is performed using a small to moderate size configuration list containing the dominant configurations of the calculation. In the second step, a CI calculation is carried out using the MC SCF orbitals of step one but with a configuration list which is larger than that used in the MC SCF calculation [18].

The CI wavefunction at the displaced geometry may be parameterized in terms of simultaneous unitary transformations in the orbital and configuration spaces of the CI wavefunction $|CI\rangle$ at the undisplaced geometry. The orbital response parameters are determined exclusively through the MC SCF calculation and the configuration amplitude response parameters are subsequently determined by the CI calculation of step two. The CI wavefunction at the displaced geometry $|CI\rangle$ may therefore be written as [9,14,15]

$$|\overline{\mathrm{CI}}\rangle = \exp(\mathrm{i}\kappa) \exp(\mathrm{i}S)|\mathrm{CI}\rangle,$$
(46)

where the operator

$$\kappa = i \sum_{r>s} \kappa_{rs} \left(a_r^+ a_s - a_s^+ a_r \right) \tag{47}$$

contains the non-redundant set of orbital excitation operators of the MC SCF calculation and the operator

$$S = i \sum_{n} S_{n} (|n\rangle \langle CI| - |CI\rangle \langle n|)$$
(48)

contains the set of state transfer operators $\{|n\rangle\langle CI|\}$ where $\{|n\rangle\}$ denotes the orthogonal complement set of states of the CI wavefunction. The total CI energy at the displaced geometry $R^0 + \mu$ becomes

$$E(R^{0} + \mu) = \langle \operatorname{CI}|\exp(-\mathrm{i}S) \exp(-\mathrm{i}\kappa) H(R^{0} + \mu) \exp(\mathrm{i}\kappa) \exp(\mathrm{i}S)|\operatorname{CI}\rangle.$$
⁽⁴⁹⁾

The CI total energy of eq. (49) contains a μ dependence in the electronic hamiltonian $H(R^0 + \mu)$, in the orbital rotation parameters $\{\kappa_{rs}\}$, and in the configuration amplitude rotation parameters $\{S_n\}$. The μ dependence of the hamiltonian has already been determined and explicitly written out as a power series in μ in eq. (6). The μ dependence of the orbital and configuration amplitude rotation parameters may also be power-series expanded

$$\kappa_{rs} = \mu \kappa_{rs}^{(1)} + \frac{1}{2} \mu \mu \kappa_{rs}^{(2)} + \frac{1}{6} \mu \mu \mu \kappa_{rs}^{(3)} + \frac{1}{24} \mu \mu \mu \mu \kappa_{rs}^{(4)} + \dots,$$
(50)

$$S_n = \mu S_n^{(1)} + \frac{1}{2} \mu \mu S_n^{(2)} + \frac{1}{6} \mu \mu \mu S_n^{(3)} + \frac{1}{24} \mu \mu \mu \mu S_n^{(4)} + \dots$$
(51)

The parameters $\{\kappa_{rs}^{(i)}\}\$ are determined as the orbital response parameters in the first (MC SCF) step of the

calculation, while the parameters $\{S_n^{(i)}\}\$ can be determined in the second (CI) step once the orbital response parameters are known.

To evaluate the parameters $\{S_n^{(i)}\}$ efficiently it is convenient to combine the μ dependence of the orbital rotation parameters $\{\kappa_{rs}\}$ and of the electronic hamiltonian $H(R^0 + \mu)$ in an "effective hamiltonian"

$$\overline{H}(R^{0}+\mu) = \exp(-i\kappa)H(R^{0}+\mu)\exp(i\kappa),$$
(52)

which explicitly takes into account both the reorthonormalization effect due to the nuclear distortion of the molecular orbitals and the reoptimization effect which results from optimizing the orbitals in the MC SCF calculation of step one. In this way all defects arising from the use of a finite basis set and an incomplete CI expansion are isolated in an effective hamiltonian.

In terms of this effective hamiltonian the expression for the CI total energy in eq. (49) becomes

$$E(R^{0} + \mu) = \langle \operatorname{CI}|\exp(-\mathrm{i}S)\overline{H}(R^{0} + \mu) \exp(\mathrm{i}S)|\operatorname{CI}\rangle.$$
(53)

Once the power-series expansion of the effective hamiltonian

$$H(R^{0} + \mu) = H_{0} + \mu H_{1} + \frac{1}{2}\mu\mu\overline{H}_{2} + \frac{1}{6}\mu\mu\mu\overline{H}_{3} + \frac{1}{24}\mu\mu\mu\mu\overline{H}_{4} + \dots$$
(54)

has been obtained by combining the expansions in eqs. (6) and (50), it is straightforward to determine the CI response parameters $\{S_n^{(i)}\}$ of eq. (51) using the fact that the total energy has to be stationary through each power in μ ($\delta E(R^0 + \mu) = 0$). The CI derivatives can then be determined by identifying in the CI total energy terms through the individual powers in μ :

$$E(R^{0} + \mu) = E_{0} + \mu E_{1} + \frac{1}{2}\mu\mu E_{2} + \frac{1}{6}\mu\mu\mu E_{3} + \frac{1}{24}\mu\mu\mu\mu E_{4} + \dots$$
(55)

In this expression E_1 and E_2 represent the CI molecular gradient and hessian, respectively, while E_3 and E_4 yield successively higher CI anharmonicity terms.

In section 3.1 we present the formulas needed to determine the MC SCF orbital response parameters $\{\kappa_{rs}^{(i)}\}$ of eq. (50), and in section 3.2 these parameters are combined with the power-series expansion of $H(R^0 + \mu)$ of section 2 to give the expansion in eq. (54) of the effective hamiltonian. The configuration amplitude response parameters $\{S_n^{(i)}\}$ are determined in section 3.4 and the CI molecular gradient, hessian and anharmonicity expressions $\{E_i\}$ are finally identified.

3.1. Treatment of the MC SCF orbital response

Eq. (50) above expresses the μ dependence of the orbital response parameters $\{\kappa_{rs}\}$ as a power series in μ . The orbital response parameters which enter into this expansion have either explicitly been derived in refs. [9,13] or may straightforwardly be derived based on equations in ref. [19]. To express these results in a compact notation the orbital (κ) and configuration state function amplitudes (^{MC}S) and the corresponding excitation operators $\{a_r^+a_s - a_s^+a_r\}$ and $\{|^{MC}n\rangle\langle MC| - |MC\rangle\langle {}^{MC}n|\}$ are collected together as column vectors

$$\lambda = \begin{pmatrix} \kappa \\ MC_S \end{pmatrix},$$

$$^{MC}T = \begin{pmatrix} a_r^+ a_s - a_s^+ a_r \\ |^{MC}n\rangle\langle MC| - |MC\rangle\langle ^{MC}n| \end{pmatrix},$$
(57)

where $\{|^{MC}n\rangle\}$ denotes the orthogonal complement space to the multiconfiguration self-consistent-field

state |MC> which is determined in step one. It is also convenient to introduce the following definitions of matrices which enter into the equations which determine the κ_{rs} parameters:

$${}^{\mathrm{MC}}F^{(i)} = \langle \mathrm{MC}|[{}^{\mathrm{MC}}T, H_i]|\mathrm{MC}\rangle, \tag{58}$$

$${}^{\mathrm{MC}}G^{(i)} = \langle \mathrm{MC} | [{}^{\mathrm{MC}}T, {}^{\mathrm{MC}}T, H_i] | \mathrm{MC} \rangle, \tag{59}$$

$${}^{\mathrm{MC}}K^{(i)} = \langle \mathrm{MC} | [{}^{\mathrm{MC}}T, {}^{\mathrm{MC}}T, {}^{\mathrm{MC}}T, {}^{\mathrm{MC}}T, {}^{\mathrm{MC}}T, {}^{\mathrm{MC}}T \rangle,$$
(60)

$${}^{AC}L^{(i)} = \langle \mathrm{MC}|[{}^{\mathrm{MC}}T, {}^{\mathrm{MC}}T, {}^{\mathrm{MC}}T, {}^{\mathrm{MC}}T, {}^{H_i}]|\mathrm{MC}\rangle,$$
(61)

$${}^{\mathrm{MC}}M^{(i)} = \langle \mathrm{MC} | [{}^{\mathrm{MC}}T, {}^{\mathrm{MC}}T, {}^{\mathrm{MC}}T$$

In eqs. (59)-(62) we have used the *n*-tuple symmetric commutators defined in ref. [20]. The orbital response parameters { $\kappa_{c_i}^{(i)}$ } are then obtained, as shown in refs. [9,13,19], as the orbital parts of the vector $\lambda^{(i)}$ given below

$$-{}^{MC}G^{(0)}\lambda^{(1)} = {}^{MC}F^{(1)}.$$
(63)

$$-\frac{1}{2} {}^{MC} G^{(0)} \lambda^{(2)} = \frac{1}{2} {}^{MC} F^{(2)} + {}^{MC} G^{(1)} \lambda^{(1)} + \frac{1}{2} {}^{MC} K^{(0)} \lambda^{(1)} \lambda^{(1)},$$
(64)

$$-\frac{1}{6}{}^{MC}G^{(0)}\lambda^{(3)} = \frac{1}{6}{}^{MC}F^{(3)} + \frac{1}{2}{}^{MC}G^{(1)}\lambda^{(2)} + \frac{1}{2}{}^{MC}G^{(2)}\lambda^{(1)} + \frac{1}{2}{}^{MC}K^{(0)}\lambda^{(2)}\lambda^{(1)} + \frac{1}{2}{}^{MC}K^{(1)}\lambda^{(1)}\lambda^{(1)} + \frac{1}{2}{}^{MC}L^{(0)}\lambda^{(1)}\lambda^{(1)}\lambda^{(1)}.$$
(65)

$$-\frac{1}{24}{}^{MC}G^{(0)}\lambda^{(4)} = \frac{1}{24}{}^{MC}F^{(4)} + \frac{1}{6}{}^{MC}G^{(1)}\lambda^{(3)} + \frac{1}{6}{}^{MC}G^{(3)}\lambda^{(1)} + \frac{1}{4}{}^{MC}G^{(2)}\lambda^{(2)} + \frac{1}{6}{}^{MC}K^{(0)}\lambda^{(3)}\lambda^{(1)} + \frac{1}{8}{}^{MC}K^{(0)}\lambda^{(2)}\lambda^{(2)} + \frac{1}{2}{}^{MC}K^{(1)}\lambda^{(2)}\lambda^{(1)} + \frac{1}{4}{}^{MC}K^{(2)}\lambda^{(1)}\lambda^{(1)} + \frac{1}{6}{}^{MC}L^{(1)}\lambda^{(1)}\lambda^{(1)}\lambda^{(1)} + \frac{1}{4}{}^{MC}L^{(0)}\lambda^{(2)}\lambda^{(1)}\lambda^{(1)} + \frac{1}{24}{}^{MC}M^{(0)}\lambda^{(1)}\lambda^{(1)}\lambda^{(1)}\lambda^{(1)}$$
(66)

In section 4 we will elaborate about how these equations might best be solved.

The kind of MC SCF calculation outlined here does not determine a unique set of orbitals in the sense that the orbitals, for example, are only determined to within an arbitrary rotation among the completely occupied orbitals and an arbitrary rotation among the unoccupied orbitals [14]. As a result, CI calculations in which a chosen set of electronic configurations are employed may not be consistent when performed with this type of MC SCF orbitals at two neighboring geometries. In particular, if the two geometries are only infinitesimally displaced, the resultant CI energy change may not be infinitesimally small. One solution to this problem is to uniquely determine all of the MC SCF orbitals by diagonalizing the redundant part of the Fock potential with an exponential operator containing the redundant orbital excitation operators and to then determine the resulting orbital responses [9]. Another solution may be to only consider CI calculations of the type where the CI energy is invariant with respect to rotations among orbitals that are not uniquely determined by the MC SCF procedure. Such a CI calculation could, for example, be one consisting of all single and double excitations out of the MC SCF configuration space used in determining the orbitals which are employed in the subsequent CI calculation.

3.2. The effective hamiltonian and its geometry dependence

1 N

We will now use the orbital responses $\{\kappa_{rs}^{(i)}\}$ obtained in the previous section to construct the effective hamiltonian expansion in eq. (54). To do this we simplify the hamiltonian in eq. (52) using the conventional Baker-Campbell-Hausdorf expansion expressed in terms of symmetric commutators

$$\overline{H}(R^{0} + \mu) = \exp(-i\kappa)H(R^{0} + \mu)\exp(i\kappa)$$

$$= H(R^{0} + \mu) - i[\kappa, H(R^{0} + \mu)] - \frac{1}{2}[\kappa, \kappa, H(R^{0} + \mu)] + \frac{1}{6}i[\kappa, \kappa, \kappa, H(R^{0} + \mu)]$$

$$+ \frac{1}{24}[\kappa, \kappa, \kappa, \kappa, H(R^{0} + \mu)] + \dots$$
(67)

(65)

The power-series expansion of $H(R^0 + \mu)$ is given in eq. (6) and earlier in eqs. (63)-(66) expressions are given for the μ -expansion of the κ parameters. Substituting these expansions into eq. (67) and collecting together factors multiplying each power of μ , we may identify each term in the order-by-order expansion of \overline{H} in eq. (54). Expressions for the \overline{H}_k operators are as follows

$$H_0 = H_0,$$
(68)
$$\overline{H_1} = H_1 - i [\kappa^{(1)}, H_0],$$
(69)

$$\frac{1}{2}\overline{H}_{2} = \frac{1}{2}H_{2} - i[\kappa^{(1)}, H_{1}] - \frac{1}{2}[\kappa^{(1)}, \kappa^{(1)}, H_{0}] - \frac{1}{2}i[\kappa^{(2)}, H_{0}],$$
(70)

$$\frac{1}{6}\overline{H}_{3} = \frac{1}{6}H_{3} - \frac{1}{6}i[\kappa^{(3)}, H_{0}] - \frac{1}{2}i[\kappa^{(2)}, H_{1}] - \frac{1}{2}i[\kappa^{(1)}, H_{2}] - \frac{1}{2}[\kappa^{(1)}, \kappa^{(1)}, H_{1}] - \frac{1}{2}[\kappa^{(1)}, \kappa^{(2)}, H_{0}] + \frac{1}{2}i[\kappa^{(1)}, \kappa^{(1)}, \kappa^{(1)}, H_{0}],$$
(71)

$$\frac{1}{24}\overline{H}_{4} = \frac{1}{24}H_{4} - \frac{1}{24}i[\kappa^{(4)}, H_{0}] - \frac{1}{6}i[\kappa^{(3)}, H_{1}] - \frac{1}{4}i[\kappa^{(2)}, H_{2}] - \frac{1}{6}i[\kappa^{(1)}, H_{3}] - \frac{1}{8}[\kappa^{(2)}, \kappa^{(2)}, H_{0}] - \frac{1}{6}[\kappa^{(1)}, \kappa^{(3)}, H_{0}] - \frac{1}{2}[\kappa^{(1)}, \kappa^{(2)}, H_{1}] - \frac{1}{4}[\kappa^{(1)}, \kappa^{(1)}, H_{2}] + \frac{1}{6}i[\kappa^{(1)}, \kappa^{(1)}, \kappa^{(1)}, H_{1}] + \frac{1}{4}i[\kappa^{(1)}, \kappa^{(1)}, \kappa^{(2)}, H_{0}] + \frac{1}{24}[\kappa^{(1)}, \kappa^{(1)}, \kappa^{(1)}, \kappa^{(1)}, H_{0}].$$
(72)

Since a commutator as $[\kappa^{(1)}, H_1]$ can be viewed as a modified hamiltonian with integrals equal to one-index transformed H_1 integrals, $\overline{H_i}$ of eqs. (69)-(72) may be determined by carrying out a sequence of one-index transformations on the integrals of H_i . In the next section we will demonstrate this point in more detail.

3.3. Remarks on the computational implementation of \overline{H}_k

The computational evaluation of expectation or transition values involving the above \overline{H}_k operators is not nearly as difficult as one might think based upon a cursory analysis of eqs. (69)-(72). Given that one can evaluate and store the integral derivatives $\{\tilde{h}^{(i)}\}$ and $\{\tilde{g}^{(i)}\}$ which we discussed earlier, it is possible to evaluate each of the commutators appearing in eqs. (69)-(72) by carrying out further one-index transformations [20] on these integrals. Let us consider one concrete example to illustrate this essential point. The contribution $-\frac{1}{2}[\kappa^{(1)}, \kappa^{(1)}, H_1]$ appearing in $\frac{1}{6}\overline{H}_3$ is initially recognized to be equal to $-\frac{1}{2}[\kappa^{(1)}, [\kappa^{(1)}, H_1]]$ and can be computationally evaluated as follows. First, the commutator $[\kappa^{(1)}, H_1]$ is carried out for a nuclear deformation a in $\kappa^{(1)}$ and b in H_1

$$\begin{bmatrix} \kappa^{(1)}, H_1 \end{bmatrix} = i \sum_{r > s} \kappa_{rs}^{(1)}(a) \left(\sum_{pq} \begin{bmatrix} a_r^+ a_s - a_s^+ a_r, a_p^+ a_q \end{bmatrix} \tilde{h}_{pq}^{(1)}(b) + \frac{1}{2} \sum_{pqmn} \tilde{g}_{pqmn}^{(1)}(b) \begin{bmatrix} a_r^+ a_s - a_s^+ a_r, a_p^+ a_m^+ a_n a_q \end{bmatrix} \right) = i \sum_{pq} \sum_r \begin{bmatrix} \tilde{h}_{pr}^{(1)}(b) \kappa_{qr}^{(1)}(a) + \kappa_{pr}^{(1)}(a) \tilde{h}_{rq}^{(1)}(b) \end{bmatrix} a_p^+ a_q + \frac{1}{2} i \sum_{pqrs} \sum_t \begin{bmatrix} \tilde{g}_{tqrs}^{(1)}(b) \kappa_{pt}^{(1)}(a) + \tilde{g}_{ptrs}^{(1)}(b) \kappa_{qt}^{(1)}(a) + \tilde{g}_{pqrs}^{(1)}(b) \kappa_{rt}^{(1)}(a) + \tilde{g}_{pqrt}^{(1)}(b) \kappa_{st}^{(1)}(a) \end{bmatrix} a_p^+ a_r^+ a_s a_q.$$

$$(73)$$

The result in eq. (73) is nothing but a one- and two-electron operator having corresponding one- and two-electron integrals which have been subjected to one-index transformation using the $\kappa^{(1)}(a)$ matrix as transformation coefficients. Eq. (73) may thus be written as a modified hamiltonian

$$\left[\kappa^{(1)}, H_{1}\right] = i \sum_{pq} k_{pq}(ab) a_{p}^{+} a_{q} + \frac{1}{2} i \sum_{pqrs} j_{pqrs}(ab) a_{p}^{+} a_{r}^{+} a_{s} a_{q},$$
(74)

where $k_{pq}(ab)$ and $j_{pqrs}(ab)$ are the modified one-index transformed one- and two-electron integrals, respectively. We stress that it is not simply notationally convenient to write the commutator in the above form. It is, in fact, computationally relevant since one would actually carry out such a one-index transformation on the integrals in order to make the commutator computationally feasible.

Returning to the task of evaluating $-\frac{1}{2}[\kappa^{(1)}, [\kappa^{(1)}, H_1]]$ we see that once the first commutator $[\kappa^{(1)}, H_1]$ is evaluated as above, the same integral transformation device can be used to effect the next commutator with eq. (74) as the hamiltonian. The double commutator $-\frac{1}{2}[\kappa^{(1)}, \kappa^{(1)}, H_1]$ therefore corresponds to a modified hamiltonian in which the integrals of H_1 have been subjected to two successive one-index transformations. Every one of the commutators in $\overline{H_1}, \overline{H_2}, \overline{H_3}$, and $\overline{H_4}$ can be expressed in like fashion in terms of integrals or integral derivatives which have been one-index transformed.

3.4. Response of the CI energy and wavefunction

Now that we have obtained compact and computationally tractable expressions for the \overline{H}_k (k = 1, 2, 3, 4) operators, we are prepared to return to consider the dependence of the CI energy on geometrical deformation. We begin by Baker-Campbell-Hausdorf (BCH) expanding the exp($\pm iS$) factors appearing in eq. (53) which give the CI energy:

$$E = \langle CI | \overline{H} | CI \rangle - i \langle CI | [S, \overline{H}] | CI \rangle - \frac{1}{2} \langle CI | [S, [S, \overline{H}]] | CI \rangle + \dots$$

$$= \overline{E} + \overline{F}S + \frac{1}{2}\overline{G}SS + \frac{1}{6}\overline{K}SSS + \frac{1}{24}\overline{L}SSSS + \dots$$
 (75)

The matrices \overline{F} , \overline{G} , \overline{K} , and \overline{L} are introduced to represent symmetrized versions [9] of the corresponding commutators appearing in the BCH expansion. When the energy function is made stable with respect to variations in the S_n parameters, we obtain an equation to be used to solve for the optimal S_n parameters:

$$0 = \bar{F} + \bar{G}S + \frac{1}{2}\bar{K}SS + \dots$$
(76)

As we saw earlier in eqs. (58)-(62), the matrices \overline{F} , \overline{G} , \overline{K} , and \overline{L} can be expanded in powers of μ . In eq. (51) the S parameters are power-series expanded in μ . Substituting these expansions into eq. (76) and collecting terms which multiply powers of μ , we obtain equations for $S^{(i)}$. The lowest-order such equations read

$$-\bar{G}^{(0)}S^{(1)} = \bar{F}^{(1)}$$
(77)

and

$$-\frac{1}{2}\overline{G}^{(0)}S^{(2)} = \frac{1}{2}\overline{F}^{(2)} + \overline{G}^{(1)}S^{(1)} + \frac{1}{2}\overline{K}^{(0)}S^{(1)}S^{(1)}.$$
(78)

When these equations are solved for $S^{(1)}$ and $S^{(2)}$ and the results substituted back into eq. (75), we may identify the terms in the order-by-order expansion of the CI energy in eq. (55). The five lowest-order terms in this expansion are

$$E_0 = \langle \mathrm{CI} | \overline{H}_0 | \mathrm{CI} \rangle, \tag{79}$$

$$E_1 = \langle \mathrm{CI} | \overline{H}_1 | \mathrm{CI} \rangle, \tag{80}$$

$$\frac{1}{2}E_2 = \frac{1}{2}\langle \text{CI}|\overline{H}_2|\text{CI}\rangle + \overline{F}^{(1)}S^{(1)} + \frac{1}{2}\overline{G}^{(0)}S^{(1)}S^{(1)} = \frac{1}{2}\langle \text{CI}|\overline{H}_2|\text{CI}\rangle + \frac{1}{2}\overline{F}^{(1)}S^{(1)}, \tag{81}$$

$${}^{1}_{6}E_{3} = {}^{1}_{6}\langle \text{CI}|\overline{H}_{3}|\text{CI}\rangle + {}^{1}_{2}\overline{F}^{(2)}S^{(1)} + {}^{1}_{2}\overline{G}^{(1)}S^{(1)}S^{(1)} + {}^{1}_{6}\overline{K}^{(0)}S^{(1)}S^{(1)}S^{(1)},$$
(82)

$$\frac{1}{24}E_4 = \frac{1}{24}\langle CI|\overline{H}_4|CI\rangle + \frac{1}{6}\overline{F}^{(3)}S^{(1)} + \frac{1}{4}\overline{G}^{(2)}S^{(1)}S^{(1)} + \frac{1}{6}\overline{K}^{(1)}S^{(1)}S^{(1)}S^{(1)} + \frac{1}{24}\overline{L}^{(0)}S^{(1)}S^{(1)}S^{(1)}S^{(1)} - \frac{1}{8}\overline{G}^{(0)}S^{(2)}S^{(2)}.$$
(83)

The matrices $\overline{F}^{(j)}$, $\overline{G}^{(j)}$, $\overline{K}^{(j)}$, and $\overline{L}^{(j)}$ are defined in analogy with those appearing earlier in eqs. (58)-(62)

except that now only the configuration-space operators $\{|j\rangle\langle CI| - |CI\rangle\langle j|\}$ appear in the commutators. Explicit expressions for the matrices needed to evaluate E_0, E_1, \ldots, E_4 are as follows:

$$\overline{F}_{n}^{(j)} = -2\langle \operatorname{CI}|\overline{H}_{j}|n\rangle \quad (\text{note } \overline{F}_{n}^{(0)} = 0), \tag{84}$$

$$\overline{G}_{mn}^{(j)} = 2\langle m | \overline{H}_j | n \rangle - 2\delta_{nm} \langle \text{CI} | \overline{H}_j | \text{CI} \rangle,$$
(85)

$$\overline{K}_{kmn}^{(j)} = \frac{8}{3} \Big[\delta_{mn} \langle \operatorname{CI} | \overline{H}_j | k \rangle + \delta_{mk} \langle \operatorname{CI} | \overline{H}_j | n \rangle + \delta_{nk} \langle \operatorname{CI} | \overline{H}_j | m \rangle \Big] \quad (\text{note } \overline{K}_{kmn}^{(0)} = 0), \tag{86}$$

$$\overline{L}_{klmn}^{(0)} = \frac{4}{3} \Big[\delta_{nk} \Big(\delta_{ml} E_0 - \langle m | \overline{H}_0 | l \rangle \Big) + \delta_{mk} \Big(\delta_{nl} E_0 - \langle n | \overline{H}_0 | l \rangle \Big) + \delta_{mn} \Big(\delta_{kl} E_0 - \langle k | \overline{H}_0 | l \rangle \Big) \\
+ \delta_{nl} \Big(\delta_{mk} E_0 - \langle m | \overline{H}_0 | k \rangle \Big) + \delta_{ml} \Big(\delta_{nk} E_0 - \langle n | \overline{H}_0 | k \rangle \Big) + \delta_{kl} \Big(\delta_{mn} E_0 - \langle m | \overline{H}_0 | n \rangle \Big) \Big].$$
(87)

Having now derived working equations for the μ -derivatives of the CI energy up through fourth order, let us briefly review the steps which must be taken to perform such a calculation. First, one must compute and store the $U^{(i)}$ arrays in terms of overlap integral derivatives as shown in eq. (35). Second, one must form the one- and two-electron integral derivatives and their one-index transformations shown in eq. (37) in order to evaluate the modified integral derivative lists $\tilde{h}^{(i)}$ and $\tilde{g}^{(i)}$ which enter into the H_i operators. Third, it is necessary to compute the MC SCF orbital response matrices $\kappa_{rs}^{(i)}$ from eqs. (63)-(66) and to subsequently use these arrays in eqs. (69)-(72) to perform further one-index transformations on the modified integral derivatives of H_i in order to form the final integral derivative lists which define the $\overline{H_i}$ operators. Finally, the integral derivatives of $\overline{H_i}$ can be used to form the $\overline{F}^{(j)}$, $\overline{G}^{(j)}$, $\overline{K}^{(0)}$ arrays as needed in eqs. (77) and (78). Once eqs. (77) and (78) are solved for $S^{(1)}$ and $S^{(2)}$, they can be used, together with the $\overline{F}^{(j)}$, $\overline{G}^{(j)}$, $\overline{K}^{(j)}$, and $\overline{L}^{(0)}$ arrays in eqs. (80)-(83) to evaluate the desired CI energy derivatives.

In the following section, we attempt to further clarify and detail the solutions of the response equations for the $\kappa_{rs}^{(i)}$ and $S^{(1)}$ and $S^{(2)}$ parameters. In particular, we focus on situations in which the number of configurations appearing in the CI wavefunction expansion may be quite large (e.g., 5000-10⁶).

4. Computationally practical solutions to working equations

4.1. Direct methods for solving the CI response equations

In the preceding section, we derived explicit expressions for the geometrical derivatives of the CI energy. The evaluation of these expressions requires that several sets of linear equations be solved [e.g. eqs. (63)-(66) and (77) and (78)]. As they are written, these linear equations are not cast in a form which allows so-called "direct methods" to be applied [21,22] and, consequently, only small configuration spaces can straightforwardly be treated.

In this section we re-express the sets of linear equations in forms that allow direct methods to be used and which therefore allow treatment of very large $(5000-10^6)$ configuration state function spaces. Let us begin by considering how the set of linear equations in eq. (77) determining the $S^{(1)}$ amplitudes

$$\bar{G}^{(0)}S^{(1)} = -\bar{F}^{(1)} \tag{88}$$

can be solved in a direct fashion. Eq. (88) is written in terms of the set of basis vectors spanning the orthogonal complement space $\{|j\rangle\}$ of the |CI⟩ wavefunction. To express eq. (88) in a form where direct methods can be used we transform eq. (88) to the configuration state function basis using a method similar to the one described by Lengsfield and Liu [23]. To do this we follow the treatment of Helgaker and Almlöf [16] and introduce the augmented hessian $aug\overline{G}^{(0)}$ which has exactly the same structure as $\overline{G}^{(0)}$ but which is of one larger dimension since it is defined in terms of the orthogonal complement states and the reference state $\{|CI\rangle, |j\rangle\}$. Since the generalized Brillouin theorem is valid,

$$^{\text{aug}}\overline{G}_{|\text{CI}\rangle|k\rangle}^{(0)} = 2\langle \text{CI}|\overline{H}_0|k\rangle = 0, \tag{89}$$

and since, from eq. (85),

$${}^{\text{aug}}\overline{G}^{(0)}_{|\text{CI}\rangle,|\text{CI}\rangle} = 2\langle \text{CI}|\overline{H}_0|\text{CI}\rangle - 2\langle \text{CI}|\overline{H}_0|\text{CI}\rangle = 0,$$
(90)

we obtain

$${}^{\operatorname{aug}}\overline{G}^{(0)} = \begin{pmatrix} 0 & \widetilde{0} \\ 0 & \overline{G}^{(0)} \end{pmatrix}.$$
(91)

Eq. (88) can therefore be written in the equivalent form

$$\left[\begin{pmatrix} z & \tilde{0} \\ 0 & 0 \end{pmatrix} + {}^{\operatorname{aug}}\overline{G}^{(0)} \right] \begin{pmatrix} 0 \\ S^{(1)} \end{pmatrix} = - \begin{pmatrix} 0 \\ \overline{F}^{(1)} \end{pmatrix},$$
(92)

where the variable $z \neq 0$ has been (temporarily) introduced to ensure that the matrix multiplying $\binom{0}{S^{(1)}}$ is non-singular. Arranging the expansion coefficients $\{C^{(CI)}, C^{(j)}\}$ of the states $\{|CI\rangle, |j\rangle\}$ as column vectors, we define a unitary matrix

$$U = (C^{(CI)}, C^{(j)}),$$
(93)

which then allows us to write eq. (92) as

$$\tilde{U}(z|C^{(\mathrm{C}1)}\rangle\langle C^{(\mathrm{C}1)}| + {}^{\mathrm{CSF}}\overline{G}^{(0)})U\begin{pmatrix}0\\S^{(1)}\end{pmatrix} = -\begin{pmatrix}0\\\overline{F}^{(1)}\end{pmatrix},\tag{94}$$

where $^{\text{CSF}}\overline{G}^{(0)}$ is defined as in eq. (75) but in the configuration state function basis $\{|\phi_g\rangle\}$

$$^{\text{CSF}}\overline{G}_{gf}^{(0)} = 2\left(\langle \phi_g | \overline{H}_0 | \phi_f \rangle - \overline{E}_0^{(\text{CI})} \delta_{gf}\right),\tag{95}$$

where

$$\overline{E}_{i}^{(\mathrm{CI})} = \langle \mathrm{CI} | \overline{H}_{i} | \mathrm{CI} \rangle. \tag{96}$$

Multiplying eq. (94) from the left by U and introducing the projection operator onto the one-dimensional space defined by $C^{(CI)}$

 $O = \left| C^{(\text{C1})} \right\rangle \left\langle C^{(\text{C1})} \right|,\tag{97}$

and its orthogonal complement projector

$$P = I - O, \tag{98}$$

where I is the unit matrix, allows us to write eq. (94) as

$$(zO + {}^{\rm CSF}\overline{G}{}^{(0)})P^{\rm CSF}S{}^{(1)} = - {}^{\rm CSF}\overline{F}{}^{(1)}.$$
(99)

where ${}^{\text{CSF}}\overline{F}{}^{(1)}$ is defined as in eq. (75) but in terms of the configuration state function basis

$$^{\text{CSF}}\overline{F}_{g}^{(1)} = -2\langle \phi_{g} | \overline{H}_{1} | \text{CI} \rangle + 2C_{g}^{(\text{CI})} \overline{E}_{1}^{(\text{CI})}, \qquad (100)$$

and $^{CSF}S^{(1)}$ denotes the set of configuration state function amplitudes in which the $C^{(CI)}$ component is annihilated. $P^{CSF}S^{(1)}$ contains the first-order response amplitudes in the configuration state function basis. That $P^{CSF}S^{(1)}$ is identical to the $U(^{0}_{S^{(1)}})$ column vector may be seen by straightforward multiplication

$$\left[U\binom{0}{S^{(1)}}\right]_{g} = \left[(C^{(C1)}, C^{(K)})\binom{0}{S^{(1)}}\right]_{g} = \sum_{K} C_{g}^{(K)} S_{K}^{(1)} = \sum_{Kg'} C_{g'}^{(K)} C_{g'}^{(K)CSF} S_{g'}^{(1)} = \sum_{g'} P_{gg'}^{CSF} S_{g'}^{(1)}.$$
 (101)

When the integral list appearing in \overline{H}_1 is available, $^{CSF}\overline{F}^{(1)}$ in eq. (100) is constructed by carrying out the same kind of linear transformation as is required in a direct CI calculation. A direct method can then be used to solve eq. (99) if the successive linear transformations

$$(l+1)_b = {}^{\text{CSF}}\overline{G}^{(0)(l)}_b b$$
 (102)

can be carried out. Here *l* denotes the *l*th iteration on a trial vector whose $|C^{(C1)}\rangle$ component has been removed (since the desired solution has the form $P^{CSF}S^{(1)}$). Since ${}^{CSF}\overline{G}^{(0)}$ is nothing but the hamiltonian matrix in the CSF basis with the CI total energy removed from its diagonal elements, the linear transformation in eq. (102) requires the very same linear transformation as is used in a direct CI calculation. The actual solution to eq. (99) may therefore be obtained using the reduced linear equations method [2,24], the conjugate gradient method [25] or other techniques which are applicable to large linear equations. When the solution ${}^{OC}C \equiv P {}^{CSF}S^{(1)}$ to eq. (99) is found, the second contribution to the CI hessian matrix of eq. (81) may straightforwardly be obtained by multiplying the row vector ${}^{CSF}\overline{F}$ into ${}^{OC}C$.

The hypercurvature E_3 may be evaluated when the $S^{(1)}$ parameters are known. In order to do so it is convenient to obtain an explicit expression for the $S_i^{(1)}$ parameters. Since the solution to eq. (99) (${}^{OC}C$) is spanned only by the orthogonal complement to $C^{(C1)}$, we may parameterize the orthogonal complement space such that only one $S_i^{(1)}$ parameter is non-vanishing. To do so, we re-express

$$\sum_{n} S_{n}^{(1)}(|n\rangle \langle CI| - |CI\rangle \langle n|)$$
(103)

as

$$\sum_{g} \left(\sum_{n} S_{n}^{(1)} C_{g}^{(n)} \right) \left(|\phi_{g}\rangle \langle CI| - |CI\rangle \langle \phi_{g}| \right) = \sum_{g} {}^{OC} C_{g} \left(|\phi_{g}\rangle \langle CI| - |CI\rangle \langle \phi_{g}| \right),$$
(104)

which can be thought of as $({}^{OC}\tilde{C}{}^{OC}C)^{1/2}$ ($|1\rangle\langle CI| - |CI\rangle\langle 1|$), where the normalized state $|1\rangle$ lying in the orthogonal complement space is

$$|1\rangle = \left({}^{\text{OC}}\tilde{C}{}^{\text{OC}}C\right)^{-1/2} \sum_{g} {}^{\text{OC}}C_{g} |\phi_{g}\rangle, \tag{105}$$

and $({}^{OC}\tilde{C}{}^{OC}C)^{-1/2}$ is its normalization constant. In this representation, the only non-vanishing element of $S^{(1)}$ is

$$S_1^{(1)} = \left({}^{\text{OC}}\tilde{C}{}^{\text{OC}}C\right)^{1/2}.$$
(106)

Using this parameterization of the orthogonal complement space, the actual evaluation of E_3 reduces to carrying out a few linear transformations of the same type as are performed in a direct CI calculation [21], followed by simple vector multiplications with already-available vectors.

The evaluation of E_4 requires the solution of the linear equations for $S^{(2)}$ in eq. (78) (recall that $\overline{K}^{(0)} = 0$)

$$-\frac{1}{2}\overline{G}^{(0)}S^{(2)} = \overline{G}^{(1)}S^{(1)} + \frac{1}{2}\overline{F}^{(2)}.$$
(107)

Since

$$\sum_{n} \overline{G}_{mn}^{(1)} S_{n}^{(1)} = 2 \sum_{n} \langle m | \overline{H}_{1} - \overline{E}_{1}^{(C1)} | n \rangle S_{n}^{(1)} = 2 \langle m | \overline{H}_{1} - \overline{E}_{1}^{(C1)} | 1 \rangle S_{1}^{(1)},$$
(108)

 $\overline{G}^{(1)}$ $S^{(1)}$ is a row vector of the same dimension and structure as $\overline{F}^{(1)}$ of eq. (88). $S^{(2)}$ may thus be determined directly from an equation similar to eq. (99) except that $^{\text{CSF}}\overline{F}^{(1)}$ of eq. (99) is replaced by

$$^{\rm CSF}(\bar{G}^{(1)}S^{(1)}) + \frac{1}{2} {}^{\rm CSF}\bar{F}^{(2)},\tag{109}$$

where ${}^{\text{CSF}}\overline{F}{}^{(2)}$ is defined as in eq. (100) but with \overline{H}_1 replaced by \overline{H}_2 and

$$^{\text{CSF}}(\overline{G}^{(1)}S^{(1)})_{g} = 2\langle \phi_{g} | \overline{H}_{1} - \overline{E}_{1}^{(\text{CI})} | 1 \rangle S_{1}^{(1)} - 2C_{g}^{(\text{CI})} \langle \text{CI} | \overline{H}_{1} | 1 \rangle S_{1}^{(1)}.$$
(110)

When $S^{(2)}$ is available it is a straightforward task to evaluate E_4 .

4.2. Direct methods for solving the MC SCF response equations

In this section we describe how the set of equations which determine the MC SCF orbital responses $\kappa_{rs}^{(j)}$ may be solved using the direct methods discussed above. This knowledge allows one to determine the orbital responses for MC SCF wavefunctions containing a large number of configurations.

Let us begin by considering the determination of the $\kappa_{rs}^{(1)}$ parameters which obey [eq. (63)]

$${}^{\rm MC}G^{(0)}\lambda^{(1)} = -{}^{\rm MC}F^{(1)},\tag{111}$$

where $\lambda^{(1)}$ contains the orbital response parameters defined in eq. (56) as well as the MC SCF configuration response parameters ${}^{MC}S_n^{(1)}$. To apply direct methods to eq. (111) we have to transform this equation to the configuration state function basis. This can be done by using the very same technique used to transform eq. (88). The result of this transformation is the following matrix equations [23]

$$\left(z|\mathrm{MC}\rangle\langle\mathrm{MC}|+{}^{\mathrm{CMC}}G^{(0)}\right)Q^{\mathrm{CMC}}\lambda^{(1)}=-{}^{\mathrm{CMC}}F^{(1)},\tag{112}$$

where

$${}^{CMC}G_{f,g}^{(0)} = 2\langle \phi_f | H_0 | \phi_g \rangle - 2E_0^{(MC)}\delta_{fg}, \tag{113}$$

$${}^{\rm CMC}G^{(0)}_{g,rs} = -2\langle \phi_g | \left[a_r^+ a_s - a_s^+ a_r, H_0 \right] | {\rm MC} \rangle, \tag{114}$$

$${}^{CMC}G^{(0)}_{r_s,t\mu} = \langle MC | [a_r^+ a_s - a_s^+ a_r, a_t^+ a_\mu - a_\mu^+ a_t, H_0] | MC \rangle,$$
(115)

$${}^{CMC}F_{-}^{(1)} = -2\langle \phi_{-}|H_{1}|MC\rangle + 2E_{1}^{(MC)}C_{-}^{(MC)},$$
(116)

$${}^{\rm CMC}F_{rs}^{(1)} = \langle {\rm MC} | [a_r^+ a_s - a_s^+ a_r, H_1] | {\rm MC} \rangle, \tag{117}$$

and where

$$E_i^{(\mathrm{MC})} = \langle \mathrm{MC} | H_i | \mathrm{MC} \rangle \tag{118}$$

and $Q^{CMC}\lambda^{(1)}$ is a vector containing both configuration- and orbital-response amplitudes. Q is the projector that annihilates the $|MC\rangle$ component of the configuration state function amplitude. Solving eq. (112) by a direct approach requires successive linear transformations of the form

$$^{(l+1)}X = {}^{CMC}G^{(0\chi)}X,$$
 (119)

to be carried out, where ${}^{(l)}X = {}^{(l)C}_{(l)x}$ is a vector in which the $|MC\rangle$ component has been annihilated. Such a linear transformation procedure has recently been described in refs. [20,26], and can be more explicitly written as

$${}^{(l+1)}C_i^{(1)} = 2\langle \phi_i | H_0 | {}^{(l)}\mathrm{MC}^{(1)} \rangle - 2E_0^{(\mathrm{MC})(l)}C_i^{(1)} - 2\langle \phi_i | H_0 ({}^{(l)}\kappa^{(1)}) | \mathrm{MC} \rangle,$$
(120)

$${}^{(l+1)}\kappa_{rs}^{(1)} = -2\langle \mathrm{MC}|[a_r^+a_s - a_s^+a_r, H_0]|{}^{(l)}\mathrm{MC}{}^{(1)}\rangle + \langle \mathrm{MC}|[a_r^+a_s - a_s^+a_r, H_0{}^{(l)}\kappa{}^{(1)})]|\mathrm{MC}\rangle,$$
(121)

where

$$\left| {}^{(l)}\mathrm{MC}^{(1)} \right\rangle = \sum_{g} {}^{(l)}C_{g}^{(1)} \left| \phi_{g} \right\rangle, \tag{122}$$

and $H_0({}^{(l)}\kappa^{(1)})$ is the one-index transformed hamiltonian defined with ${}^{(l)}\kappa^{(1)}$ as the transformation matrix as in eq. (74). Using the above techniques, the coupled multiconfiguration set of linear equations may be solved for very large configuration spaces. Once $\kappa^{(1)}$ and $C^{(1)}$ (or equivalently $S^{(1)}$) [see eqs. (103)–(106)] are available, it is straightforward to actually evaluate the MC SCF molecular hessian ${}^{MC}E_2$ and the first MC SCF anharmonicity term ${}^{MC}E_3$. Direct evaluation of $\kappa^{(2)}$ may be performed in a manner very similar to that described for $\kappa^{(1)}$. The first task would be to express the right-hand side of eq. (64)

$$\left({}^{MC}G^{(1)}\lambda^{(1)} + \frac{1}{2}{}^{MC}K^{(0)}\lambda^{(1)}\lambda^{(1)} + \frac{1}{2}{}^{MC}F^{(2)}\right),\tag{123}$$

as a vector of the same structure as ${}^{MC}F^{(1)}$ analogous to using the transformation that was applied to $\overline{G}^{(1)}S^{(1)}$ in eq. (108) to bring it to the same form as $\overline{F}^{(1)}$ in eq. (88). This transformation is described in some detail in ref. [20]. With this transformation available, it is straightforward to directly evaluate $\kappa^{(2)}$, and then ${}^{MC}E_4$ may consequently be evaluated. $\kappa^{(2)}$ is also required in order to evaluate the hessian (E_2) of the CI energy. A direct evaluation of the $\kappa^{(3)}$ and $\kappa^{(4)}$ parameters, which are required for E_3 and E_4 , becomes increasingly more difficult because of the larger μ -index dimensionality of the equations which determine these parameters. In our opinion it is, at the present time, necessary to accept that $\kappa^{(3)}$ and $\kappa^{(4)}$ be evaluated without using direct-method algorithms. This, of course, restricts the evaluation of CI third and fourth derivatives to configuration spaces of the MC SCF calculation of up to a few hundred configuration state functions (i.e. those for which $\kappa^{(3)}$ and $\kappa^{(4)}$ can be computed using in-core methods).

5. Summary and overview

In this paper we have given analytical expressions for derivatives of the CI energy with respect to molecular deformation up through the fourth derivative. To implement the results which we have derived, several steps are required:

(1) The overlap-based matrices $U^{(i)}$ must be computed and stored.

(2) The integral derivatives (e.g., $g^{(3)}$) and the one-index transformed integrals and integral derivatives (e.g., $\{g^{(1)}, U^{(2)}\}$) must be computed and used to assemble the modified integral derivative arrays (e.g., $\tilde{g}^{(3)}$) which define the various hamiltonian derivatives $H_1 \dots H_4$.

(3) The response of the MC SCF orbitals to molecular deformation, as described through the parameters $\kappa_{rs}^{(j)}$, j = 1, 2, 3, 4, must be evaluated. For large configuration expansion lengths in the MC SCF wavefunction, this step may require the use of "direct methods" as described in section 4.2.

(4) The modified integral derivative lists which appear in the $H_1
dots H_4$ operators must be subjected to further one-index transformations, using the $\kappa_{rs}^{(j)}$ as transformation matrices, in order to generate the integral derivative lists which define the final working hamiltonian operators $\overline{H}_1 \dots \overline{H}_4$ in terms of which all final CI-based energy derivatives are expressed.

(5) The response of the CI wavefunction's configuration expansion parameters $S^{(1)}$ and $S^{(2)}$ must be evaluated by solving the sets of linear equations which define them. Because we have in mind CI wavefunctions whose configuration expansion lengths are large (e.g., $5000-10^6$), the solution of these sets of linear equations requires the use of the direct methods treated in section 4.1.

(6) The CI gradient (E_1) , hessian (E_2) and higher energy derivatives (E_3, E_4) can then be evaluated by performing linear transformations similar to the ones occurring in direct CI calculations, followed by simple vector multiplications.

Before closing, we examine in some detail the computational effort which is required to compute the various CI-energy derivatives and we compare this effort with what is needed to perform MC SCF-based energy-derivative calculations.

The analytical expressions for the CI and MC SCF energy derivatives are very much alike. The MC SCF

energy derivatives through fourth order are given in refs. [9,13]. The CI energy derivatives in eqs. (80)–(83) can be obtained by simply replacing in refs. [9,13] the MC SCF matrices ${}^{MC}F^{(i)}$, ${}^{MC}G^{(i)}$, ${}^{MC}K^{(i)}$ and ${}^{MC}L^{(i)}$ of eqs. (58)–(61) by the corresponding CI matrices $\overline{F}^{(i)}$, $\overline{G}^{(i)}$, $\overline{K}^{(i)}$ and $\overline{L}^{(i)}$. The MC SCF matrices ${}^{MC}F^{(i)}$,... contain the hamiltonians H_i , i = 1-4 of eq. (6) and have both orbital excitation and state transfer excitation parts. The CI matrices contain the modified hamiltonians \overline{H}_i , i = 1-4 of eq. (54) and have only state transfer excitation parts. In carrying out a comparison of MC SCF and CI energy derivatives we concentrate on describing the differences which occur due to the fact that orbital responses are required to a lower level in MC SCF calculations than in corresponding CI calculations. As a result, MC SCF calculations can be carried out by constructing matrices (${}^{MC}F^{(i)}$...) of lower order than is required in a corresponding CI calculation. We shall now address each of the four energy derivatives separately.

 E_1 : The CI gradient $\langle CI | \overline{H}_1 | CI \rangle$ requires the evaluation of the $\kappa_{rs}^{(1)}$ orbital response parameters and the one-index transformation of the integrals in H_1 with $\kappa^{(1)}$ to generate \overline{H}_1 . The MC SCF gradient $\langle MC | H_1 | MC \rangle$ does not require knowledge of any orbital response parameters.

 E_2 : The CI hessian requires evaluation of $\kappa_{rs}^{(1)}$ and $\kappa_{rs}^{(2)}$ as well as the one-index transformations required to obtain \overline{H}_1 and \overline{H}_2 . Furthermore, to evaluate the CI hessian, the configuration amplitude response parameters $S^{(1)}$ of eq. (51) need to be evaluated. The MC SCF hessian requires that the simultaneous set of orbital and state response parameters $\lambda^{(1)}$ of eq. (63) be evaluated; no second-order responses are needed.

 E_3 : The evaluation of E_3 in the CI method requires knowledge of $\kappa_{rs}^{(1)}$, $\kappa_{rs}^{(2)}$ and $\kappa_{rs}^{(3)}$ in order to perform the one-index transformations necessary to evaluate \overline{H}_1 , \overline{H}_2 and \overline{H}_3 . As was the case for the CI hessian, the E_3 also requires that the linear equations of eq. (77) be solved for $S^{(1)}$. The MC SCF hessian requires only that the linear set of equations for $\lambda^{(1)}$ in eq. (63) be solved. The evaluation of E_3 in CI simplifies a little because $\overline{K}^{(0)}$ is zero.

 E_4 : Evaluation of E_4 in CI requires that the orbital response parameters $\kappa_{rs}^{(1)}$, $\kappa_{rs}^{(2)}$, $\kappa_{rs}^{(3)}$ and $\kappa_{rs}^{(4)}$ be evaluated and that the resulting one-index transformations be carried out to obtain \overline{H}_1 , \overline{H}_2 , \overline{H}_3 and \overline{H}_4 . The configuration amplitude responses $S^{(1)}$ and $S^{(2)}$ also have to be evaluated. To obtain E_4 in the MC SCF method requires evaluation of the $\lambda^{(1)}$ and $\lambda^{(2)}$ parameters of eqs. (63) and (64) respectively.

As discussed above, the major differences between evaluating energy derivatives in CI and in MC SCF is that orbital responses $\kappa_{rs}^{(j)}$ are required to a higher level in CI than in MC SCF. The lowest orbital responses $\kappa_{rs}^{(1)}$ and $\kappa_{rs}^{(2)}$ can relatively straightforwardly be evaluated using direct methods. However, it becomes increasingly difficult to evaluate the higher-order orbital responses as $\kappa_{rs}^{(3)}$ and $\kappa_{rs}^{(4)}$ using direct methods. These higher responses are required in the evaluation of the CI E_3 and E_4 . Therefore, it is likely that presently E_3 and E_4 can only be evaluated if the orbital responses $\kappa_{rs}^{(3,4)}$ are obtained from MC SCF calculations involving only moderate size configuration spaces (≈ 300) so that in-core solution methods can be used. In the MC SCF approach, the simultaneous orbital and state response parameter set $\lambda^{(1)}$ is capable of determining ${}^{MC}E_3$; no higher-order response parameters are needed. Evaluation of ${}^{MC}E_4$ in MC SCF requires also that $\lambda^{(2)}$ be computed. Both $\lambda^{(1)}$ and $\lambda^{(2)}$ can relatively straightforwardly be evaluated for very large configuration spaces (10^3-10^6). With the technology which has recently become available [23,26], MC SCF wavefunctions reliably can be obtained for large configuration spaces (10^3-10^6). Therefore, it appears that accurate energy derivatives preferentially might be achieved using large MC SCF wavefunctions rather than with the CI wavefunction approach.

Acknowledgement

We wish to acknowledge the financial support of the National Science Foundation (Grant No. 8206845) and the Donors of the Petroleum Research Fund administered by the American Chemical Society (PRF 14446 AC6). PJ thanks the Danish Natural Sciences Research Council for travel support.

J. Simons et al. / Molecular - deformation derivatives of the CI energy

References

- [1] P. Pulay, in: Modern theoretical chemistry, ed. H.F. Schaefer III (Plenum Press, New York, 1977) ch. 4.
- [2] J.A. Pople, R. Krishnan, H.B. Schlegel and J.S. Binkley, Intern. J. Quantum Chem. S 13 (1979) 225;
- R. Krishnan, H.B. Schlegel and J. A. Pople, J. Chem. Phys. 72 (1980) 4654.
 [3] H.F. King and M. Dupuis, J. Comput. Phys. 21 (1976) 144;
- M. Dupuis, J. Rys and H.F. King, J. Chem. Phys. 65 (1976) 111;
 M. Dupuis and H.F. King, J. Chem. Phys. 68 (1978) 3998;
 R.N. Camp, H.F. King, J.W. McIver Jr. and D. Mullally, J. Chem. Phys. 79 (1983) 1088.
- [4] J.D. Goddard, N.C. Handy and H.F. Schaefer III, J. Chem. Phys. 71 (1979) 1525;
 Y. Osamura, Y. Yamaguchi and H.F. Schaefer III, J. Chem. Phys. 75 (1981) 2919; 77 (1982) 383;
 B.R. Brooks, W.D. Laidig, P. Saxe, J.D. Goddard, Y. Yamaguchi and H.F. Schaefer III, J. Chem. Phys. 72 (1980) 4652;
 Y. Yamaguchi, Y. Osamura, G. Fitzgerald and H.F. Schaefer III, J. Chem. Phys. 78 (1983) 1607.
- [5] D. Poppinger, Chem. Phys. Letters 34 (1975) 332; 35 (1975) 550.
- [6] H.B. Schlegel, S. Wolfe and F. Bernardi, J. Chem. Phys. 63 (1975) 3632; 67 (1977) 4181, 4194.
- [7] A. Komornicki, K. Ishida, K. Morokuma, R. Ditchfield and M. Conrad, Chem. Phys. Letters 45 (1977) 595;
 K. Ishida, K. Morokuma and A. Komornicki, J. Chem. Phys. 66 (1977) 2153.
- [8] S. Kato and K. Morokuma, Chem. Phys. Letters 65 (1979) 19.
- [9] P. Jørgensen and J. Simons, J. Chem. Phys. 79 (1983) 334.
- [10] G. Herzberg, Spectra of diatomic molecules (Van Nostrand, Princeton, 1950).
- [11] S. Jorna, ed., Topics in nonlinear dynamics, A.I.P. Conference Proceedings No. 46 (American Institute of Physics, New York, 1978).
- [12] P. Pulay, J. Chem. Phys. 78 (1983) 5043.
- [13] J. Simons and P. Jørgensen, J. Chem. Phys. 79 (1983) 3599.
- [14] P. Jørgensen and J. Simons, Second quantization-based methods in quantum chemistry (Academic Press, New York, 1981).
- [15] E. Dalgaard and P. Jørgensen, J. Chem. Phys. 69 (1978) 3833;
 D.L. Yeager and P. Jørgensen, J. Chem. Phys. 71 (1979) 755;
 E. Dalgaard, Chem. Phys. Letters 65 (1979) 559;
 J. Olsen, D.L. Yeager and P. Jørgensen, Advan. Chem. Phys. 54 (1983) 1.
- [16] T.U. Helgaker and J. Almlöf, Intern. J. Quantum. Chem., to be published.
- [17] A. Banerjee, J. Jensen and J. Simons, Chem. Phys., to be published.
- [18] I. Shavitt, in: Modern theoretical chemistry, Vol. 3, eds. H.F. Schaefer III and W.H. Miller (Plenum Press, New York, 1977).
- [19] P. Jørgensen, P. Swanstrøm, D.L. Yeager and J. Olsen, Intern. J. Quantum Chem. 23 (1983) 959.
- [20] P. Jørgensen, J. Olsen and D.L. Yeager, J. Chem. Phys. 75 (1981) 5802.
- [21] B. Roos, P. Siegbahn, in: Methods of electronic structure, ed. H.F. Schaefer III (Plenum Press, New York, 1977).
- [22] E.R. Davidson, J. Comput. Phys. 17 (1975) 87.
- [23] B.H. Lengsfield III and B. Liu, J. Chem. Phys. 75 (1981) 478;
- B.H. Lengsfield III, J. Chem. Phys. 77 (1982) 4073.
- [24] G.D. Purvis III and R.J. Bartlett, J. Chem. Phys. 75 (1981) 1284.
- [25] P.E.S. Wormer, F. Visser and J. Paldus, J. Comput. Phys. 48 (1982) 23.
- [26] H.J. Aa. Jensen and P. Jørgensen, J. Chem. Phys., to be published.