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MC SCF MOLECULAR GRADIENTS AND HESSIANS: COMPUTATIONAL ASPECTS

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Molecular gradients and hessians for multiconfigurational self-consistent-field wavefunctions are derived in terms of the generators of the unitary group using exponential unitary operators to describe the response of the energy to a geometrical deformation. Final expressions are cast in forms which contain reference only to the primitive non-orthogonal atomic basis set and to the final orthonormal molecular orbitals; all reference to intermediate orthogonalized orbitals is removed. All of the deformation-dependent terms in the working equations reside in the one- and two-electron integral derivatives involving the atomic basis orbitals. The deformation-independent terms, whose contributions can be partially summed, involve symmetrized density matrix elements which have the same eight-fold index permutational symmetry as the one- and two-electron integral derivatives they multiply. This separation of deformation-dependent and -independent factors allows for single-pass integral-derivative-driven implementation of the gradient and hessian expressions.

1. Introduction

In recent years quantum chemists have devoted much effort toward obtaining computationally tractable analytical formulas for the gradients (forces), hessians (force constants), and higher energy derivatives appropriate to single Born–Oppenheimer electronic energy surfaces. Such knowledge is of use in locating minima and saddle points on such surfaces and characterizing, by local normal-mode vibrational frequencies, these stationary-point geometries. Integration of classical equations of motion also requires knowledge of the local force (energy gradient) and can be made even more efficient given higher energy-derivative information.

Much of the history of the development of this research topic is reviewed by Pulay [1]. The very substantial early contributions of Gerratt and Mills [2], Bratoz [3], Meyer and Pulay [4], Thomsen and Swanstrøm [5], and Pulay [6] himself are spelled out clearly in ref. [1]. Somewhat more recent developments have been made by Pople et al. [7], King and Dupuis [8], Goddard et al. [9], Poppinger [10], Schlegel et al. [11], and Komornicki et al. [12]. The most recent developments have stressed the treatment of open-shell cases [4,7,9] and multiconfigurational wavefunctions as treated by configuration interaction [7,9] (CI), multiconfigurational self-consistent-field [9,13–15] (MC SCF), and Møller–Plesset perturbation theory [7] (MPPT) techniques.

Recently Jørgensen and Simons [16,17] have given analytical expressions for the energy gradient and hessian of SCF, MC SCF, CI, MPPT, and coupled-cluster (CC) wavefunctions as well as the third and fourth derivatives of the MC SCF energy. Pulay has also recently derived [14] the MC SCF third energy derivative, and Camp et al. [15] and Helgaker and Almlöf [18] also made use of explicitly *unitary*

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transformations to describe how the molecular orbital $\{C_{\mu i}\}$ and configuration $\{C_g\}$ mixing coefficients of the MC SCF wavefunction $|0\rangle = \Sigma_g C_g \Phi_g$ vary as the molecule's nuclei are displaced from $\boldsymbol{R}$ to $\boldsymbol{R}+\boldsymbol{\mu}$. By using such a unitary formulation, these authors avoided the imposition, via Lagrange multipliers, of constraints on variations of the $\{C_{\mu i}\}$ and $\{C_g\}$ which appear [1–14] in most earlier developments. In our opinion, this makes the *derivation* of such energy derivatives more straightforward although, of course, the final results should be independent of the method of derivation.

It is a purpose of the present work to address the computational implementation of working MC SCF and CI gradient and hessian formulas. We also wish to make clear connection between the derivation of Jørgensen and Simons [16,17] (JS) and that presented here. In particular we show how the symmetrically orthogonalized atomic-orbital basis used in ref. [16] can be used as a convenient derivational tool but removed from final working formulas in favor of the more convenient primitive atomic-orbital basis.

Consideration of efficient computer implementation of the analytical expressions for energy derivatives is very important because of the extremely large number of derivatives of atomic-orbital based integrals which arise in these expressions. Given n primitive (gaussian or Slater) atomic basis functions and a molecule with N nuclei which are permitted to move, one has of the order of $12 \times n^4$ first derivatives of the atomic-orbital (AO) two-electron integrals and $78 \times n^4$ second derivatives. Each two-electron integral over atomic orbitals localized on atomic centers involves at most four centers. Thus, the only derivatives which give non-zero results when operating on such an integral are the x, y or z coordinates of the four atoms. There are twelve such coordinates. Such integral derivative arrays are, except for quite small basis sets, too large to be conveniently computed and stored even on modern high-speed high-volume disks. As a result, strategies for implementing energy gradient, hessian, and higher energy derivatives must, where possible, make use of these integral derivatives as they are generated. That is, in our opinion, successful computational schemes must be single-pass integral-derivative driven.

2. Derivation of working equations for the MC SCF case

2.1. The effect of nuclear displacement on the wavefunction

We begin by supposing that the MC SCF wavefunction $|0\rangle$ at geometry $\boldsymbol{R}$ has had its energy made stable with respect to variations in the expansion coefficients $\{C_{\mu i}\}$ of its molecular orbitals (MOs) $\{\phi_i\}$ and in its configuration mixing amplitudes $\{C_g\}$. The wavefunction $|\tilde{0}\rangle$ at the displaced geometry $\boldsymbol{R}+\boldsymbol{\mu}$ is described in terms of two unitary operators [exp(iκ) and exp(iS)] operating on $|0\rangle$

$$|\tilde{0}\rangle = \exp(\mathrm{i}\kappa)\exp(\mathrm{i}S)|0\rangle. \tag{1}$$

The first operator exp(iS) brings about changes [16,19] in the configuration mixing coefficients of $|0\rangle$. The exp(iκ) operator, when acting on each configuration Φ_g in $|0\rangle = \Sigma_{g=1}^{M} C_g \Phi_g$, achieves a unitary transformation among the MOs appearing in Φ_g and all other MOs in the basis being employed. These two operators

$$\kappa = \mathrm{i}\sum_{r>s}\kappa_{rs}(e_{rs}-e_{sr}), \qquad S = \mathrm{i}\sum_{n\neq 0} S_n(|n\rangle\langle 0| - |0\rangle\langle n|), \tag{2}$$

contain parameters (κ_{rs}, S_n) whose values are chosen to make the energy of the displaced wavefunction $|\tilde{0}\rangle$ stable. In eqs. (2), the e_{rs} are unitary generators given in terms of the MO-based spin-orbital creation $a^+_{r\sigma}$ and annihilation $a_{s\sigma}$ operators as

$$e_{rs} = a^+_{r\alpha}a_{s\alpha} + a^+_{r\beta}a_{s\beta}, \tag{3}$$

and the set $\{|n\rangle\}$ consists of $M-1$ orthonormal linear combinations

$$|n\rangle = \sum_{g=1}^{M} C_{gn}\Phi_g, \tag{4}$$

of the M configurations $\{\Phi_g\}$ appearing in $|0\rangle$.

2.2. *Response of the energy to changes in geometry*

The second quantized expression for the electron hamiltonian $H(\boldsymbol{\mu})$ at $\boldsymbol{R}+\boldsymbol{\mu}$ can be used together with eq. (1) to express the energy at $\boldsymbol{R}+\boldsymbol{\mu}$:

$$E(\boldsymbol{\mu}) = \langle\tilde{0}|H(\boldsymbol{\mu})|\tilde{0}\rangle. \tag{5}$$

Using the well known Baker–Campbell–Hausdorf expansion of the two exponential operators, one obtains an expansion for E in powers of the κ_{rs} and S_n parameters (which, for notational ease, we collect together as a single set $\{\kappa_{rs}, S_n\} \equiv \{\lambda_i\}$):

$$E(\lambda, \boldsymbol{\mu}) = \langle 0|H(\boldsymbol{\mu})|0\rangle + \lambda_i F_i(\boldsymbol{\mu}) + \tfrac{1}{2}\lambda_i G_{ij}(\boldsymbol{\mu})\lambda_j + \dots + \tfrac{1}{6}\lambda_i\lambda_j\lambda_k K_{ijk}(\boldsymbol{\mu}) + \dots . \tag{6}$$

Here, the Einstein summation convention over i, j, k is assumed. The Brillouin F_i, hessian G_{ij} and superhessian K_{ijk} matrices [*] are defined in terms of commutators of the operators $\{T_i\} \equiv \{e_{rs} - e_{sr}, |n\rangle\langle 0| - |0\rangle\langle n|\}$ with the hamiltonian $H(\boldsymbol{\mu})$

$$F_i(\boldsymbol{\mu}) = \langle 0|[T_i, H(\boldsymbol{\mu})]|0\rangle, \quad G_{ij}(\boldsymbol{\mu}) = \langle 0|\big[T_i, [T_j, H(\boldsymbol{\mu})]\big]|0\rangle,$$
$$K_{ijk}(\boldsymbol{\mu}) = \langle 0|\big[T_i, \big[T_j, [T_k, H(\boldsymbol{\mu})]\big]\big]|0\rangle. \tag{7}$$

Eq. (7) displays the $\boldsymbol{\mu}$ and λ_i dependence of the MC SCF energy. Choosing the λ_i parameters to make E stable ($\partial E/\partial\lambda_i = 0$) gives rise to a set of equations which can be used to solve for the optimal λ_i as functions of $\boldsymbol{\mu}$:

$$0 = F_i + G_{ij}\lambda_j + \tfrac{1}{2}K_{ijk}\lambda_j\lambda_k + \dots . \tag{8}$$

Since the λ_i are now functions of $\boldsymbol{\mu}$, $|\tilde{0}\rangle$ and H are functions of the only remaining independent variable, $\boldsymbol{\mu}$. The hamiltonian H can be expanded in powers of $\boldsymbol{\mu}$,

$$H(\boldsymbol{\mu}) = H(0) + \boldsymbol{\mu}\,\boldsymbol{H}_1 + \tfrac{1}{2}\boldsymbol{\mu}\,\mathbf{H}_2\,\boldsymbol{\mu} + \dots . \tag{9}$$

Notice that the displacement $\boldsymbol{\mu}$ is a vector whose dimension equals the number of geometrical degrees of freedom which are allowed to vary. Hence $\boldsymbol{H}_1$ is a vector of this same dimension, and $\mathbf{H}_2$ is a second-rank tensor in this same dimension. In what follows, we often delete the vector and tensor notation but keep it in mind.

This expansion of $H(\boldsymbol{\mu})$ allows each of the F_i, G_{ij}, K_{ijk} to also be expanded in powers of $\boldsymbol{\mu}$. For example,

$$F_j = \sum_{n=0} F_j^{(n)}\mu^n = \sum_{n=0} \frac{\mu^n}{n!}\langle 0|\big[T_j, H_n\big]|0\rangle. \tag{10}$$

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[*] As treated in eq. (33) of ref. [16], these commutators should be appropriately symmetrized if one wishes to generate G, K,… matrices which have proper index symmetry. Such symmetrization occurs naturally when the Baker–Campbell–Hausdorf expansion is carried out. We view this as a technical detail which we shall not dwell further on here.

Since each of F_i, G_{ij} and K_{ijk} contain all powers of $\boldsymbol{\mu}$, the λ_j solutions to eq. (8) contain all powers of $\boldsymbol{\mu}$:

$$\lambda_j = \lambda_j^{(0)} + \boldsymbol{\lambda}_j^{(1)}\boldsymbol{\mu} + \tfrac{1}{2}\boldsymbol{\mu}\boldsymbol{\lambda}_j^{(2)}\boldsymbol{\mu} + \ldots, \tag{11}$$

so $\boldsymbol{\lambda}_j^{(1)}$ is a vector, $\boldsymbol{\lambda}_j^{(2)}$ a second-rank tensor, etc. Substituting this order-by-order expansion of λ_j into eq. (8) and collecting powers of $\boldsymbol{\mu}$ allows one to solve for the $\lambda_j^{(n)}$. Low-order solutions of importance here are

$$\lambda_j^{(0)} = 0, \tag{12a}$$

since $F_j^{(0)} = 0$ according to the generalized Brillouin condition,

$$\boldsymbol{\lambda}_j^{(1)} = -\left(G^{(0)}\right)_{ji}^{-1} \boldsymbol{F}_i^{(1)}, \tag{12b}$$

and

$$\boldsymbol{\lambda}_j^{(2)} = -\left(G^{(0)}\right)_{ji}^{-1} \left(\mathbf{F}_i^{(2)} + 2\boldsymbol{\lambda}_k^{(1)}\boldsymbol{G}_{ik}^{(1)} + K_{ikl}^{(0)}\boldsymbol{\lambda}_k^{(1)}\boldsymbol{\lambda}_l^{(1)}\right). \tag{12c}$$

These results, when substituted back into eq. (7) give an expression for the $\boldsymbol{\mu}$ dependence of E:

$$E = E^{(0)} + \boldsymbol{E}^{(1)}\boldsymbol{\mu} + \tfrac{1}{2}\boldsymbol{\mu}\mathbf{E}^{(2)}\boldsymbol{\mu} + \ldots, \tag{13a}$$

where

$$E^{(0)} = \langle 0|H(0)|0\rangle, \tag{13b}$$

the gradient is

$$\boldsymbol{E}^{(1)} = \langle 0|\boldsymbol{H}_1|0\rangle + \boldsymbol{\lambda}_i^{(1)}F_i^{(0)}, \tag{13c}$$

the hessian is

$$\mathbf{E}^{(2)} = \langle 0|\mathbf{H}_2|0\rangle + \boldsymbol{\lambda}_i^{(2)}F_i^{(0)} + 2\boldsymbol{\lambda}_i^{(1)}\boldsymbol{F}_i^{(1)} + \boldsymbol{\lambda}_i G_{ij}^{(0)}\boldsymbol{\lambda}_j^{(1)}, \tag{13d}$$

etc.

Because the MC SCF wavefunction at $\boldsymbol{R}$ was presumed to have been optimized, $\partial E/\partial\lambda = 0$ at $\boldsymbol{\mu} = 0$. Hence the generalized Brillouin condition

$$F_i^{(0)} = \langle 0|\left[T_i, H(\boldsymbol{0})\right]|0\rangle = 0, \tag{14}$$

holds and the above eqs. (13) simplify to our final working equations for the MC SCF gradient:

$$\boldsymbol{E}^{(1)} = \langle 0|\boldsymbol{H}_1|0\rangle, \tag{15a}$$

and hessian

$$\mathbf{E}^{(2)} = \langle 0|\mathbf{H}_2|0\rangle + \boldsymbol{F}_i^{(1)}\boldsymbol{\lambda}_i^{(1)}. \tag{15b}$$

Clearly one must be able to evaluate the $\boldsymbol{F}_i^{(1)}$ and $G_{ij}^{(0)}$ matrices as well as $\langle 0|\boldsymbol{H}_1|0\rangle$ and $\langle 0|\mathbf{H}_2|0\rangle$ in order to compute the MC SCF gradient and hessian. $G_{ij}^{(0)}$ is nothing but the wavefunction-optimization hessian which can safely be presumed to be available because it is necessary for the MC SCF calculation at $\boldsymbol{R}$. It is written in terms of one- and two-electron integrals and density matrices over the MC SCF orbitals in eqs. (2.38), (2.42) and (2.44) of ref. [19]. The elements $\boldsymbol{F}_i^{(1)} = \langle 0|[T_i, \boldsymbol{H}_1]|0\rangle$ are generalized Brillouin matrix elements but with $\boldsymbol{H}_1$ replacing $H(0)$, respectively. Their computational evaluation is addressed in more detail in section 3, but first we must obtain more concrete expressions for the operators $\boldsymbol{H}_1$ and $\mathbf{H}_2$.

2.3. Molecular orbital-level expressions for the H_K

Because the operators e_{rs} appearing in the T_i refer to transformations among the orthonormal MC SCF molecular orbitals, it would be convenient for carrying out further derivation to express $\boldsymbol{H}_1$ and $\mathbf{H}_2$ in terms of operators e_{ij} which also refer to the MC SCF orbitals. In ref. [16], $\boldsymbol{H}_1$ and $\mathbf{H}_2$ were given in terms of symmetrically orthogonalized orbitals (SOs). The fact that $H(\boldsymbol{\mu})$ and $\boldsymbol{\kappa}$ (and hence T_i) are given in terms of *different* orthonormal bases (symmetrically orthogonalized and MC SCF orbitals, respectively) would seem to complicate the practical evaluation of $\boldsymbol{F}_i^{(1)}$, $\langle 0|\boldsymbol{H}_1|0\rangle$ and $\langle 0|\mathbf{H}_2|0\rangle$. However, as we now demonstrate, it is indeed possible to describe the H_K in terms of creation and annihilation operators which refer to the MC SCF orbital basis.

Our strategy is to show that the derivatives of the SO orbitals appearing in ref. [16] can be conveniently re-expressed as derivatives of the MC SCF orbitals themselves. Once we have established this relation between SO and MO derivatives it will be straightforward to express $\boldsymbol{H}_1$ and $\mathbf{H}_2$ in terms of MC SCF orbital derivatives, and it will become clear that the SOs can be viewed as a convenient derivational tool which need not appear in final working formulas.

Let us begin by considering the $\boldsymbol{\mu}$ dependence of the symmetrically orthogonalized (SO) orbitals $\{\xi_\alpha\}$ which consist of combinations of the atomic basis orbitals $\{\chi_\nu\}$

$$\xi_\alpha = \sum_\nu S_{\nu\alpha}^{-1/2}\chi_\nu, \tag{16}$$

where the atomic-orbital (AO) overlap matrix $S_{\alpha\nu}$ has elements $\langle\chi_\alpha|\chi_\nu\rangle$. The second quantized expression for any operator (the hamiltonian, in particular) involves sums of orthonormal spin orbitals multiplied by their associated creation or annihilation operators. It is well known and easily demonstrated that such sums are independent of a unitary transformation among the orthonormal orbitals; that is, the sum is the same for all orthonormal bases. In particular, the sum of SO orbitals and operators a_α in terms of which $H(\boldsymbol{\mu})$ is analyzed in ref. [16] can be replaced by an MO-level sum

$$\sum_\alpha \xi_\alpha a_\alpha = \sum_{i\alpha} U_{\alpha i}^* \phi_i a_\alpha = \sum_i \phi_i a_i, \tag{17}$$

by making use of the expansion coefficients $\{U_{\alpha i}\}$ relating the SOs $\{\xi_\alpha\}$ to the MC SCF MOs $\{\phi_i\}$. It is this kind of relationship which we shall use to move from an SO-level expression for $H(\boldsymbol{\mu})$ to the MO-level result, but first we need to further analyze the $\boldsymbol{\mu}$ dependence of. the $\{\xi_\nu\}$ since this gives rise to $\boldsymbol{\mu}$ dependence in $H(\boldsymbol{\mu})$.

The SOs $\{\xi_\nu\}$ can be expanded in powers of $\boldsymbol{\mu}$ around $\boldsymbol{\mu} = \boldsymbol{0}$ by writing them in the following manner:

$$\xi_\nu = \sum_{\alpha,\nu'} (1+\Delta)_{\nu'\nu}^{-1/2} \left(S_0^{-1/2}\right)_{\alpha\nu'} \chi_\alpha, \tag{18}$$

where the $\{\chi_\alpha\}$ are the primitive atomic orbitals (AOs) (gaussian- or Slater-type), S_0 is the overlap matrix over these AOs at $\boldsymbol{\mu} = \boldsymbol{0}$, and

$$(1+\Delta)_{\nu'\nu} \equiv \sum_{\alpha\beta} \left(S_0^{-1/2}\right)_{\nu\alpha} S_{\alpha\beta} \left(S_0^{-1/2}\right)_{\beta\nu'}. \tag{19}$$

Eq. (18) simply provides a convenient parameterization of the $\boldsymbol{\mu}$ dependence of $\boldsymbol{\mu} = \boldsymbol{0}$. Notice that as $\boldsymbol{\mu} \to \boldsymbol{0}$, $\Delta_{\nu'\nu} \to 0$, and that derivatives of $(1+\Delta)$ involve simply derivatives of the overlap S itself:

$$(\nabla)^n (1+\Delta)_{\nu'\nu} = (\nabla)^n \Delta_{\nu'\nu} = \sum_{\alpha\beta} \left(S_0^{-1/2}\right)_{\nu\alpha} (\nabla)^n S_{\alpha\beta} \left(S_0^{-1/2}\right)_{\beta\nu'}. \tag{20}$$

Using eq. (18), we can now express $\nabla\xi_\nu$ in a convenient form. To do so we first evaluate the first derivatives [*] of $(1+\Delta)^{-1/2}$ at $\boldsymbol{\mu}=\boldsymbol{0}$:

$$\nabla(1+\Delta)_{\nu'\nu}^{-1/2}=\nabla\Big(\delta_{\nu'\nu}-\tfrac{1}{2}\Delta_{\nu'\nu}+\tfrac{3}{8}\sum_{\alpha}\Delta_{\nu'\alpha}\Delta_{\alpha\nu}-\dots\Big)=-\tfrac{1}{2}\nabla(\Delta_{\nu'\nu}). \tag{21}$$

The desired derivative of ξ_ν can now be written (at $\boldsymbol{\mu}=\boldsymbol{0}$)

$$\nabla\xi_\nu=\sum_{\alpha}\big(S_0^{-1/2}\big)_{\nu\alpha}\nabla\chi_\alpha-\tfrac{1}{2}\sum_{\substack{\alpha,\nu'\\ \beta\gamma}}\big(S_0^{-1/2}\big)_{\nu\beta}\nabla S_{\beta\gamma}\big(S_0^{-1/2}\big)_{\gamma\nu'}\big(S_0^{-1/2}\big)_{\nu'\alpha}\chi_\alpha. \tag{22}$$

In ref. [16] the derivatives H_1 and $\mathbf{H}_2$ of the hamiltonian $H(\boldsymbol{\mu})$ with respect to $\boldsymbol{\mu}$ were given in terms of sums $\Sigma_\nu\nabla\xi_\nu a_\nu$ and $\Sigma_\nu\nabla\nabla\xi_\nu\, a_\nu$ analogous to those discussed in eq. (17). From eq. (17) one sees that the SO-level annihilation operators a_ν can be related to their MO-level counterparts a_i:

$$a_\nu=\sum_i U_{\nu i}a_i. \tag{23}$$

This then allows the above sums involving $\nabla\xi_\nu$ and $\nabla\nabla\xi_\nu$ to be rewritten as follows:

$$\sum_\nu\nabla\xi_\nu a_\nu=\sum_i a_i\sum_\nu U_{\nu i}\nabla\xi_\nu,\qquad \sum_\nu\nabla\nabla\xi_\nu a_\nu=\sum_i a_i\sum_\nu U_{\nu i}\nabla\nabla\xi_\nu. \tag{24}$$

Eqs. (24) allow us to move from the SO-level operators $\{a_\nu\}$ to the MO-level operators $\{a_i\}$. The combinations $\Sigma_\nu U_{\nu i}\nabla\xi_\nu$ and $\Sigma_\nu U_{\nu i}\nabla\nabla\xi_\nu$, which can be viewed as MO-level derivatives $\nabla\phi_i$ and $\nabla\nabla\phi_i$ in which the expansion coefficients $U_{\nu i}$ are held fixed, will from now on be denoted $\nabla\phi_i$ and $\nabla\nabla\phi_i$ for notational ease.

When eq. (22) is premultiplied by the MO-to-SO expansion coefficient $U_{\nu i}$ and summed over ν, we obtain a useful expression for the derivative of the MO ϕ_i in which its MO-to-SO expansion coefficients are held fixed:

$$\nabla\phi_i\equiv\sum_\nu U_{\nu i}\nabla\xi_\nu=\sum_\alpha C_{\alpha i}\nabla\chi_\alpha-\tfrac{1}{2}\sum_{\alpha,\beta\gamma}C_{\beta i}\nabla S_{\beta\gamma}S_{\gamma\alpha}^{-1}\chi_\alpha, \tag{25}$$

where

$$C_{\alpha i}=\sum_\nu U_{\nu i}\big(S^{-1/2}\big)_{\nu\alpha} \tag{26}$$

is the expansion coefficient of MO ϕ_i in the primitive AO basis $\{\chi_\alpha\}$ at $\boldsymbol{\mu}=\boldsymbol{0}$. Using this relation between the MOs and AOs ($\phi_i=\Sigma_\alpha C_{\alpha i}\chi_\alpha$) it is straightforward to show that

$$\sum_\alpha S_{\gamma\alpha}^{-1}\chi_\alpha=\sum_i C_{\gamma i}\phi_i. \tag{27}$$

This allows eq. (25) for $\nabla\phi_i$ to be rewritten in our final working form as

$$\nabla\phi_i=\sum_\alpha C_{\alpha i}\nabla\chi_\alpha-\tfrac{1}{2}\sum_k\Big(\sum_{\alpha\beta}C_{\beta i}\nabla S_{\beta\alpha}C_{\alpha k}\Big)\phi_k. \tag{28}$$

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[*] When $\nabla_1\nabla_2$ operates on a product of factors (such as $(1+\Delta)_{\nu\nu'}^{-1/2}\chi_\alpha$) one obtains four terms [e.g., $(1+\Delta)^{-1/2}\nabla_1\nabla_2\chi$, $\chi\nabla_1\nabla_2(1+\Delta)^{-1/2}$ and both $\nabla_1(1+\Delta)^{-1/2}\,\nabla_2\chi$ and $\nabla_2(1+\Delta)^{-1/2}\nabla_1\chi$]. The subscripts 1 and 2 on ∇_1 and ∇_2 remind us that these differential operators have components. For example, when $(\mathrm{d}/\mathrm{d}x_a)(\mathrm{d}/\mathrm{d}y_b)$ operates one obtains four terms including both "cross terms" $(\mathrm{d}/\mathrm{d}x_a)(1+\Delta)^{-1/2}(\mathrm{d}/\mathrm{d}y_b)\chi$ and $(\mathrm{d}/\mathrm{d}y_b)(1+\Delta)^{-1/2}(\mathrm{d}/\mathrm{d}x_a)\chi$. In this manuscript we will simply write $\nabla(1+\Delta)^{-1/2}\,\nabla\chi$ but keep in mind that both cross terms are present.

This result is especially important and easy to interpret. It states that $\nabla\phi_i$ contains a contribution from the basis-set dependence and a contribution due to changes in the $C_{\alpha i}$ coefficients arising from the orthogonality condition $C^{\mathrm{T}}SC=1$. Even though the $\nabla\phi_i$ which eq. (28) expresses has its MO-to-SO expansion coefficients ($U_{\nu i}$) held fixed, the MO-to-AO coefficients $C_{\nu i}$ vary through their $S_{\nu\alpha}^{-1/2}$ dependence as given in eq. (26). This variation is, however, only an effect of the maintenance of the orthonormality of the MOs. Because $\phi_i=\Sigma_\alpha C_{\alpha i}\chi_\alpha$, one can alternatively view $\nabla\phi_i$ as

$$\nabla\phi_i=\sum_\alpha\left(C_{\alpha i}\nabla\chi_a+\chi_\alpha\nabla C_{\alpha i}\right). \tag{29}$$

When compared to eq. (28) one sees that

$$\sum_\alpha\chi_\alpha\nabla C_{\alpha i}=-\tfrac{1}{2}\sum_{\substack{k\\ \beta\gamma}}\left(C_{\beta i}\nabla S_{\beta\gamma}C_{\gamma k}\right)\phi_k, \tag{30}$$

from which it is straightforward to show that

$$\nabla C_{\alpha i}=-\tfrac{1}{2}\sum_k\left(C^{\mathrm{T}}\nabla SC\right)_{ik}C_{\alpha k}, \tag{31}$$

Eq. (31) provides us with a very important tool for expressing the change in the MO-to-AO expansion coefficients which arises from the MO orthonormality constraint $C^{\mathrm{T}}SC=1$.

If JS had, in ref. [16], realized our eq. (28) they could have avoided using the SO basis as an intermediate device in their derivation. We chose to show the relation of the $S_{\alpha\beta}^{-1/2}$ array which arises in the SO basis to the direct MO-to-AO result given in eq. (28) so as to clarify the derivation of ref. [16]. However, it should be clear that because eq. (28) contains *no reference* to the intermediate SO orbitals, it is a general result. Because eq. (23) refers only to the AO-level orbital derivatives and to the AO-to-MO expansion coefficients, its validity is independent of the SO basis which was used in ref. [16]. That is, the SO basis can be viewed as a perhaps convenient intermediate; eqs. (25) and (31) are, however, more useful because they allow all orbital derivatives to involve only the primitive AOs.

To obtain an expression for $\nabla\nabla\phi_i$ analogous to eq. (28) for $\nabla\phi_i$ we simply differentiate eq. (28) once more and make use of eqs. (28) and (31) to obtain

$$\begin{aligned}\nabla\nabla\phi_i=&\sum_\alpha C_{\alpha i}\nabla\nabla\chi_\alpha-\tfrac{1}{2}\sum_k\left(C^{\mathrm{T}}\nabla\nabla SC\right)_{ik}\phi_k-\tfrac{1}{2}\sum_{k,\alpha}\left(C^{\mathrm{T}}\nabla SC\right)_{ik}C_{\alpha k}\nabla\chi_\alpha\\&+\tfrac{3}{8}\sum_k\left[\left(C^{\mathrm{T}}\nabla SC\right)\left(C^{\mathrm{T}}\nabla SC\right)\right]_{ik}\phi_k.\end{aligned} \tag{32}$$

We are now ready to use our expressions [eqs. (23) and (32)] for $\Sigma_\nu U_{\nu i}\nabla\xi_\nu$ and $\Sigma_\nu U_{\nu i}\nabla\nabla\xi_\nu$ to write down $\boldsymbol{H}_1$ and $\mathbf{H}_2$. Within the SO basis $H(\boldsymbol{\mu})$ is given as

$$\begin{aligned}H(\boldsymbol{\mu})&=\sum_{\nu,\sigma}\langle\xi_\nu|-\tfrac{1}{2}\nabla^2-\Sigma_a Z_a/|\boldsymbol{r}-\boldsymbol{R}_a-\boldsymbol{\mu}||\xi_\sigma\rangle a_\nu^+a_\sigma+\tfrac{1}{2}\sum_{\alpha\nu\sigma\tau}\left(\xi_\alpha\xi_\nu|\xi_\sigma\xi_\tau\right)a_\alpha^+a_\sigma^+a_\nu a_\tau\\&\equiv\sum_{\nu,\sigma}h_{\nu\sigma}a_\nu^+a_\sigma+\tfrac{1}{2}\sum_{\alpha\nu\sigma\tau}(\alpha\nu|\sigma\tau)a_\alpha^+a_\sigma^+a_\nu a_\tau,\end{aligned} \tag{33}$$

where the shorthand one- and Mulliken two-electron integral notations, $h_{\nu\sigma}$ and $(\alpha\nu|\sigma\tau)$ have been introduced. The first and second $\boldsymbol{\mu}$-derivatives of $H(\boldsymbol{\mu})$ (evaluated at $\boldsymbol{\mu}=\boldsymbol{0}$) give $\boldsymbol{H}_1$ and $\mathbf{H}_2$. These derivatives clearly involve $\Sigma_\nu\nabla\xi_\nu a_\nu$ and $\Sigma_\nu\nabla\nabla\xi_\nu a_\nu$ which, by eqs. (24), can be rewritten as $\Sigma_i a_i\nabla\phi_i$ and $\Sigma_i a_i\nabla\nabla\phi_i$. The results of taking the required derivatives of the H shown in eq. (33), using eqs. (24), and substituting eqs. (28) and (32) for $\nabla\phi_i$ and $\nabla\nabla\phi_i$ are given as follows:

$$\boldsymbol{H}_1=\sum_{rs}\sum_{\mu\nu}C_{\mu r}C_{\nu s}\left(d_{rs}\nabla h_{\mu\nu}-E_{rs}\nabla S_{\mu\nu}\right)+\tfrac{1}{2}\sum_{rspq}\sum_{\mu\nu\lambda\sigma}C_{\mu r}C_{\nu s}C_{\lambda p}C_{\sigma q}d_{rspq}\nabla(\mu\nu|\lambda\sigma), \tag{34}$$

where the E_{rs} are elements of a Fock-like operator

$$E_{rs} = \sum_k h_{rk} d_{sk} + \sum_{pqk} (sk|pq) d_{rkpq} \tag{35}$$

(which is symmetric if the MC SCF wavefunction obeys the generalized Brillouin condition) and the d_{sk} and d_{rkpq} are symmetrized density operators

$$d_{rs} = \tfrac{1}{2}(e_{rs} + e_{sr}), \qquad d_{rspq} = \tfrac{1}{4}(e_{rspq} + e_{rsqp} + e_{srpq} + e_{srqp}), \tag{36}$$

which have the same index permutational symmetries as the integrals which they multiply in H. The $e_{ij} = a^+_{i\alpha} a_{j\alpha} + a^+_{i\beta} a_{jb}$ and $e_{ijkl} = e_{ij} e_{kl} - \delta_{jk} e_{il}$ are the well-known unitary generators. Note that in eq. (34) all integral derivatives involve atomic-orbital integrals (labeled with Greek indices α, β γ, δ) whereas all creation and annihilation operators (in d_{ij}) involve molecular orbitals (labeled p, q, r, s). These facts are of crucial importance to the efficient computational implementation of eqs. (15a) and (15b).

The corresponding expression for $\mathbf{H}_2$ is

$$\begin{aligned} \mathbf{H}_2 = {} & \sum_{\mu\nu} \sum_{rs} C_{\mu r} C_{\nu s} d_{rs} \nabla\nabla h_{\mu\nu} - \sum_{\mu\nu rs} C_{\mu r} C_{\nu s} (\nabla E_{rs} \nabla S_{\mu\nu} + E_{rs} \nabla\nabla S_{\mu\nu}) \\ & + \tfrac{3}{8} \sum_{\substack{\mu\nu \\ rs \\ \alpha\beta}} C_{\mu r} C_{\nu s} E_{rs} \left(\nabla S_{\mu\alpha} \sum_i C_{i\alpha} C_{i\beta} \nabla S_{\beta\nu} \right) + \tfrac{1}{2} \sum_{\substack{\mu\nu\lambda\sigma \\ rspq}} C_{\mu r} C_{\nu s} C_{\lambda p} C_{\sigma q} d_{rspq} \nabla\nabla(\mu\nu|\lambda\sigma), \end{aligned} \tag{37}$$

with

$$\nabla E_{rs} = \sum_{k\alpha\beta} C_{\alpha r} C_{\beta k} \nabla h_{\alpha\beta} d_{sk} + \sum_{kpq} \sum_{\alpha\beta\mu\nu} C_{\alpha s} C_{\beta k} C_{\mu p} C_{\nu q} \nabla(\alpha\beta|\mu\nu) d_{rkpq}. \tag{38}$$

Eqs. (34) and (37) represent our final expressions for $\boldsymbol{H}_1$ and $\mathbf{H}_2$.

2.4. MC SCF gradient and hessian

When used in eqs. (15a) and (15b) these results provide working equations for the gradient $\boldsymbol{E}^{(1)}$ and hessian $\mathbf{E}^{(2)}$:

$$\boldsymbol{E}^{(1)} = \langle 0|\boldsymbol{H}_1|0\rangle = \sum_{\mu\nu} \langle d_{\mu\nu}\rangle \nabla h_{\mu\nu} - \sum_{\mu\nu} \langle E_{\mu\nu}\rangle \nabla S_{\mu\nu} + \tfrac{1}{2} \sum_{\mu\nu\lambda\sigma} \langle d_{\mu\nu\lambda\sigma}\rangle \nabla(\mu\nu|\lambda\sigma), \tag{39}$$

where the following quantities involve density matrices which are first computed in the MO basis and then transformed to the AO basis:

$$\langle d_{\mu\nu}\rangle = \sum_{rs} C_{\mu r} C_{\nu s} \langle d_{rs}\rangle, \quad \langle d_{\mu\nu\lambda\sigma}\rangle = \sum_{rspq} C_{\mu r} C_{\nu s} C_{\lambda p} C_{\sigma q} \langle d_{rspq}\rangle, \tag{40}$$

$$\langle E_{\mu\nu}\rangle = \sum_{rs} C_{\mu r} C_{\nu s} \langle E_{rs}\rangle, \quad \langle E_{rs}\rangle = \sum_k h_{rk} \langle d_{sk}\rangle + \sum_{pqk} (sk|pq) \langle d_{rkpq}\rangle. \tag{41}$$

The MC SCF hessian is given in like fashion by

$$\mathbf{E}^{(2)} = \langle 0|\mathbf{H}_2|0\rangle - \left(\boldsymbol{F}^{(1)}_{rs}, \boldsymbol{F}^{(1)}_{n}\right) \left(G^{(0)}\right)^{-1} \begin{pmatrix} \boldsymbol{F}^{(1)}_{tu} \\ \boldsymbol{F}^{(1)}_{m} \end{pmatrix}, \tag{42}$$

where its constituent parts are

$$\langle 0|\mathbf{H}_2|0\rangle = \sum_{\mu\nu} \langle d_{\mu\nu}\rangle \nabla\nabla h_{\mu\nu} - \sum_{\substack{rs\\ \mu\nu}} \langle \nabla E_{rs}\rangle \nabla S_{\mu\nu} C_{\mu r} C_{\nu s} - \sum_{\substack{rs\\ \mu\nu}} \langle E_{rs}\rangle \nabla\nabla S_{\mu\nu} C_{\mu r} C_{\nu s}$$
$$+ \tfrac{3}{8} \sum_{\mu\nu rs} C_{\mu r} C_{\nu s} \langle E_{rs}\rangle \sum_{\alpha\beta} \nabla S_{\mu\alpha} \sum_{i} C_{i\alpha} C_{i\beta} \nabla S_{\beta\nu} + \tfrac{1}{2} \sum_{\mu\nu\lambda\sigma} \langle d_{\mu\nu\lambda\sigma}\rangle \nabla\nabla(\mu\nu|\lambda\sigma), \tag{43}$$

$$\boldsymbol{F}_{mn}^{(1)} = 2(1 - P_{mn}) \Bigg(\sum_{\mu\nu} C_{\mu n} \nabla h_{\mu\nu} \sum_{i} C_{\nu i} \langle d_{mi}\rangle - \sum_{\mu\nu} \nabla S_{\mu\nu} \sum_{ij} \left(\langle d_{mi}\rangle C_{\mu j} C_{\nu n} h_{ji} + \langle d_{mi}\rangle C_{\mu j} C_{\nu i} h_{nj} \right)$$
$$- \sum_{\mu\nu} \nabla S_{\mu\nu} \sum_{ijkl} \langle d_{mi,jk}\rangle C_{\mu l} \left[C_{\nu n}(li|jk) + C_{\nu i}(nl|jk) + C_{\nu j}(ni|lk) + C_{\nu k}(ni|jl) \right]$$
$$+ \sum_{\substack{\mu\nu\\ \lambda\sigma}} C_{\mu n} \nabla(\mu\nu|\lambda\sigma) \sum_{ijk} \langle d_{mi,jk}\rangle C_{\nu i} C_{\lambda j} C_{\sigma k} \Bigg), \tag{44}$$

where P_{mn} represents permuting indices m and n, and

$$\boldsymbol{F}_{n}^{(1)} = \langle 0|[\,|n\rangle\langle 0| - |0\rangle\langle n|, \boldsymbol{H}_1]|0\rangle = -\langle n|\boldsymbol{H}_1|0\rangle - \langle 0|\boldsymbol{H}_1|n\rangle$$
$$= -\sum_{\mu\nu} \left(\nabla h_{\mu\nu} \langle d_{\mu\nu}\rangle_n - \nabla S_{\mu\nu} \langle E_{\mu\nu}\rangle_n \right) - \tfrac{1}{2} \sum_{\mu\nu\lambda\sigma} \langle d_{\mu\nu\lambda\sigma}\rangle_n \nabla(\mu\nu|\lambda\sigma). \tag{45}$$

Here the subscript n means that all such density matrices are evaluated as *transition* density matrices. For example,

$$\langle d_{\mu\nu}\rangle_n = 2 \sum_{rs} C_{\mu r} C_{\nu s} \langle 0|d_{rs}|n\rangle. \tag{46}$$

As mentioned earlier, G_0 is the usual hessian matrix of MC SCF theory [19].

2.5. CI gradient

Before closing this derivation section, we would point out how the results of this work allow one to also compute molecular gradients for configuration interaction (CI) wavefunctions $|\mathrm{CI}\rangle$. Eq. (13c) still holds for this case, but the generalized Brillouin condition [eq. (14)] only holds in the variable space $\{S_n\}$ for which the CI energy has been variationally optimized. That is $F_n^{(0)} = 0$ but $F_{rs}^{(0)} \neq 0$. As a result, the CI molecular gradient has a non-vanishing second term in eq. (13c)

$$\boldsymbol{E}^{(1)} = \langle \mathrm{CI}|\boldsymbol{H}_1|\mathrm{CI}\rangle + \kappa_{rs}^{(1)} F_{rs}^{(0)} = \langle \mathrm{CI}|\boldsymbol{H}_1|\mathrm{CI}\rangle - \sum_{\substack{r>s\\ t>u}} F_{rs}^{(0)} (G^{(0)})_{rs,tu}^{-1} \boldsymbol{F}_{tu}^{(1)}. \tag{47}$$

The computation of $\langle \mathrm{CI}|\boldsymbol{H}_1|\mathrm{CI}\rangle$ is treated exactly as outlined above relative to eq. (39) except that all density matrix elements $\langle d_{rs}\rangle$ and $\langle d_{rspq}\rangle$ are evaluated relative to the CI wavefunction. Because the combination $-\sum_{t>u}(G^{(0)})_{rs,tu}^{-1}\boldsymbol{F}_{tu}^{(1)}$ gives the response $\kappa_{rs}^{(1)}$ of the orthonormal orbitals to nuclear displacement [see eq. (12b)], the calculation of this quantity depends upon the nature of the *orbitals* being used in the CI calculation, not the configurations included in $|\mathrm{CI}\rangle$. That is, $F_{rs}^{(0)}$ described the changes in the CI energy due to variation of the κ_{rs} orbital parameters; $\kappa_{rs}^{(1)}$ gives the change in the orbitals due to displacement. Clearly, the orbital change only depends on what the orbitals are, not on the CI configurations. The most commonly used choices are Hartree–Fock (HF) molecular orbitals and orbitals resulting from an MC SCF calculation of considerably smaller dimension (i.e. number of configurations) than the CI calculation under study. For either of these two cases, the evaluation of $F_{tu}^{(1)}$ and $(G^{(0)})^{-1}_{rs,tu}$ proceeds as follows: $F_{tu}^{(1)}$ is computed as discussed above in eq. (47) except that the density matrices are taken relative either to the HF or MC SCF function which was used to compute the orbitals. Likewise, $G^{(0)}_{rs,tu}$ is evaluated as in eq. (2.42) of ref. [19] but with HF or MC SCF density matrices. To evaluate $F_{rs}^{(0)}$ one used the well-known expressions (e.g., eq. (2.41) of ref. [19]) for these generalized Brillouin matrix elements except that one computes the density matrices with respect to the CI wavefunction whose molecular gradient is being sought.

3. Computational implementation of working equations

In writing eqs. (39) and (42) for the molecular gradient and hessian, care has been taken to group together those factors (e.g., $\nabla h_{\mu\nu}$, $\nabla(\mu\nu|\lambda\sigma)$, $\nabla\nabla(\mu\nu|\lambda\sigma)$, $\nabla S_{\mu\nu}$) which depend upon the components of the displacement derivatives and those which are independent of displacement. This facilitates our computational strategy: (1) to compute, sort, and store on disk all quantities (performing as many intermediate sums as possible) which are deformation independent, (2) to carry out a *single* shell-by-shell pass through the AO-based integral derivatives during which these derivatives are generated and the corresponding displacement-independent quantities are read into the computer's core from disk and multiplied by the integral derivatives. This strategy allows us to generate and use the AO-level integral derivatives without storing them.

Let us consider a few examples of how this procedure works. In the last term of eq. (39) we see that the AO-based two-electron integral derivatives $\nabla(\mu\nu|\lambda\sigma)$ are multiplied by $\langle d_{\mu\nu\lambda\sigma}\rangle$ which is displacement-independent. The MO-level density matrix $\langle d_{rspq}\rangle$, which has full eight-fold index permutational symmetry, is evaluated within our unitary-group MC SCF computer program; it is a necessary ingredient of the MC SCF process itself. This array $\langle d_{rs,pq}\rangle$ can then be transformed, using the conventional n^5 procedure employed to transform two-electron integrals, to give $\langle d_{\mu\nu,\lambda\sigma}\rangle$ as shown in eq. (40). This latter array also has full eight-fold index permutation symmetry. It can be sorted and stored on disk in the same order in which the integral derivatives $\lambda(\mu\nu|\lambda\sigma)$ are evaluated. Notice that it is our desire to perform only a single pass through the integral derivatives and not to store these integral derivatives which require us to have access to the AO-level density matrices $\langle d_{\mu\nu,\lambda\sigma}\rangle$. It is true that the density matrices are likely to be much sparser, and thus more easily handled, in the MO basis, however our computing strategy requires us to evaluate and store the $\langle d_{\mu\nu,\lambda\sigma}\rangle$ in the same shell-by-shell blocks as we used to generate the integral derivatives. One could alternatively compute $\langle d_{ijkl}\rangle$ in the MO basis and multiply these density matrix elements by the integral derivatives which have been transformed to the MO basis $\nabla(ij|kl) = \sum_{\mu\nu\lambda\sigma} C_{i\mu}C_{j\nu}C_{k\lambda}C_{l\sigma}\nabla(\mu\nu|\lambda\sigma)$. However, this transformation results in an integral derivative list of dimension $3N \times O^4$, where O is the number of MOs which are occupied in the MC SCF wavefunction and N is the number of atoms which are allowed to move. Notice that the sparseness of the AO-level integral derivative list (whose size is $\approx 12 \times n^4$) is lost once the AO-to-MO transformation is effected. For molecules with more than a few geometrical degrees of freedom, the storage difference between $12 \times n^4$ and $3N \times O^4$ can be so large as to offset the density matrix transformation and storage difference (n^4 for $\langle d_{\mu\nu\lambda\sigma}\rangle$ versus O^4 for $\langle d_{ijkl}\rangle$)

Most of the terms in $\boldsymbol{E}_1$ and $\mathbf{E}_2$ can be straightforwardly evaluated following the above outlined strategy. However, the computation of $F_{mn}^{(1)}$ involves special difficulties which are worth focusing attention on. The last term in eq. (44) requires an n^5 three-index transformation

$$\sum_{ijk}\langle d_{mi,jk}\rangle C_{\nu i}C_{\lambda j}C_{\sigma k} \equiv X_{m\nu,\lambda\sigma}, \tag{48}$$

to form, sort and store the $X_{m\nu,\lambda\sigma}$ array. As the integral derivatives $\nabla(\mu\nu|\lambda\sigma)$ are generated, the appropriate groups of $X_{m\nu,\lambda\sigma}$ and $C_{\mu n}$ are brought into the computer's core and contributions to the quadruple (i.e. n^5) sum $\boldsymbol{Z}_{m\mu} \equiv \Sigma_{\nu,\lambda\sigma} X_{m\nu,\lambda\sigma} \nabla(\mu\nu|\lambda\sigma)$ are generated. It is possible to reduce the amount of disk-to-core input/output required to evaluate the $\boldsymbol{Z}_{m\mu}$ array. By allowing oneself to compute integral derivatives more than once, one can minimize IO of the density matrix elements $X_{m\nu,\lambda\sigma}$. Alternatively, by insisting that integral derivatives $N(\mu\nu|\lambda\sigma)$ be computed only once, one must be willing to do more IO of the $X_{m\nu,\lambda\sigma}$ array. Once $\boldsymbol{Z}_{m\mu}$ is in hand it can be multiplied by $C_{\mu n}$ and summed over μ to give $\boldsymbol{F}_{mn}^{(1)}$. The next to the last terms in eq. (44) can be handled in like fashion.

The last terms in eq. (45) present the most challenges. As written, its evaluation would require the evaluation and storage of transition density matrices over the AO basis. Since there are one fewer transition density matrices than there are configurations (N_c) in the MC SCF wavefunction $|0\rangle$, there may be very many such arrays. Therefore, for any but quite small ($\lesssim 10$) configuration expansion lengths, it is not practical to evaluate this term as it is written. Instead, it may be preferable to transform the integral derivatives to the MO basis and to evaluate the transition density matrices in this same MO basis. Evaluation of the MO-level transition density matrices is relatively straightforward. Transformation of the AO-level integral derivatives $\nabla(\mu\nu|\lambda\sigma)$ to the MO basis is tedious and storage intensive (since there are $3N \times O^4$ such MO integral derivatives, where N is the number of atoms and O is the number of occupied MOs). Nevertheless, the requirements for transforming this array of length $3Nn^4$ may, for moderate to large configuration expansion lengths (N_c), be less than is needed to evaluate the $\langle d_{\mu\nu,\lambda\sigma}\rangle_n$ array whose dimension is $(N_c - 1)n^4$. Thus, it may be wiser to evaluate the last term in eq. (45) via transformation of the integral derivatives to the MO basis.

We feel that the working equations given in eqs. (39) and (44) together with the above strategy for their implementation provide an efficient and computationally feasible procedure for generating molecular gradients and hessians via ab initio MC SCF-based wavefunctions. We presently have at Utah and at Argonne [☆] a working program based upon this approach in which the gradient routines are fully operative. We are currently working on bringing the second integral derivatives [e.g., $\nabla\nabla(\mu\nu|\lambda\sigma)$] and the $\boldsymbol{F}_{mn}^{(1)}$ routines into production.

These remarks conclude our treatment of MC SCF and CI molecular gradients and hessians. We feel that our working expressions are given in computationally tractable form and that our derivation was carried out in a manner which other workers will find enlightening. It is possible to use the connections which we demonstrated between derivatives of the SOs and the MO-level derivatives $\nabla\phi_i$ and $\nabla\nabla\phi_i$ given in eqs. (28) and (32) to express the Møller–Plesset and coupled-cluster gradients and hessians of ref. [16] in terms of AO-level integral derivatives and MO-level density matrices. In fact, by using eqs. (28) and (32) for $\nabla\phi_i$ and $\nabla\nabla\phi_i$ it should be possible to efficiently derive any gradient, hessian, or higher energy-derivative formula in computationally tractable form.

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