

Ab initio analytical molecular gradients and Hessians

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Molecular gradients and Hessians have been derived for MCSCF, CI, coupled cluster, and Møller–Plesset wave functions. In deriving the gradients and Hessians, atomic orbital basis set effects have been incorporated into the finite basis Hamiltonian, and unitary exponential operators have been used to determine the wave function's configuration and orbital responses. The gradients and Hessians are expressed in terms of products of configuration and orbital responses and matrices of the same form as the gradient and Hessian matrices appearing in energy and wave function optimizations. The molecular gradients and Hessians have also been cast into forms that are computationally very tractable.

I. INTRODUCTION

In recent years quantum chemists have devoted much effort toward obtaining computationally tractable analytical formulas for the gradients (forces) and Hessians (force constants) appropriate to single Born–Oppenheimer electronic energy surfaces. Such forces and curvatures are of primary use in locating minima and saddle points and characterizing, by vibrational frequencies, these stationary-point geometries. Much of the history (until 1977) of the development of this research topic is reviewed by Pulay in his chapter¹ in *Modern Theoretical Chemistry*. The very substantial early contributions of Gerratt and Mills,² Bratoz,³ Meyer and Pulay,⁴ Thomsen and Swanstrøm,⁵ and Pulay⁶ himself are spelled out clearly in that chapter. Somewhat more recent developments have been made by Pople,⁷ Dupuis and King,⁸ Schaefer,⁹ Poppinger,¹⁰ Schlegel,¹¹ and Kormonicki.¹²

The most recent developments have stressed the treatment of open-shell cases^{4,7,9} and multiconfigurational wave functions as treated by configuration interaction^{7,9} (CI), multiconfigurational self-consistent field^{9,13} (MCSCF), and Møller–Plesset perturbation theory⁷ (MPPT) techniques. At present, there seems to exist analytical results for the gradient within the SCF, CI, MCSCF, and MPPT theories and for the Hessian within the SCF framework.

In the present paper we obtain analytical gradient and Hessian expressions for SCF, MCSCF, CI, MPPT, and coupled-cluster (CC) wave functions. By using symmetrically orthogonalized orbitals, we localize all explicit basis-set overlap dependence in the one- and two-electron integrals appearing in the Hamiltonian. All one- and two-particle density matrices then contain no explicit geometry dependence. The symmetrically orthogonalized atomic orbitals also allow us to make use of exponential unitary operators to describe the changes in orbitals arising from an infinitesimal displacement of the nuclei. By employing the exponential unitary operators which have recently proven so useful in formulating quadratically convergent MCSCF wave function optimization theory,^{14,15} we eliminate the need to introduce constraints among the configuration and molecular orbital expansion coefficients. By using the

exponential unitary operators, the responses¹⁶ of the wave function's configuration and molecular orbital expansion amplitudes can be expressed in terms of parameters all of which are linearly independent; in contrast to previous developments,¹ no additional constraints need be applied. The use of such constraints and their accompanying Lagrange multipliers has, in our opinion, given rise to unnecessary difficulties in developing all previous expressions for the molecular gradients and Hessians of correlated wave functions.

In addition to eliminating the need for Lagrange multipliers and constraint equations, the exponential operator techniques used here have allowed us to bring all of the wave function cases (SCF, MCSCF, CI, MPPT, CC) very much under one umbrella. That is, we have been able to express the gradients and Hessians for all of the above wave functions in terms of a few fundamental response matrices. In this way, we have achieved at least a pedagogical goal; we allow the reader to more easily identify similarities and differences among the gradient and Hessian expressions of the various wave function cases.

In addition to using the above mentioned exponential unitary operator methods, we have chosen to make use of the second quantization notation.¹⁴ In this language the dependence of the electronic energy on the locations of the atomic orbital basis functions is isolated in the Hamiltonian. The wave function contains only the configuration expansion amplitude and molecular orbital expansion coefficient dependence.

In obtaining final working expressions for each gradient and Hessian case, we have made reasonable efforts to direct the reader to literature where explicit expressions for all contributions, in terms of one- and two-electron integrals and density matrix elements, can be found. We have also shown how¹⁷ most of the matrices which arise in our gradient and Hessian expressions can be recast in a manner which makes their computational evaluation equivalent to computing Hamiltonian average values and conventional Brillouin-type and wave function Hessian-type matrices which arise in, e.g., MCSCF optimization calculations. For these reasons, we feel that the expressions given in this paper represent computationally tractable working equations which efficiently describe how to evaluate gradients and Hessians.

It should be stressed that most of the computational

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effort needed to evaluate the molecular gradients and Hessians as described here is involved in setting up the first and second derivatives of the atomic-orbital basis integrals described in Sec. II A. These integral derivatives, which are used to evaluate the first H_1 and second H_2 order Hamiltonian responses, are not individually difficult to compute, but there are so many of them that efficient evaluation and file management procedures must be employed. Because the majority of the cost involved in any gradient or Hessian calculation arises in evaluating H_1 and H_2 , there should be very little differences among the noncorrelated and correlated wave function methods treated here (HF, CI, MCSCF, MPPT, CC) as far as *total* computational effort is concerned.

In Sec. II of this paper, we describe how to expand the electronic Hamiltonian to powers of the displacement of the nuclei (μ). We also show how to derive the response of HF or MCSCF orbitals and of MCSCF or CI configuration expansion coefficients in powers of μ . These Hamiltonian, orbital, and configuration amplitude responses are then used in Secs. III–VIII to generate expressions for the response of the electronic energy to nuclear displacement for each class of wave function. In Sec. IX we briefly compare our derived molecular gradients and Hessians with those already existing in the literature. The last section contains some concluding remarks.

In Appendix A we show how to generate derivatives of the symmetrically orthogonalized Gaussian atomic orbital basis which we assume are being used in the actual calculation. We also show how, under certain circumstances, these basis-set derivative contributions can be cast in a form which other workers have used in their molecular gradient work.

In Appendix B we show how most of the terms which arise in our gradient and Hessian formulas can be computationally evaluated in a form which requires effort of the same magnitude as that needed to compute the Hamiltonian average values, Generalized Brillouin, and wave function Hessian matrices arising in MCSCF optimization theory.

II. BASIS SET, WAVE FUNCTION, AND HAMILTONIAN DEPENDENCE ON NUCLEAR DISPLACEMENT

We begin by describing the notation and outlining the procedures used for deriving analytical expressions for the molecular gradients and Hessians appropriate to various approximate wave functions. We use the words *molecular* gradient and *molecular* Hessian to describe the linear (slope) and quadratic (curvature) terms in the expansion of the electronic energy of a molecule in powers of nuclear displacements. The adjective *molecular* is used to distinguish these terms from the gradients and Hessians which may arise in electronic wave function optimizations with respect to variations in molecular orbital and configuration expansion coefficients.

The total electronic energy of the molecular system has both an *explicit* dependence on the positions of the nuclei (via the Hamiltonian) and an *implicit* dependence

(via parameters characterizing the wave function). For most correlated wave functions, the dependence of the wave function on nuclear locations involves both molecular-orbital and configuration interaction-coefficient dependence. When a finite atomic orbital basis set is used to evaluate the total energy, the space spanned by the basis set also contains a dependence on the nuclear positions. All of these factors give rise to changes in the electronic energy when one or more atomic centers (nuclei) are displaced. Let us now turn to consider each such term in some detail. We first consider how the above mentioned basis set dependence may be expressed as a change in the finite-basis Hamiltonian.

A. Hamiltonian dependence on nuclear position

Let us denote the normalized atomic basis functions by $|\chi\rangle = \{\chi_i\}$. These atomic basis functions may be nonorthogonal and they may or may not be symmetry adapted. Their overlap matrix will be denoted

$$\langle \chi | \chi \rangle = S. \quad (1)$$

The atomic basis functions may be symmetrically orthogonalized¹⁸

$$|\phi\rangle = |\chi\rangle S^{-1/2} \quad (2)$$

to yield a new orthonormal atomic orbital (AO) basis $\{\phi_i\}$. Note that both the original atomic basis functions and the overlap matrix S depend on the location of the nuclei.

The electronic Hamiltonian H is conveniently expressed, in second quantization language,¹⁹ in terms of the symmetrically orthogonalized basis functions

$$H = \sum_{rs} h_{rs} a_r^\dagger a_s + \frac{1}{2} \sum_{\substack{rs \\ tu}} \langle \phi_r \phi_s | \phi_t \phi_u \rangle a_r^\dagger a_s^\dagger a_u a_t, \quad (3)$$

where

$$\langle \phi_r \phi_s | \phi_t \phi_u \rangle = \int \phi_r^*(1) \phi_s^*(2) \frac{1}{r_{12}} \phi_t(1) \phi_u(2) d\tau_1 d\tau_2, \quad (4)$$

$$h_{rs} = \langle \phi_r | h_1 | \phi_s \rangle, \quad (5)$$

and h_1 contains all of the usual one-electron operators

$$h_1 = -\frac{1}{2} \nabla^2 - \sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} + \frac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}. \quad (6)$$

Z_A denotes the charge and \mathbf{R}_A the position of nucleus A . We shall, for convenience, omit the vector arrows from now on when writing the vectors describing the locations of the nuclei and of the electrons. In Eq. (6), we have included the nuclear–nuclear interaction energies. However, we will, from now on, omit these terms as well as their contributions to the molecular gradient and Hessian which are straightforward to evaluate.

We have written the Hamiltonian out in terms of the symmetrically orthogonalized basis because this basis allows the annihilation (a_s) and creation (a_s^\dagger) operators to satisfy the usual anticommutation relations (with no overlap). If we had chosen to express the Hamiltonian in terms of the original (nonorthogonal) atomic basis the anticommutation relations would contain an overlap matrix, which would introduce an additional and unnecessary complication into the derivations to follow. In Appendix A, we discuss in more detail consequences of

using creation and annihilation operators that refer to a nonorthogonal basis and the simplifications that occur when an orthonormal basis is used.

The above Hamiltonian depends on the nuclear positions ($\mathbf{R} \equiv R_1 \cdots R_N$) through the second term in Eq. (6) and through the fact that the basis functions appearing in the integrals in Eqs. (4) and (5) sit on the nuclear centers. To explore how H changes as the nuclei are moved, let us consider the nuclear displacement

$$\mathbf{R}^0 \rightarrow \mathbf{R}^0 + \boldsymbol{\mu}, \quad (7)$$

where $\boldsymbol{\mu}$ is a row vector

$$\boldsymbol{\mu} = (\mu_A^x \mu_A^y \mu_A^z \mu_B^x \mu_B^y \cdots) \quad (8)$$

containing the (small) magnitudes of the displacements in the X , Y , and Z components of all nuclei A, B, \dots . The Hamiltonian at the displaced coordinates may be expressed in terms of the Hamiltonian at the undisplaced coordinate system plus terms that are linear, quadratic, cubic, \dots , etc. in the nuclear displacements

$$H(\mathbf{R}^0 + \boldsymbol{\mu}) = H_0 + \boldsymbol{\mu} \mathbf{H}_1 + \frac{1}{2} \boldsymbol{\mu} \mathbf{H}_2 \boldsymbol{\mu} + \cdots \quad (9)$$

To derive explicit expressions for the linear (\mathbf{H}_1) and quadratic (\mathbf{H}_2) perturbation operators, we need to examine how each component in Eq. (3) can be expanded in powers of $\boldsymbol{\mu}$.

The electron-nuclear interaction in Eq. (6) depends explicitly on the nuclear coordinates. Carrying out a Taylor series expansion of this potential

$$\begin{aligned} |r - R_A|^{-1} &= |r - R_A^0 - \mu_A|^{-1} \\ &= |r - R_A^0|^{-1} + \mu_A (\nabla_A |r - R_A^0|^{-1}) \\ &\quad + \frac{1}{2} \mu_A (\nabla_A \nabla_A |r - R_A^0|) \mu_A + \cdots \end{aligned} \quad (10)$$

we display the order-by-order dependence of this potential on the nuclear displacements $\boldsymbol{\mu}$. In Eq. (10) terms are explicitly written out through second order since these are the only terms which are required in the following analysis.

The symmetrically orthogonalized functions, which in general are combinations of basis functions centered on all nuclei, also depend on the nuclear coordinates. This dependence may be clearly described through carrying out a Taylor series expansion of $\phi_i(r - \mathbf{R}^0 - \boldsymbol{\mu})$ around $\phi_i(r - \mathbf{R}^0)$. We obtain

$$\begin{aligned} \phi_i(r - \mathbf{R}^0 - \boldsymbol{\mu}) &= \phi_i(r - \mathbf{R}^0) + \boldsymbol{\mu} [\nabla \phi_i(r - \mathbf{R}^0)] \\ &\quad + \frac{1}{2} \boldsymbol{\mu} [\nabla \nabla \phi_i(r - \mathbf{R}^0)] \boldsymbol{\mu} + \cdots, \end{aligned} \quad (11)$$

where again terms are written out explicitly only through second order in the nuclear displacement. The vector ∇ contains derivatives with respect to all coordinates of

all nuclei: $\nabla = \{\nabla_A, \nabla_B, \dots\}$.

The linear and quadratic terms in Eq. (11) may straightforwardly be evaluated. Using Eq. (2) we rewrite the linear term in Eq. (11) as

$$\begin{aligned} \nabla \phi_j(r - \mathbf{R}^0) &= \nabla \sum_i \chi_i(r - \mathbf{R}^0)_i S(\mathbf{R}^0)^{-1/2}_{ij} \\ &= \sum_i [(\nabla \chi_i(r - \mathbf{R}^0))_i S(\mathbf{R}^0)^{-1/2}_{ij} \\ &\quad + \chi_i(r - \mathbf{R}^0)_i \nabla S(\mathbf{R}^0)^{-1/2}_{ij}] . \end{aligned} \quad (12)$$

In finite-basis-set calculations using Gaussian basis functions centered on the individual atoms, $\nabla \chi_i(r - R_A)$ can be expressed as a sum of two new basis functions, one having an orbital angular momentum quantum number one higher than $\chi_i(r - R_A)$ and the other having an orbital angular momentum one lower (see Appendix A). The second term in Eq. (12) multiplies the original basis function by the gradient of the $S^{-1/2}$ matrix. In Appendix A we derive the explicit expression for $\nabla \phi_i(r - \mathbf{R}^0)$ and for the second term $\nabla \nabla \phi_i(r - \mathbf{R}^0)$ in the case where the $\chi_j(r - R_A^0)$ refers to a set of Gaussian basis functions. We also give there the explicit formula for $\nabla S^{-1/2}$ and $\nabla \nabla S^{-1/2}$.

Using Eqs. (10) and (11), we may now identify all of the changes in the electronic Hamiltonian through second order in the nuclear displacement $\boldsymbol{\mu}$. The linear term in Eq. (9) becomes

$$\begin{aligned} \mathbf{H}_1 &= \sum_{rs} \nabla (\langle \phi_r | h_1 | \phi_s \rangle) a_r^\dagger a_s \\ &\quad + \frac{1}{2} \sum_{rs} \nabla \nabla (\langle \phi_r \phi_s | \phi_t \phi_u \rangle) a_r^\dagger a_s^\dagger a_u a_t, \end{aligned} \quad (13)$$

where

$$\begin{aligned} \nabla_A (\langle \phi_r | h_1 | \phi_s \rangle) &= -Z_A \langle \phi_r | (\nabla_A |r - R_A^0|^{-1}) | \phi_s \rangle \\ &\quad + \langle (\nabla_A \phi_r) | h_1 | \phi_s \rangle + \langle \phi_r | h_1 | (\nabla_A \phi_s) \rangle \end{aligned} \quad (14)$$

and

$$\begin{aligned} \nabla_A (\langle \phi_r \phi_s | \phi_t \phi_u \rangle) &= \langle (\nabla_A \phi_r) \phi_s | \phi_t \phi_u \rangle + \langle \phi_r (\nabla_A \phi_s) | \phi_t \phi_u \rangle \\ &\quad + \langle \phi_r \phi_s | (\nabla_A \phi_t) \phi_u \rangle + \langle \phi_r \phi_s | \phi_t (\nabla_A \phi_u) \rangle. \end{aligned} \quad (15)$$

The quadratic term may similarly be identified as

$$\begin{aligned} \mathbf{H}_2 &= \sum_{rs} \nabla \nabla (\langle \phi_r | h_1 | \phi_s \rangle) a_r^\dagger a_s \\ &\quad + \frac{1}{2} \sum_{rs} \nabla \nabla (\langle \phi_r \phi_s | \phi_t \phi_u \rangle) a_r^\dagger a_s^\dagger a_u a_t, \end{aligned} \quad (16)$$

where

$$\begin{aligned} \nabla \nabla (\langle \phi_r | h_1 | \phi_s \rangle) &= \sum_A -Z_A \langle \phi_r | (\nabla \nabla |r - R_A^0|^{-1}) | \phi_s \rangle + \langle \phi_r | h_1 | (\nabla \nabla \phi_s) \rangle + \langle (\nabla \nabla \phi_r) | h_1 | \phi_s \rangle \\ &\quad - 2 \sum_A Z_A \langle (\nabla \phi_r) | (\nabla |r - R_A^0|^{-1}) | \phi_s \rangle + 2 \langle (\nabla \phi_r) | h_1 | (\nabla \phi_s) \rangle - 2 \sum_A Z_A \langle \phi_r | (\nabla |r - R_A^0|^{-1}) | (\nabla \phi_s) \rangle \end{aligned} \quad (17)$$

and

$$\begin{aligned} \nabla \nabla (\langle \phi_r \phi_s | \phi_t \phi_u \rangle) &= \langle (\nabla \nabla \phi_r) \phi_s | \phi_t \phi_u \rangle + \langle \phi_r (\nabla \nabla \phi_s) | \phi_t \phi_u \rangle + \langle \phi_r \phi_s | (\nabla \nabla \phi_t) \phi_u \rangle + \langle \phi_r \phi_s | \phi_t (\nabla \nabla \phi_u) \rangle \\ &\quad + 2 \langle (\nabla \phi_r) \phi_s | (\nabla \phi_t) \phi_u \rangle + 2 \langle (\nabla \phi_r) \phi_s | \phi_t (\nabla \phi_u) \rangle + 2 \langle \phi_r (\nabla \phi_s) | (\nabla \phi_t) \phi_u \rangle + 2 \langle \phi_r (\nabla \phi_s) | \phi_t (\nabla \phi_u) \rangle. \end{aligned} \quad (18)$$

The first term in Eq. (14) is the Hellmann–Feynman force. The residual terms in H_1 originate from the basis set dependence. The first term of H_2 in Eq. (17) describes the electric field gradient induced by the movement of the nuclei. The residual part of H_2 contains basis-set-dependence terms. In Appendix A we show that the contributions to the molecular gradient and Hessian due to basis-set dependence vanish as the AO basis approaches completeness.

Having now seen how H can be decomposed into terms linear and quadratic in the nuclear displacements, we move on to examine how the components of the electronic wave function vary when the nuclei move. When carrying out a molecular gradient or Hessian calculation, it is most convenient to work in the basis defined by the set of orthonormal molecular orbitals (MO's) appropriate to that calculation (e.g., a set of MCSCF or HF orbitals). The transformation of H_0 , H_1 , and H_2 to this basis may be carried out straightforwardly since this MO basis is obtained just by carrying out a unitary transformation of the symmetrically orthogonalized AO basis functions defined above. However, it still remains to determine how these unitary transformation coefficients and the wave function's configuration expansion coefficients vary with μ .

B. Orbital and state responses

In this section we describe the dependence of the electronic wave function on μ for specific commonly employed choices of correlated wave functions. Because the wave functions are assumed to be expressed in terms of configurations constructed from a set of multiconfiguration self-consistent field (MCSCF) or Hartree–Fock (HF) orbitals, the linear and quadratic responses of these orbitals must be determined. We also need expressions for the linear and quadratic responses of the configuration amplitudes of the wave function. By first examining the response of an MCSCF state to a nuclear displacement, we achieve information which also covers one other case. In the limit of a single-configuration wave function, the resultant expressions can be used to describe the Hartree–Fock orbital response. Later in this paper, we also consider how molecular gradients and Hessians may be evaluated in the CI method in Møller–Plesset perturbation theory and in the coupled cluster method. In Møller–Plesset perturbation theory (MPPT), analytical expressions for the molecular gradients and Hessians may be derived from knowledge only of how the HF orbitals respond to nuclear displacement. This is so because the MPPT correlation coefficients are analytically expressed, in each order, in terms of the HF orbitals and orbital energies. Coupled cluster (CC) evaluation of molecular gradients and Hessians requires knowledge of how the orbitals (e.g., HF) respond to a nuclear displacement. However, the coupled cluster amplitudes are, in contrast to the MPPT amplitudes (i.e., correlation coefficients), not analytically expressed in terms of orbitals and orbital energies but are determined through a set of coupled-cluster equations. The coupled-cluster amplitudes therefore implicitly depend on nuclear position and

this dependency has to be addressed. We postpone the actual derivation of the linear and quadratic response of the CC amplitudes until later. Here we consider only the evaluation of the linear and quadratic responses of an MCSCF state to nuclear displacement.

1. Unitary transformation of the MCSCF state

Variations in the molecular orbitals and in the configuration amplitudes of a MCSCF state $|0\rangle$ may be defined^{14,15} in terms of a set of rotational parameters that describe how the MCSCF state is rotated simultaneously in the orbital and configuration or state spaces. The MCSCF state $|0\rangle$ may be regarded as a member of the set of states $\{|j\rangle\} = \{|0\rangle, |k\rangle\}$,

$$|0\rangle = \sum_g |\Phi_g\rangle C_{g0}, \quad (19)$$

$$|k\rangle = \sum_g |\Phi_g\rangle C_{gk}, \quad (20)$$

where the coefficient matrix C is unitary. The configuration state functions $|\Phi_g\rangle$ may be expressed as simple linear combinations of determinants $\{|\Phi_f^D\rangle\}$,

$$|\Phi_f^D\rangle = \prod_{r \in f} a_r^\dagger |\text{vac}\rangle, \quad (21)$$

where $\prod_{r \in f} a_r^\dagger$ refers to an ordered product of creation operators which relate to the set of orthonormal molecular orbitals occupied in $|\Phi_f^D\rangle$. For the sake of simplicity, we assume in the following development that all of the above orbitals and states are real.

A detailed discussion of how a simultaneous unitary transformation (rotation) of the orbitals and state expansion coefficients of the MCSCF function may be carried out is given in Refs. 14 and 15. Below we briefly summarize the essential results of these references stressing the aspects which pertain to the present development.

An arbitrary unitary transformation among the states $\{|j\rangle\}$ may be described in terms of the exponential operator

$$\exp(i\hat{S})|j\rangle = \sum_k |k\rangle [\exp(-S)]_{kj}, \quad (22)$$

where

$$\hat{S} = i \sum_{k \neq 0} S_{k0} (|k\rangle\langle 0| - |0\rangle\langle k|) \quad (23)$$

and $\exp(-S)$ is a unitary matrix because S is a real antisymmetric matrix with nonvanishing elements S_{k0} and $S_{0k} (= -S_{k0})$ and zero elements elsewhere.

A unitary transformation of the creation operators corresponding to the MCSCF orbitals may similarly be parametrized as

$$\tilde{a}_r^\dagger = \exp(i\hat{\kappa}) a_r^\dagger \exp(-i\hat{\kappa}) \quad (24)$$

with

$$\hat{\kappa} = i \sum_{rs} \kappa_{rs} (a_r^\dagger a_s - a_s^\dagger a_r). \quad (25)$$

From Eqs. (24) and (25) we can show (see Ref. 14) that

$$\bar{a}_r^\dagger = \sum_s a_s^\dagger [\exp(-\kappa)]_{sr}, \quad (26)$$

where $\exp(-\kappa)$ is a unitary matrix because κ is an anti-symmetric matrix with elements κ_{rs} and $\kappa_{sr} (= -\kappa_{rs})$.

A unitary transformation of the MCSCF state $|0\rangle$ which simultaneously gives a unitary transformation in the orbital and in the configurational spaces may be therefore described as

$$|\bar{0}\rangle = \exp(i\hat{\kappa}) \exp(i\hat{S}) |0\rangle. \quad (27)$$

The other states spanned by the multiconfiguration space

$$|\bar{k}\rangle = \exp(i\hat{\kappa}) \exp(i\hat{S}) |k\rangle \quad (28)$$

can be shown, together with $|\bar{0}\rangle$, to form an orthonormal set given that the unrotated states $|0\rangle$ and $|k\rangle$ do so. Through specifying the set of parameters κ and S we may generate an arbitrary state $|\bar{0}\rangle$ and assure that this state together with the states $\{|\bar{k}\rangle\}$ form an orthonormal set of states $\{|\bar{j}\rangle\}$. The set of rotational parameters $(\kappa, S) = (0, 0)$ represents, of course, the untransformed states $\{|0\rangle, |k\rangle\}$.

The set of functions $(a_r^\dagger a_s - a_s^\dagger a_r)|0\rangle$, $(|k\rangle\langle 0| - |0\rangle\langle k|)|0\rangle$, which arises when powers of $\hat{\kappa}$ or \hat{S} act on $|0\rangle$, may be linearly dependent. Furthermore, some variables κ_{rs} may be redundant when used to carry out an orbital optimization. Such linear dependencies and redundant operators have to be eliminated from the $\hat{\kappa}$ and \hat{S} operator spaces before we can describe simultaneous variations in the orbitals and configuration space amplitudes. The elimination of such linear dependencies and redundant operators is discussed in detail in Refs. 14 and 15 and is important because redundant operators may result in zero Hessian eigenvalues. We will, from now on, assume that such problems have been eliminated in determining $|0\rangle$ and, therefore, need not be dealt with further here.

2. Variation of the total MCSCF energy

To lead up to examining how the MCSCF wave function changes when the nuclei are displaced by μ , we look at the total energy of the MCSCF wave function in the presence of the potential field due to the nuclear displacement described in Eq. (9). The wave function $|\bar{0}\rangle$ dependence on the nuclear displacement is then determined by requiring that the energy at the displaced geometry has to be stationary. The total electronic energy as a function of nuclear displacement can be written as

$$E(\mu) = \langle \bar{0} | H(\mathbf{R}^0 + \mu) | \bar{0} \rangle \\ = \langle \bar{0} | H_0 + \mu \mathbf{H}_1 + \frac{1}{2} \mu \mathbf{H}_2 \mu | \bar{0} \rangle. \quad (29)$$

Once the dependence of $|\bar{0}\rangle$ on μ has been determined, the total energy may be written as a power series expansion in μ ,

$$E(\mu) = E(0) + \mu \mathbf{E}_1 + \frac{1}{2} \mu \mathbf{E}_2 \mu + \dots, \quad (30)$$

where \mathbf{E}_1 is identified as the molecular gradient and \mathbf{E}_2 as the molecular Hessian. The task therefore is to first determine the dependence of $|\bar{0}\rangle$ on μ and subsequently to use the power series expansion of $E(\mu)$ in μ to then identify the gradient and Hessian matrices.

Let us therefore begin by determining the response of the MCSCF state to nuclear displacement. Using Eqs. (24) and (27) we write the MCSCF energy as

$$E(\kappa, S, \mu) = \langle \bar{0} | H_0 + \mu \mathbf{H}_1 + \frac{1}{2} \mu \mathbf{H}_2 \mu | \bar{0} \rangle \\ = \langle 0 | \exp(-i\hat{S}) \exp(-i\hat{\kappa}) (H_0 + \mu \mathbf{H}_1 + \frac{1}{2} \mu \mathbf{H}_2 \mu) \\ \times \exp(i\hat{\kappa}) \exp(i\hat{S}) | 0 \rangle, \quad (31)$$

where the parameters S and κ depend implicitly on μ in a manner which is determined below. The total energy may be expanded around $(\kappa, S) = (0, 0)$ (the parameter set characterizing the MCSCF state belonging to undisplaced nuclei) as

$$E(\kappa, S, \mu) = \langle 0 | H(\mu) | 0 \rangle - i \langle 0 | [\hat{S} + \hat{\kappa}, H(\mu)] | 0 \rangle - \frac{1}{2} \langle 0 | [\hat{S}, [\hat{S}, H(\mu)]] | 0 \rangle - \frac{1}{2} \langle 0 | [\hat{\kappa}, [\hat{\kappa}, H(\mu)]] | 0 \rangle - \langle 0 | [\hat{S}, [\hat{\kappa}, H(\mu)]] | 0 \rangle \\ + \frac{i}{6} \langle 0 | [\hat{\kappa}, [\hat{\kappa}, [\hat{\kappa}, H(\mu)]]] | 0 \rangle + \frac{i}{2} \langle 0 | [\hat{S}, [\hat{S}, [\hat{\kappa}, H(\mu)]]] | 0 \rangle + \frac{i}{6} \langle 0 | [\hat{S}, [\hat{S}, [\hat{S}, H(\mu)]]] | 0 \rangle + \frac{i}{2} \langle 0 | [\hat{S}, [\hat{\kappa}, [\hat{\kappa}, H(\mu)]]] | 0 \rangle + \dots \quad (32)$$

All terms through third order in $\hat{\kappa}$ and \hat{S} are written out explicitly in Eq. (32). In order to obtain matrix elements which have permutational symmetries with respect to their subscripts, we can define, as in Ref. 17, the n -tuple symmetric commutator for the operators D_1, D_2, \dots, D_n as

$$[D_1, D_2, \dots, D_n, H] = \frac{1}{n!} P(1, 2, \dots, n) [D_1, [D_2, \dots [D_n, H] \dots]], \quad (33)$$

where $P(1, 2, \dots, n)$ is a permutation operator which contains the $n!$ permutations of the indices $1, 2, \dots, n$. Using this definition allows us to rewrite Eq. (32) as

$$E(\kappa, S, \mu) = \langle 0 | H(\mu) | 0 \rangle - i \langle 0 | [\hat{S} + \hat{\kappa}, H(\mu)] | 0 \rangle - \frac{1}{2} \langle 0 | [\hat{S}, \hat{S}, H(\mu)] | 0 \rangle - \frac{1}{2} \langle 0 | [\hat{\kappa}, \hat{\kappa}, H(\mu)] | 0 \rangle - \langle 0 | [\hat{S}, [\hat{\kappa}, H(\mu)]] | 0 \rangle \\ + \frac{i}{6} \langle 0 | [\hat{S}, \hat{S}, \hat{S}, H(\mu)] | 0 \rangle + \frac{i}{6} \langle 0 | [\hat{\kappa}, \hat{\kappa}, \hat{\kappa}, H(\mu)] | 0 \rangle + \frac{i}{2} \langle 0 | [\hat{S}, \hat{S}, [\hat{\kappa}, H(\mu)]] | 0 \rangle + \frac{i}{2} \langle 0 | [\hat{S}, [\hat{\kappa}, \hat{\kappa}, H(\mu)]] | 0 \rangle + \dots, \quad (34)$$

where we have used the fact that each of the operators $\hat{\kappa}$ and \hat{S} commute among one another.

Introducing a notation in which the variational parameters $\{\kappa_{rs}\}$ and $\{S_{n0}\}$ and the excitation operators

$$\mathbf{Q}^\dagger = \{a_r^\dagger a_s\}, \quad r > s; \quad \mathbf{R}^\dagger = \{|n\rangle\langle 0|\} \quad (35)$$

both are arranged as column vectors

$$\lambda = \begin{pmatrix} \kappa \\ S \end{pmatrix}, \quad (36)$$

$$T = \begin{pmatrix} Q^\dagger - Q \\ R^\dagger - R \end{pmatrix}, \quad (37)$$

allows us to write the total energy in Eq. (34) as (Einstein summation convention is used with respect to the subscripts i, j, k)

$$\begin{aligned} E(\lambda, \mu) = & E(0) + \mu \langle 0 | \mathbf{H}_1 | 0 \rangle + \frac{1}{2} \mu \langle 0 | \mathbf{H}_2 | 0 \rangle \mu + \mu (\mathbf{F}_i^{(1)} \lambda_i) \\ & + \frac{1}{2} \mu (\mathbf{F}_i^{(2)} \lambda_i) \mu + \frac{1}{2} G_{ij}^{(0)} \lambda_i \lambda_j + \frac{1}{2} \mu (\mathbf{G}_{ij}^{(1)} \lambda_i \lambda_j) \\ & + \frac{1}{6} K_{ijk}^{(0)} \lambda_i \lambda_j \lambda_k + \dots, \end{aligned} \quad (38)$$

where the generalizations of the MCSCF Generalized Brillouin matrix elements are defined as

$$F^{(i)} = \langle 0 | [T, H_i] | 0 \rangle, \quad i = 0, 1, 2, \quad (39)$$

the generalizations of the MCSCF Hessian matrix elements are

$$G^{(i)} = \langle 0 | [T, T, H_i] | 0 \rangle, \quad i = 0, 1, 2 \quad (40)$$

and the cubic derivative matrix elements are

$$K^{(i)} = \langle 0 | [T, T, T, H_i] | 0 \rangle, \quad i = 0, 1, 2. \quad (41)$$

The H_i are the Hamiltonian contributions H_0 , \mathbf{H}_1 , and \mathbf{H}_2 employed in Eqs. (13)–(18).

The matrices defined in Eqs. (39)–(41) form the fundamental units in terms of which most of the molecular gradients and Hessians described here are expressed. The explicit evaluation of $F^{(i)}$ and $G^{(i)}$ is given in terms of one- and two-electron integrals (for the $i=0$ cases) or their derivatives (for $i=1, 2$) over the MCSCF orbitals and density matrices of $|0\rangle$ in Eqs. (2.38)–(2.44) of Ref. 14. These expressions are also valid for computing matrices analogous to those of Eqs. (39) and (40) but in which $|0\rangle$ is not an MCSCF function and the orbitals are not MCSCF orbitals. For example, when $|0\rangle$ is a CI wave function, these equations may still be used if the density matrices are simply replaced by the CI density matrices. As will be shown later in this paper, construction of the three-indexed $K^{(i)}$ matrix is impractical and unnecessary. Devices can be used¹⁷ (see Appendix B) to reduce the terms in which $K^{(0)}$ appears to terms which require no more effort than the evaluation of the $G^{(0)}$ matrices.

The term due to $F^{(0)}$ does not occur in Eq. (38) due to the generalized Brillouin theorem (GBT). The λ parameters have no zeroth order μ dependence [see Eqs. (44) and (45)] since it is assumed that $(\kappa, S) = (0, 0)$ properly describes the $\mu = 0$ case. All terms in the n -tuple commutators in Eqs. (40) and (41) which couple the configuration and orbital space are defined such that the Hamiltonian first operates on the orbital space excitation operators and then on the configuration space operators. The matrices $G_{ki}^{(i)}$, $K_{lmn}^{(i)}$ are symmetric in indices k, l ,

and m because of the use of the symmetrized commutators introduced via Eq. (33). In Eq. (38) all terms that depend on μ through second order have been written out as will be more clear from the discussion that follows in the next subsection.

3. Linear and quadratic response of the MCSCF state

The explicit dependence of the rotational parameters on the nuclear displacement is determined from the requirement that the above total energy has to be stationary in the field described by the nuclear displacement. Taking the derivative of Eq. (38) with respect to λ equal to zero, we obtain

$$\mu \mathbf{F}_i^{(1)} + \frac{1}{2} \mu \mathbf{F}_i^{(2)} \mu + G_{ij}^{(0)} \lambda_j + \mu (\mathbf{G}_{ij}^{(1)} \lambda_j) + \frac{1}{2} K_{ijk}^{(0)} \lambda_j \lambda_k + \dots = 0. \quad (42)$$

Equation (42) can be solved order-by-order in the nuclear displacement. To do so, we write the rotational parameters as power series in μ ,

$$\lambda = \lambda^{(0)} + \mu \lambda^{(1)} + \frac{1}{2} \mu \lambda^{(2)} \mu + \dots \quad (43)$$

and rearrange Eq. (42) as

$$\begin{aligned} \lambda_i = & -\mu (\mathbf{G}_{ij}^{(0)-1} \mathbf{F}_j^{(1)}) - \frac{1}{2} \mu (\mathbf{G}_{ij}^{(0)-1} \mathbf{F}_j^{(2)}) \mu \\ & - \mu (\mathbf{G}_{ij}^{(0)-1} \mathbf{G}_{jk}^{(1)} \lambda_k) - \frac{1}{2} \mu (\mathbf{G}_{ij}^{(0)-1} K_{jkl} \lambda_k \lambda_l). \end{aligned} \quad (44)$$

From Eq. (44) it should be clear that

$$\lambda^{(0)} = 0. \quad (45)$$

The terms in Eq. (44) which are linear in μ may be easily identified as

$$\lambda_i^{(1)} = -G_{ij}^{(0)-1} \mathbf{F}_j^{(1)}. \quad (46)$$

Equation (46) describes the linear response of the MCSCF wave function to the nuclear displacement. Inserting Eq. (46) into the right-hand side of Eq. (44) and collecting terms through second order in μ gives

$$\begin{aligned} \lambda_i^{(2)} = & -G_{ij}^{(0)-1} \mathbf{F}_j^{(2)} \\ & - 2G_{ij}^{(0)-1} G_{jk}^{(1)} \lambda_k^{(1)} - G_{ij}^{(0)-1} K_{jkl}^{(0)} \lambda_k^{(1)} \lambda_l^{(1)}, \end{aligned} \quad (47)$$

the quadratic response of the MCSCF wave function to nuclear displacement. These expressions for $\lambda^{(1)}$ and $\lambda^{(2)}$ play important roles in all subsequent developments. Their components $\kappa^{(1)}$, $\mathbf{S}^{(1)}$, $\kappa^{(2)}$, $\mathbf{S}^{(2)}$ are the fundamental units in terms of which orbitals and configuration responses are given.

Only the matrix elements of $F^{(i)}$, $i=1, 2$; $G^{(i)}$, $i=0, 1$; and $K^{(i)}$, $i=0$ enter into the above linear and quadratic response equations. The labor involved in computing the $F^{(i)}$ and $G^{(i)}$ is no more than that arising in MCSCF GBT and MCSCF Hessian computations described in Refs. 14 and 15. The evaluation of the three-indexed matrix $K^{(0)}$ is rather cumbersome, especially when large dimensions are considered. However, the two-indexed product $K_{ijk}^{(0)} \lambda_k^{(1)}$ may be reexpressed¹⁷ relatively easy in a form which has the structure of a modified Hessian matrix in which modified one- and two-electron integrals and density matrices are used. In Appendix B, we demonstrate how to evaluate $K_{ijk}^{(0)} \lambda_k^{(1)}$ as such a modified Hessian matrix, and we show how the one-indexed product $K_{ijk}^{(0)} \lambda_j^{(1)} \lambda_k^{(1)}$ may alternatively be recast as a modified GBT matrix element.

4. CI response

We now derive expressions for the responses of the configuration amplitudes of a CI state assuming that MCSCF orbitals are used to construct the configuration list used in the CI calculation. At a displaced geometry $\mathbf{R}^0 + \boldsymbol{\mu}$, the CI state $|\tilde{\text{CI}}\rangle$ may be expressed in terms of a unitary transformation of the CI state $|\text{CI}\rangle$ at the undisplaced geometry because all basis-set effects are contained in the Hamiltonian in Eq. (9):

$$|\tilde{\text{CI}}\rangle = \exp(i^{\text{MC}}\hat{\kappa}) \exp(i^{\text{CI}}\hat{S}) |\text{CI}\rangle, \quad (48a)$$

$i^{\text{MC}}\hat{\kappa}$ contains the orbital excitation operators of the MCSCF calculation used to determine the set of MCSCF orbitals, and $i^{\text{CI}}\hat{S}$ contains the state transfer operators involving the state $|\text{CI}\rangle$ and its orthogonal complement

$$\begin{aligned} E(^{\text{CI}}S, \boldsymbol{\mu}) &= \langle \text{CI} | \exp(-i^{\text{CI}}\hat{S}) \exp(-i^{\text{MC}}\hat{\kappa}) H(\boldsymbol{\mu}) \exp(i^{\text{MC}}\hat{\kappa}) \exp(i^{\text{CI}}\hat{S}) | \text{CI} \rangle \\ &= \langle \text{CI} | \exp(-i^{\text{CI}}\hat{S}) \bar{H}(\boldsymbol{\mu}) \exp(i^{\text{CI}}\hat{S}) | \text{CI} \rangle \\ &= \langle \text{CI} | \bar{H} | \text{CI} \rangle - i \langle \text{CI} | [i^{\text{CI}}\hat{S}, \bar{H}(\boldsymbol{\mu})] | \text{CI} \rangle - \frac{1}{2} \langle \text{CI} | [i^{\text{CI}}\hat{S}, i^{\text{CI}}\hat{S}, \bar{H}(\boldsymbol{\mu})] | \text{CI} \rangle + \frac{i}{6} \langle \text{CI} | [i^{\text{CI}}\hat{S}, i^{\text{CI}}\hat{S}, i^{\text{CI}}\hat{S}, \bar{H}(\boldsymbol{\mu})] | \text{CI} \rangle + \dots, \end{aligned} \quad (48b)$$

where we have introduced the shorthand notation

$$\bar{H}(\boldsymbol{\mu}) = \exp(-i^{\text{MC}}\hat{\kappa}) H(\boldsymbol{\mu}) \exp(i^{\text{MC}}\hat{\kappa}). \quad (48c)$$

The total energy at a displaced geometry thus contains an explicit dependence on $\boldsymbol{\mu}$ in $\bar{H}(\boldsymbol{\mu})$ and an implicit dependence on $\boldsymbol{\mu}$ in the parameters $^{\text{CI}}S$. The implicit dependence of $^{\text{CI}}S$ on $\boldsymbol{\mu}$ may be determined by requiring that the total CI energy be stationary in the presence of the nuclear displacement. Setting the derivative of Eq. (48b) with respect to $^{\text{CI}}S$ equal to zero we obtain

$$\begin{aligned} \langle \text{CI} | [R^\dagger - R, \bar{H}(\boldsymbol{\mu})] | \text{CI} \rangle - i \langle \text{CI} | [R^\dagger - R, i^{\text{CI}}\hat{S}, \bar{H}(\boldsymbol{\mu})] | \text{CI} \rangle \\ - \frac{1}{2} \langle \text{CI} | [R^\dagger - R, i^{\text{CI}}\hat{S}, i^{\text{CI}}\hat{S}, \bar{H}(\boldsymbol{\mu})] | \text{CI} \rangle + \dots = 0. \end{aligned} \quad (48d)$$

Equation (48d) may be solved through each power in $\boldsymbol{\mu}$. To do so, we first write out the $\boldsymbol{\mu}$ dependence of $\bar{H}(\boldsymbol{\mu})$ in Eq. (48c) through each power in $\boldsymbol{\mu}$. Expanding the exponential operators in Eq. (48c) and introducing Eq. (9) then given

$$\bar{H}(\boldsymbol{\mu}) = \bar{H}_0 + \boldsymbol{\mu} \bar{H}_1 + \frac{1}{2} \boldsymbol{\mu} \bar{H}_2 \boldsymbol{\mu} + \dots, \quad (49a)$$

where

$$\bar{H}_0 = H_0, \quad (49b)$$

$$\bar{H}_1 = H_1 - i [i^{\text{MC}}\hat{\kappa}^{(1)}, H_0], \quad (49c)$$

$$\begin{aligned} \bar{H}_2 = H_2 - i2[i^{\text{MC}}\hat{\kappa}^{(1)}, H_1] - i2[i^{\text{MC}}\hat{\kappa}^{(2)}, H_0] \\ - [i^{\text{MC}}\hat{\kappa}^{(1)}, [i^{\text{MC}}\hat{\kappa}^{(1)}, H_0]], \end{aligned} \quad (49d)$$

where $i^{\text{MC}}\hat{\kappa}^{(1)}$ denotes the orbital excitation operator of Eq. (25) containing the MCSCF orbital response parameters of Eq. (46). We note that \bar{H}_1 and \bar{H}_2 may be determined simply by carrying out one-index Hamiltonian transformations on H_1 and H_2 as described in Appendix B.

Carrying out a power series expansion of the $^{\text{CI}}S$ parameters

$$^{\text{CI}}S = ^{\text{CI}}S^{(0)} + \boldsymbol{\mu} ^{\text{CI}}S^{(1)} + \frac{1}{2} \boldsymbol{\mu} ^{\text{CI}}S^{(2)} \boldsymbol{\mu} + \dots \quad (49e)$$

and collecting terms in Eq. (42d) through individual powers in $\boldsymbol{\mu}$ gives the response equations

space. Equation (48a) shows how a simultaneous unitary transformation can be carried out in the MCSCF orbital and configuration spaces of the CI calculation.

$\exp(i^{\text{MC}}\hat{\kappa})$ describes how the MCSCF orbitals at the undisplaced geometry relate to those of the displaced geometry. This dependence is determined entirely by the MCSCF calculation carried out *prior* to the CI calculation. Through second order in $\boldsymbol{\mu}$ the responses of the parameters $^{\text{MC}}\kappa$ are given as the orbital parts of Eqs. (44)–(47).

The responses of the $^{\text{CI}}S$ parameters to a nuclear displacement $\boldsymbol{\mu}$ may be determined in a way very similar to that used to determine the responses of the parameters λ of the MCSCF calculation. At the displaced geometry, the total CI energy may be written as

$$^{\text{CI}}S^{(0)} = 0, \quad (50a)$$

$$^{\text{CI}}S_i^{(1)} = - {}^{\text{CI}}\bar{G}_{ij}^{(0)-1} {}^{\text{CI}}\bar{F}_j^{(1)}, \quad (50b)$$

$$\begin{aligned} ^{\text{CI}}S_i^{(2)} = & - {}^{\text{CI}}\bar{G}_{ij}^{(0)-1} {}^{\text{CI}}\bar{F}_j^{(2)} - 2 {}^{\text{CI}}\bar{G}_{ij}^{(0)-1} {}^{\text{CI}}\bar{G}_{jk}^{(1)} {}^{\text{CI}}S_k^{(1)} \\ & - {}^{\text{CI}}\bar{G}_{ij}^{(0)-1} {}^{\text{CI}}K_{jkl}^{(0)} {}^{\text{CI}}S_k^{(1)} {}^{\text{CI}}S_l^{(1)}, \end{aligned} \quad (50c)$$

where the F , G , and K matrices are defined by Eqs. (39)–(41). The index CI on F , G , and K denotes that the orbital parts of these matrices are neglected and the $-$ denotes that the Hamiltonians entering these matrices are those of Eqs. (49). The responses of the configuration amplitudes of a CI state thus are given explicitly through second order in Eq. (50).

Explicit expressions for the linear and quadratic responses of the MCSCF, Hartree–Fock and CI wave functions have thus been derived. In the following sections, we use these results to derive analytical expressions for molecular gradients and Hessians as evaluated in finite-basis-set calculations within several more commonly used wave function approximations. All of these wave function cases (HF, CI, MCSCF, MPPT, and CC) are outlined in pedagogical style in Chaps. II–IV of Ref. 14.

III. GRADIENT AND HESSIAN FOR A HARTREE-FOCK WAVE FUNCTION

A. The electronic energy

We have chosen to describe the Hartree–Fock case first since it is very simple yet it illustrates most of the points used in the subsequent derivations and it defines much of the notation and format for the other developments. Let us assume that a Hartree–Fock calculation has been carried out (and converged) at a geometry \mathbf{R}^0 and let us denote the Hartree–Fock (HF) state at this geometry by $|\text{HF}\rangle$. The HF state at a displaced geometry $\mathbf{R}^0 + \boldsymbol{\mu}$ (denoted by $|\tilde{\text{HF}}\rangle$) may be expressed in terms of a unitary transformation of the HF orbitals at the undisplaced geometry \mathbf{R}^0 because all basis set effects are contained in the Hamiltonian expansion in Eq. (9)

$$|\tilde{\text{HF}}\rangle = \exp(i^{\text{HF}}\hat{\kappa})|\text{HF}\rangle. \quad (51)$$

The orbital rotation operator $\hat{\kappa}$ is defined in Eq. (25) and contains the nonredundant set of orbital excitation operators ($a_r^\dagger a_s - a_s^\dagger a_r$). In this HF case, these nonredundant operators consist of the particle-hole excitations in which s labels an occupied orbital (hole) and r labels an unoccupied orbital (particle). The dependence of ${}^{\text{HF}}\kappa$ on nuclear displacement μ was determined explicitly through second order in μ in Sec. II B.3 and is given in Eqs. (46) and (47). The total HF energy at the displaced geometry may be written as

$$\begin{aligned} E(\mathbf{R}^0 + \mu) &= \langle \tilde{\text{HF}} | H(\mathbf{R}^0 + \mu) | \tilde{\text{HF}} \rangle \\ &= \langle \text{HF} | \exp(-i^{\text{HF}}\hat{\kappa}) (H_0 + \mu \mathbf{H}_1 \\ &\quad + \tfrac{1}{2} \mu \mathbf{H}_2 \mu) \exp(i^{\text{HF}}\hat{\kappa}) | \text{HF} \rangle, \end{aligned} \quad (52)$$

where the Hamiltonian's dependence on nuclear displacement μ given in Eq. (9) has been introduced. In Eqs. (51) and (52) we have explicitly labeled the $\hat{\kappa}$ operator as ${}^{\text{HF}}\hat{\kappa}$ to make clear the point that the orbitals utilized in the present response calculation are assumed to be HF molecular orbitals. In subsequent sections we will similarly use ${}^{\text{HF}}\hat{\kappa}$, ${}^{\text{MC}}\hat{\kappa}$, ${}^{\text{CI}}\hat{S}$, and ${}^{\text{MC}}\hat{S}$ to stress the nature of the orbitals (HF or MCSCF) and configuration amplitudes (CI or MCSCF) whose responses we are treating. This notation will be used in writing all wave function and energy expressions analogous to Eqs. (51) and (52), but the superscripts will then be dropped for the duration of the respective section. This action is taken for notational simplicity once we have made clear the nature of the orbital and configuration responses.

The HF total energy in Eq. (52) contains a dependence on μ both in the orbital rotation parameters κ and in the Hamiltonian H . According to Eq. (30) the HF molecular gradient and Hessian may be determined as the first and second derivatives with respect to μ of the Hartree-Fock energy in Eq. (52).

B. The HF molecular gradient

The first derivative of the HF energy with respect to nuclear displacement evaluated at zero displacement becomes (in all such derivatives in this paper the $\mu = 0$ limit will be implied)

$$\frac{dE(\mathbf{R}^0 + \mu)}{d\mu} = \frac{\partial E(\mathbf{R}^0 + \mu)}{\partial \kappa} \frac{\partial \kappa}{\partial \mu} + \langle \text{HF} | \mathbf{H}_1 | \text{HF} \rangle, \quad (53)$$

where we have used the chain rule to obtain the total derivative. The partial derivatives of the energy with respect to the κ parameters are given by

$$\frac{\partial E(\mathbf{R}^0 + \mu)}{\partial \kappa_{rs}} = \langle \text{HF} | [a_r^\dagger a_s - a_s^\dagger a_r, H_0] | \text{HF} \rangle = 0, \quad (54)$$

which vanishes because of the Brillouin theorem, thereby reducing the right-hand side of Eq. (53) to its last term only,

$$\frac{dE(\mathbf{R}^0 + \mu)}{d\mu} = \langle \text{HF} | \mathbf{H}_1 | \text{HF} \rangle. \quad (55)$$

Therefore, the HF gradient contains the Hellmann-Feynman force term and terms that describe the finiteness of the atomic orbital basis set, both of which are contained in \mathbf{H}_1 .

C. The HF molecular Hessian

The Hartree-Fock molecular Hessian is the second derivative of the HF energy with respect to nuclear displacement evaluated at zero displacement. Using the chain rule for obtaining the total derivative we obtain (all derivatives are evaluated at $\mu = 0$)

$$\begin{aligned} \frac{d^2 E(\mathbf{R}^0 + \mu)}{d\mu d\mu} &= \frac{\partial^2 \kappa}{\partial \mu \partial \mu} \frac{\partial E^{(0)}}{\partial \kappa} + \frac{\partial \kappa}{\partial \mu} \frac{\partial^2 E^{(0)}}{\partial \kappa^2} \frac{\partial \kappa}{\partial \mu} \\ &\quad + 2 \frac{\partial E^{(1)}}{\partial \kappa} \frac{\partial \kappa}{\partial \mu} + \langle \text{HF} | \mathbf{H}_2 | \text{HF} \rangle. \end{aligned} \quad (56)$$

We have introduced in Eq. (56) the shorthand notation

$$E^{(i)} = \langle \text{HF} | \exp(-i^{\text{HF}}\hat{\kappa}) H_i \exp(i^{\text{HF}}\hat{\kappa}) | \text{HF} \rangle, \quad i = 0, 1, 2, \quad (57)$$

which, at $\mu = 0$, reduces to $E^{(i)} = \langle \text{HF} | H_i | \text{HF} \rangle$ since $\kappa = 0$ at $\mu = 0$.

The first term in Eq. (56) vanishes because $\partial E^{(0)}/\partial \kappa$ is zero due to the Brillouin theorem [Eq. (54)]. Furthermore, Eqs. (38) and (43) allow us to recognize that

$$\frac{\partial^2 E^{(0)}}{\partial \kappa^2} = {}^{\text{HF}}G^{(0)} \quad (58)$$

which is nothing but the orbital-space Hessian matrix for the HF state and that

$$\partial \kappa / \partial \mu = {}^{\text{HF}}\kappa^{(1)} \quad (59)$$

which is the first-order κ response for the HF orbitals as given in Eq. (46). Equation (56) can therefore be rewritten as

$$\begin{aligned} \frac{d^2 E(\mathbf{R}^0 + \mu)}{d\mu d\mu} &= {}^{\text{HF}}\kappa^{(1)} {}^{\text{HF}}G^{(0)} {}^{\text{HF}}\kappa^{(1)} \\ &\quad + 2 {}^{\text{HF}}\kappa^{(1)} {}^{\text{HF}}\mathbf{F}^{(1)} + \langle \text{HF} | \mathbf{H}_2 | \text{HF} \rangle \end{aligned} \quad (60)$$

which reduces, after introducing Eq. (46) for ${}^{\text{HF}}\kappa^{(1)}$, to

$$\frac{d^2 E(\mathbf{R}^0 + \mu)}{d\mu d\mu} = - {}^{\text{HF}}\mathbf{F}^{(1)} ({}^{\text{HF}}G^{(0)})^{-1} {}^{\text{HF}}\mathbf{F}^{(1)} + \langle \text{HF} | \mathbf{H}_2 | \text{HF} \rangle. \quad (61)$$

The first term in Eq. (61) describes the response of the HF state to a nuclear displacement in a finite basis. The second term contains the field gradient factor and basis set dependence effects. Notice that both the molecular gradient and Hessian have been expressed in terms of expectation values of \mathbf{H}_1 and \mathbf{H}_2 as well as response matrices involving the Hessians $G^{(0)}$ and Brillouin-type matrix elements $\mathbf{F}^{(1)}$. In conventional wave function optimizations, the same matrices appear with \mathbf{H}_1 and \mathbf{H}_2 replaced by H_0 . However, \mathbf{H}_1 and \mathbf{H}_2 are also, as is H_0 , sums of one- and two-electron operators.

IV. GRADIENT AND HESSIAN FOR A MULTICONFIGURATION SELF-CONSISTENT FIELD WAVE FUNCTION

A. The MCSCF energy

Paralleling the development of the last section, let us assume that a MCSCF calculation has been carried out at a geometry \mathbf{R}^0 and that we have a set of MCSCF orbitals, the MCSCF state $|\text{MC}\rangle$, and its orthogonal complement set of states. The MCSCF state $|\text{MC}\rangle$ at a displaced geometry $\mathbf{R}^0 + \mu$ may be expressed in terms of the result of the undisplaced MCSCF function as follows:

$$|\tilde{MC}\rangle = \exp(i^{MC}\hat{\kappa}) \exp(i^{MC}\hat{S}) |MC\rangle. \quad (62)$$

The operators $\hat{\kappa}$ and \hat{S} are defined in Eqs. (25) and (23), respectively. The dependence of the parameters κ_{rs} and S_{n0} on μ is given explicitly through second order in Eqs. (45)–(47). Using these response values, the MCSCF total energy at the displaced geometry may be written as

$$\begin{aligned} E(\mathbf{R}^0 + \mu) &= \langle \tilde{MC} | H(\mathbf{R}^0 + \mu) | \tilde{MC} \rangle \\ &= \langle MC | \exp(-i^{MC}\hat{S}) \exp(-i^{MC}\hat{\kappa}) (H_0 + \mu H_1 \\ &\quad + \frac{1}{2} \mu H_2 \mu) \exp(i^{MC}\hat{\kappa}) \exp(i^{MC}\hat{S}) | MC \rangle. \end{aligned} \quad (63)$$

The total MCSCF energy at the displaced geometry has an implicit dependence on μ in the parameters κ and S and an explicit dependence on μ in the Hamiltonian.

B. The MCSCF molecular gradient

The molecular gradient is defined as the first derivative of the MCSCF energy given in Eq. (63),

$$\begin{aligned} \frac{dE(\mathbf{R}^0 + \mu)}{d\mu} &= \frac{\partial E(\mathbf{R}^0 + \mu)}{\partial \kappa} \frac{\partial \kappa}{\partial \mu} + \frac{\partial E(\mathbf{R}^0 + \mu)}{\partial S} \frac{\partial S}{\partial \mu} \\ &\quad + \langle MC | H_1 | MC \rangle = \langle MC | H_1 | MC \rangle. \end{aligned} \quad (64)$$

To obtain the last equality in Eq. (64) we have used that the MCSCF state $|MC\rangle$ satisfies the generalized Brillouin theorem in both the orbital and state spaces; i. e.,

$$\frac{\partial E(\mathbf{R}^0 + \mu)}{\partial \kappa} = \langle MC | [Q^\dagger - Q, H_0] | MC \rangle = 0 \quad (65)$$

and

$$\frac{\partial E(\mathbf{R}^0 + \mu)}{\partial S} = \langle MC | [R^\dagger - R, H_0] | MC \rangle = 0. \quad (66)$$

These last equations simply state that $|MC\rangle$ has been variationally optimized at $\mu = 0$ both with respect to the κ and S variables. The MCSCF molecular gradient in Eq. (64) contains only the Hellman–Feynmann force term and terms that describe the finiteness of the atomic orbital basis set, both of which are in H_1 . There is no need to evaluate either $\kappa^{(1)} = \partial \kappa / \partial \mu$ or $S^{(1)} = \partial S / \partial \mu$ when computing the MCSCF molecular gradient. This fact makes the MCSCF wave function the most straightforward to use in correlated-wave function molecular gradient studies.

C. The MCSCF molecular Hessian

The MCSCF molecular Hessian is the second derivative of the MCSCF energy in Eq. (63):

$$\begin{aligned} \frac{d^2 E(\mathbf{R}^0 + \mu)}{d\mu d\mu} &= {}^{MC}\mathbf{S}^{(2)} {}^{MC}\mathbf{\kappa}^{(2)} \begin{pmatrix} \frac{\partial E^{(0)}}{\partial S} \\ \frac{\partial E^{(0)}}{\partial \kappa} \end{pmatrix} \\ &\quad + {}^{MC}\mathbf{S}^{(1)} {}^{MC}\mathbf{\kappa}^{(1)} \begin{pmatrix} \frac{\partial^2 E^{(0)}}{\partial S^2} & \frac{\partial^2 E^{(0)}}{\partial \kappa \partial S} \\ \frac{\partial^2 E^{(0)}}{\partial S \partial \kappa} & \frac{\partial^2 E^{(0)}}{\partial \kappa^2} \end{pmatrix} \begin{pmatrix} {}^{MC}\mathbf{S}^{(1)} \\ {}^{MC}\mathbf{\kappa}^{(1)} \end{pmatrix} \\ &\quad + 2({}^{MC}\mathbf{S}^{(1)} {}^{MC}\mathbf{\kappa}^{(1)}) \begin{pmatrix} \frac{\partial \mathbf{E}^{(1)}}{\partial S} \\ \frac{\partial \mathbf{E}^{(1)}}{\partial \kappa} \end{pmatrix} + \langle MC | H_2 | MC \rangle. \end{aligned} \quad (67)$$

Here we have used $\partial \kappa / \partial \mu = {}^{MC}\mathbf{\kappa}^{(1)}$, $\partial S / \partial \mu = {}^{MC}\mathbf{S}^{(1)}$, $\partial^2 \kappa / \partial \mu \partial \mu = {}^{MC}\mathbf{\kappa}^{(2)}$, and $\partial^2 S / \partial \mu \partial \mu = {}^{MC}\mathbf{S}^{(2)}$ [see Eq. (43)] and introduced the shorthand notation

$$E^{(i)} = \langle MC | \exp(-i^{MC}\hat{S}) \exp(-i^{MC}\hat{\kappa}) H_i \exp(i^{MC}\hat{\kappa}) \times \exp(i^{MC}\hat{S}) | MC \rangle, \quad i = 0, 1, 2$$

analogous to that [Eq. (57)] used in the HF case. The generalized Brillouin theorem [Eqs. (65) and (66)] immediately says that the first term in Eq. (67) is equal to zero. Equation (38) further allows us to recognize the MCSCF wave function Hessian matrix ${}^{MC}\mathbf{G}^{(0)}$:

$$\begin{pmatrix} \frac{\partial^2 E^{(0)}}{\partial S^2} & \frac{\partial^2 E^{(0)}}{\partial \kappa \partial S} \\ \frac{\partial^2 E^{(0)}}{\partial S \partial \kappa} & \frac{\partial^2 E^{(0)}}{\partial \kappa^2} \end{pmatrix} = {}^{MC}\mathbf{G}^{(0)} \quad (68)$$

as well as MCSCF Generalized Brillouin-type (with H_1 in place of H_0) elements

$$\begin{pmatrix} \frac{\partial \mathbf{E}^{(1)}}{\partial S} \\ \frac{\partial \mathbf{E}^{(1)}}{\partial \kappa} \end{pmatrix} = {}^{MC}\mathbf{F}^{(1)}. \quad (69)$$

Introducing the explicit forms of ${}^{MC}\mathbf{\kappa}^{(1)}$ and ${}^{MC}\mathbf{S}^{(1)}$ given in Eq. (46) into Eq. (67) and using Eqs. (68) and (69) allows the MCSCF molecular Hessian to be written as

$$\frac{d^2 E(\mathbf{R}^0 + \mu)}{d\mu d\mu} = - {}^{MC}\mathbf{F}^{(1)} ({}^{MC}\mathbf{G}^{(0)})^{-1} {}^{MC}\mathbf{F}^{(1)} + \langle MC | H_2 | MC \rangle. \quad (70)$$

The first term above describes the response of the MCSCF state to a nuclear displacement. The second term contains the field gradient term and terms caused by the finiteness of the basis set. In the special case of a single configuration state function, the MCSCF molecular gradients and Hessians of Eqs. (64) and (70) reduce to the Hartree–Fock expressions given in Eqs. (55) and (61), respectively. Again, we remind the reader that explicit expressions for the $F^{(i)}$ and $G^{(i)}$ matrices are given in Ref. 14.

V. GRADIENT AND HESSIAN FOR A CONFIGURATION INTERACTION WAVE FUNCTION CONSTRUCTED FROM HARTREE-FOCK ORBITALS

A. The CI energy function

We assume that we have carried out a Hartree–Fock calculation at an internuclear geometry \mathbf{R}^0 and used the set of Hartree–Fock orbitals to perform a CI calculation to determine the CI state $|CI\rangle$.

The CI state at the displaced geometry $|\tilde{CI}\rangle$ may be expressed in terms of the Hartree–Fock orbitals and CI states $(|CI\rangle)$ and its orthogonal complement $|n\rangle$ of the undisplaced geometry as

$$|\tilde{CI}\rangle = \exp(i^{HF}\hat{\kappa}) \exp(i^{CI}\hat{S}) |CI\rangle. \quad (71)$$

The dependence of the parameters ${}^{HF}\mathbf{\kappa}$ and ${}^{CI}\mathbf{S}$ on nuclear displacement has been given explicitly through second order in Eqs. (46), (47), and (50). The total energy of the CI state at the displaced geometry becomes

$$E(\mathbf{R}^0 + \boldsymbol{\mu}) = \langle \tilde{\text{CI}} | H(\mathbf{R}^0 + \boldsymbol{\mu}) | \tilde{\text{CI}} \rangle \\ = \langle \text{CI} | \exp(-i \text{CI} \hat{S}) \exp(-i \text{HF} \hat{\kappa}) (H_0 + \boldsymbol{\mu} \mathbf{H}_1 + \frac{1}{2} \boldsymbol{\mu} \mathbf{H}_2 \boldsymbol{\mu}) \\ \times \exp(i \text{HF} \hat{\kappa}) \exp(i \text{CI} \hat{S}) | \text{CI} \rangle. \quad (72)$$

The total CI energy at displaced geometry thus contains an implicit dependence on $\boldsymbol{\mu}$ in $\text{HF} \hat{\kappa}$ and $\text{CI} \hat{S}$ and an explicit dependence on $\boldsymbol{\mu}$ in the Hamiltonian.

B. The CI molecular gradient

The molecular gradient is determined as the first derivative of the CI total energy in Eq. (72) with respect to $\boldsymbol{\mu}$,

$$\frac{dE(\mathbf{R}^0 + \boldsymbol{\mu})}{d\boldsymbol{\mu}} = \frac{\partial E}{\partial S} \frac{\partial S}{\partial \boldsymbol{\mu}} + \frac{\partial E}{\partial \kappa} \frac{\partial \kappa}{\partial \boldsymbol{\mu}} + \langle \text{CI} | \mathbf{H}_1 | \text{CI} \rangle. \quad (73)$$

The derivatives

$$\frac{\partial E}{\partial S_{n0}} = \langle \text{CI} | [|n\rangle \langle \text{CI}| - | \text{CI} \rangle \langle n|, H_0] | \text{CI} \rangle = 0 \quad (74)$$

vanish because the state $|\text{CI}\rangle$ is determined in a variational manner in the state space as a result of which the energy is stationary with respect to S . Using Eqs. (74) and (46) as well as

$$\frac{\partial E^{(0)}}{\partial \kappa_{rs}} = \text{HF} F_{rs}^{(0)} = \langle \text{CI} | [a_r^\dagger a_s - a_s^\dagger a_r, H_0] | \text{CI} \rangle, \quad (75)$$

we may rewrite Eq. (73) as

$$\frac{dE}{d\boldsymbol{\mu}} = \text{HF} F^{(0)} \text{HF} \boldsymbol{\kappa}^{(1)} + \langle \text{CI} | \mathbf{H}_1 | \text{CI} \rangle. \quad (76)$$

The factor $\text{HF} F^{(0)}$ does not vanish since it is a Brillouin theorem matrix for the HF orbital space but computed as an expectation value, with respect to the CI state. The first term in the above molecular gradient describes how the Hartree-Fock orbitals polarize in the field of a nuclear displacement. The second term contains the Hellmann-Feynmann force and the finite-basis set factors.

The first term in Eq. (76) may alternatively be written in a form which suggests a more computationally practical means of evaluation

$$\text{HF} F^{(0)} \text{HF} \boldsymbol{\kappa}^{(1)} = \sum_{r>s} \langle \text{CI} | [a_r^\dagger a_s - a_s^\dagger a_r, H_0] | \text{CI} \rangle \text{HF} \boldsymbol{\kappa}_{rs}^{(1)} \\ = -i \langle \text{CI} | [\text{HF} \hat{\kappa}^{(1)}, H_0] | \text{CI} \rangle, \quad (77)$$

where

$$\text{HF} \hat{\kappa}^{(1)} = i \sum_{r>s} \text{HF} \boldsymbol{\kappa}_{rs}^{(1)} (a_r^\dagger a_s - a_s^\dagger a_r). \quad (78)$$

In Appendix B we demonstrate how the right-hand side of Eq. (77) can be viewed as a Hamiltonian expectation value in which modified integrals appear. These modified integrals are obtained by carrying out a one-index transformation on the one- and two-electron integrals appearing in H_0 using the parameters $\text{HF} \boldsymbol{\kappa}^{(1)}$ of the linear response calculation as the transformation matrix. In the remainder of this paper we report whenever possible molecular gradient and Hessian results in a form analogous to Eq. (77) since this form allows the most computationally efficient evaluation of such terms.

C. The CI molecular Hessian

The molecular Hessian is determined as the second derivative of the total energy in Eq. (72):

$$\frac{d^2 E(\mathbf{R}^0 + \boldsymbol{\mu})}{d\boldsymbol{\mu} d\boldsymbol{\mu}} = (\text{CI} \mathbf{S}^{(2)} \text{HF} \boldsymbol{\kappa}^{(2)}) \begin{pmatrix} \frac{\partial E^{(0)}}{\partial S} \\ \frac{\partial E^{(0)}}{\partial \kappa} \end{pmatrix} \\ + (\text{CI} \mathbf{S}^{(1)} \text{HF} \boldsymbol{\kappa}^{(1)}) \begin{pmatrix} \frac{\partial^2 E^{(0)}}{\partial S^2} & \frac{\partial^2 E^{(0)}}{\partial \kappa \partial S} \\ \frac{\partial^2 E^{(0)}}{\partial S \partial \kappa} & \frac{\partial^2 E^{(0)}}{\partial \kappa^2} \end{pmatrix} \begin{pmatrix} \text{CI} \mathbf{S}^{(1)} \\ \text{HF} \boldsymbol{\kappa}^{(1)} \end{pmatrix} \\ + 2(\text{CI} \mathbf{S}^{(1)} \text{HF} \boldsymbol{\kappa}^{(1)}) \begin{pmatrix} \frac{\partial E^{(1)}}{\partial S} \\ \frac{\partial E^{(1)}}{\partial \kappa} \end{pmatrix} + \langle \text{CI} | \mathbf{H}_2 | \text{CI} \rangle, \quad (79)$$

where we have again introduced the shorthand notation

$$E^{(i)} = \langle \text{CI} | \exp(-i \text{CI} \hat{S}) \exp(-i \text{HF} \hat{\kappa}) H_i \\ \times \exp(i \text{HF} \hat{\kappa}) \exp(i \text{CI} \hat{S}) | \text{CI} \rangle, \quad i = 0, 1, 2.$$

The first component $(\partial E^{(0)}/\partial S)$ of the first term in Eq. (79) vanishes because the state $|\text{CI}\rangle$ is determined in a variational manner in which the energy is stationary with respect to S . The molecular Hessian thus does not contain terms describing the second-order response of the CI amplitudes $\text{CI} \mathbf{S}^{(2)}$. However the second-order HF orbital responses are required for the molecular Hessian since $\partial E^{(0)}/\partial \kappa$ is not equal to zero [see Eq. (75)] because average values are taken with respect to the CI reference state $|\text{CI}\rangle$ and not with respect to the Hartree-Fock state $|\text{HF}\rangle$. The second and third terms in Eq. (79) contain $\text{CI} \mathbf{S}^{(1)}$ and $\text{HF} \boldsymbol{\kappa}^{(1)}$. The explicit forms for these vectors are given in Eqs. (50) and (46), respectively. The second derivative matrix in Eq. (79) (the second term) has the same structure as the MCSCF molecular Hessian matrix $G^{(0)}$ in Eq. (40). The orbital excitation operators $a_r^\dagger a_s - a_s^\dagger a_r$, however, refer in this case, to the set of Hartree-Fock orbitals and the state transfer operators $|n\rangle\langle 0| - |0\rangle\langle n|$ are constructed from the CI state $|\text{CI}\rangle$ and its orthogonal complement set of states. The first derivative term in the third term of Eq. (79) has the same structure as $\text{MC} \mathbf{F}^{(1)}$ of Eq. (39) but again refers to HF orbital excitation operators and CI state transfer operators. The fact that the structures of the $G^{(0)}$ and $\mathbf{F}^{(1)}$ matrices are as stated allows the results given in Eqs. (2.41) and (2.42) of Ref. 14 to once again be used.

The second and third terms of Eq. (79) can not be combined as was done in the HF and MCSCF cases [see Eqs. (61) and (70)] because a simultaneous optimization in the orbital and configuration spaces has not been carried out. As a result, there exists no relationship such as Eq. (46) which allows both $\boldsymbol{\kappa}^{(1)}$ and $\mathbf{S}^{(1)}$ to be expressed in terms of a single matrix.

When large configuration expansions are considered, the most time consuming elements to evaluate in the molecular Hessian of Eq. (79) are probably $\text{CI} \mathbf{S}^{(1)}$. $\text{HF} \boldsymbol{\kappa}^{(2)}$ and $\text{HF} \boldsymbol{\kappa}^{(1)}$ may relatively easily be calculated using the procedures described in Sec. II B.3. When $\text{CI} \mathbf{S}^{(1)}$, $\text{HF} \boldsymbol{\kappa}^{(2)}$, and $\text{HF} \boldsymbol{\kappa}^{(1)}$ are available, it is relatively

straightforward to evaluate the molecular Hessian if the approach in Appendix B is used. To do so Eq. (79) may be rewritten as

$$\frac{d^2 E(\mathbf{R}^0 + \boldsymbol{\mu})}{d\boldsymbol{\mu} d\boldsymbol{\mu}} = \langle \text{CI} | -i[\mathbf{H}^{\text{F}} \hat{\mathbf{K}}^{(2)}, H_0] - [\mathbf{H}^{\text{F}} \hat{\mathbf{K}}^{(1)}, [\mathbf{H}^{\text{F}} \hat{\mathbf{K}}^{(1)}, H_0]] \\ - 2[\text{CI} \hat{\mathbf{S}}^{(1)}, [\mathbf{H}^{\text{F}} \hat{\mathbf{K}}^{(1)}, H_0]] - [\text{CI} \hat{\mathbf{S}}^{(1)}, [\text{CI} \hat{\mathbf{S}}^{(1)}, H_0]] \\ - 2i[\mathbf{H}^{\text{F}} \hat{\mathbf{K}}^{(1)}, \mathbf{H}_1] - 2i[\mathbf{H}^{\text{F}} \hat{\mathbf{S}}^{(1)}, \mathbf{H}_1] | \text{CI} \rangle. \quad (80)$$

All terms in Eq. (79) then reduce to Hamiltonian average values involving modified integrals and modified density matrices.

VI. GRADIENTS AND HESSIANS FOR CONFIGURATION INTERACTION WAVE FUNCTIONS CONSTRUCTED FROM MCSCF ORBITALS

A. The CI energy

In the calculation we shall now consider, we assume that a MCSCF calculation has been carried in a configuration space consisting of the presumed dominant configurations, and subsequently a larger CI calculation has been carried out using the resulting MCSCF orbitals and a configuration list that is larger than that used in the MCSCF calculation. This format is designed to represent the state-of-the-art large CI calculations which have recently received much attention. At geometry \mathbf{R}^0 we denote the CI reference state as $|\text{CI}\rangle$; at displaced geometry $\mathbf{R}^0 + \boldsymbol{\mu}$, the CI reference state is denoted $|\tilde{\text{CI}}\rangle$. The nuclear displaced state $|\tilde{\text{CI}}\rangle$ may be expressed in terms of the results of the undisplaced calculation as

$$|\tilde{\text{CI}}\rangle = \exp(i^{\text{MC}} \hat{\mathbf{K}}) \exp(i^{\text{CI}} \hat{\mathbf{S}}) |\text{CI}\rangle, \quad (81)$$

where $^{\text{MC}} \hat{\mathbf{K}}$ contains only the nonredundant orbital excitation operators of the MCSCF calculation and $^{\text{CI}} \hat{\mathbf{S}}$ contains the state transfer operators of the CI calculation. More is said about the treatment of redundant orbital excitation operators in Sec. IX. The total energy at the displaced coordinates may therefore be written as

$$E(\mathbf{R}^0 + \boldsymbol{\mu}) = \langle \tilde{\text{CI}} | H(\mathbf{R}^0 + \boldsymbol{\mu}) | \tilde{\text{CI}} \rangle = \langle \text{CI} | \exp(-i^{\text{CI}} \hat{\mathbf{S}}) \exp(-i^{\text{MC}} \hat{\mathbf{K}}) \\ \times (H_0 + \mathbf{H}_1 \boldsymbol{\mu} + \frac{1}{2} \mathbf{H}_2 \boldsymbol{\mu} \boldsymbol{\mu}) \exp(i^{\text{MC}} \hat{\mathbf{K}}) \exp(i^{\text{CI}} \hat{\mathbf{S}}) | \text{CI} \rangle. \quad (82)$$

The total energy of Eq. (82) contains an implicit dependence on $\boldsymbol{\mu}$ in $^{\text{CI}} \hat{\mathbf{S}}$ and $^{\text{MC}} \hat{\mathbf{K}}$ and an explicit dependence on $\boldsymbol{\mu}$ in the Hamiltonian.

B. The CI molecular gradient

The molecular gradient is determined as the first derivative of the total energy with respect to $\boldsymbol{\mu}$,

$$\frac{dE(\mathbf{R}^0 + \boldsymbol{\mu})}{d\boldsymbol{\mu}} = \frac{\partial E(\mathbf{R}^0 + \boldsymbol{\mu})}{\partial \mathbf{S}} \frac{\partial \mathbf{S}}{\partial \boldsymbol{\mu}} + \frac{\partial E(\mathbf{R}^0 + \boldsymbol{\mu})}{\partial \boldsymbol{\mu}} \frac{\partial \boldsymbol{\mu}}{\partial \boldsymbol{\mu}} + \langle \text{CI} | \mathbf{H}_1 | \text{CI} \rangle \quad (83)$$

The derivative $\partial E(\mathbf{R}^0 + \boldsymbol{\mu}) / \partial \mathbf{S}$ is zero because the configuration expansion amplitudes of the state $|\text{CI}\rangle$ have been variationally optimized. The derivative

$$\frac{\partial E^{(0)}}{\partial \kappa_{rs}} = {}^{\text{MC}} F_{rs}^{(0)} = \langle \text{CI} | [a_r^\dagger a_s - a_s^\dagger a_r, H_0] | \text{CI} \rangle \quad (84)$$

is nonvanishing since it is a generalized Brillouin theorem matrix element evaluated with respect to the state $|\text{CI}\rangle$. Using Eq. (84), Eq. (83) reduces to

$$\frac{dE(\mathbf{R}^0 + \boldsymbol{\mu})}{d\boldsymbol{\mu}} = {}^{\text{MC}} F^{(0)} {}^{\text{MC}} \boldsymbol{\kappa}^{(1)} + \langle \text{CI} | \mathbf{H}_1 | \text{CI} \rangle \\ = \langle \text{CI} | -i[{}^{\text{MC}} \hat{\mathbf{K}}^{(1)}, H_0] + \mathbf{H}_1 | \text{CI} \rangle \quad (85)$$

which then becomes the molecular gradient. Using Appendix B we may evaluate the first term in Eq. (85) as a Hamiltonian average value using modified integrals.

C. The CI molecular Hessian

The molecular Hessian is the second derivative of the total energy with respect to a nuclear displacement

$$\frac{d^2 E(\mathbf{R}^0 + \boldsymbol{\mu})}{d\boldsymbol{\mu} d\boldsymbol{\mu}} = ({}^{\text{CI}} \hat{\mathbf{S}}^{(2)} {}^{\text{MC}} \boldsymbol{\kappa}^{(2)}) \begin{pmatrix} \frac{\partial E^{(0)}}{\partial \mathbf{S}} \\ \frac{\partial E^{(0)}}{\partial \boldsymbol{\kappa}} \end{pmatrix} \\ + ({}^{\text{CI}} \hat{\mathbf{S}}^{(1)} {}^{\text{MC}} \boldsymbol{\kappa}^{(1)}) \begin{pmatrix} \frac{\partial^2 E^{(0)}}{\partial \mathbf{S}^2} & \frac{\partial^2 E^{(0)}}{\partial \boldsymbol{\kappa} \partial \mathbf{S}} \\ \frac{\partial^2 E^{(0)}}{\partial \mathbf{S} \partial \boldsymbol{\kappa}} & \frac{\partial^2 E^{(0)}}{\partial \boldsymbol{\kappa} \partial \boldsymbol{\kappa}} \end{pmatrix} \begin{pmatrix} {}^{\text{CI}} \hat{\mathbf{S}}^{(1)} \\ {}^{\text{MC}} \boldsymbol{\kappa}^{(1)} \end{pmatrix} \\ + 2({}^{\text{CI}} \hat{\mathbf{S}}^{(1)} {}^{\text{MC}} \boldsymbol{\kappa}^{(1)}) \begin{pmatrix} \frac{\partial E^{(1)}}{\partial \mathbf{S}} \\ \frac{\partial E^{(1)}}{\partial \boldsymbol{\kappa}} \end{pmatrix} + \langle \text{CI} | \mathbf{H}_2 | \text{CI} \rangle. \quad (86)$$

The first component $\partial E^{(0)} / \partial \mathbf{S}$ of the first term vanishes again because the state $|\text{CI}\rangle$ is determined variationally. The evaluation of the terms ${}^{\text{CI}} \hat{\mathbf{S}}^{(1)}$, ${}^{\text{MC}} \boldsymbol{\kappa}^{(2)}$, and ${}^{\text{MC}} \boldsymbol{\kappa}^{(1)}$ is described in some detail in Eqs. (46), (47), and (50). ${}^{\text{MC}} \boldsymbol{\kappa}^{(1)}$ is determined from a coupled set of linear equations that also have as variables ${}^{\text{MC}} \hat{\mathbf{S}}^{(1)}$. However ${}^{\text{MC}} \hat{\mathbf{S}}^{(1)}$ is not required directly when evaluating either the molecular gradient or Hessian in Eqs. (85) and (86), respectively. It is however, worth pointing out that ${}^{\text{MC}} \boldsymbol{\kappa}^{(1)}$ depends on the configurations of ${}^{\text{MC}} \hat{\mathbf{S}}$ both through the orbital-configuration coupling matrix elements in Eq. (46) and also because all matrix elements in Eqs. (46) and (47) are evaluated with respect to the MCSCF reference state $|\text{MC}\rangle$. The derivative matrices in the second and third terms in Eq. (86) have the structure of the MCSCF Hessian matrix. The state transfer operators, however, refer to the CI state $|\text{CI}\rangle$ and its orthogonal complement set of states. In both these derivative terms, average values are taken with respect to the CI state $|\text{CI}\rangle$.

The approach of Appendix B may also be used to efficiently evaluate Eq. (86). To do so we rewrite Eq. (86) as

$$\frac{d^2 E(\mathbf{R}^0 + \boldsymbol{\mu})}{d\boldsymbol{\mu} d\boldsymbol{\mu}} = \langle \text{CI} | -i[{}^{\text{MC}} \hat{\mathbf{K}}^{(2)}, H_0] - [{}^{\text{MC}} \hat{\mathbf{K}}^{(1)}, [{}^{\text{MC}} \hat{\mathbf{K}}^{(1)}, H_0]] \\ - 2[{}^{\text{CI}} \hat{\mathbf{S}}^{(1)}, [{}^{\text{MC}} \hat{\mathbf{K}}^{(1)}, H_0]] - [{}^{\text{CI}} \hat{\mathbf{S}}^{(1)}, [{}^{\text{CI}} \hat{\mathbf{S}}^{(1)}, H_0]] \\ - 2i[{}^{\text{MC}} \hat{\mathbf{K}}^{(1)}, \mathbf{H}_1] - 2i[{}^{\text{CI}} \hat{\mathbf{S}}^{(1)}, \mathbf{H}_1] | \text{CI} \rangle. \quad (87)$$

All of the terms in Eq. (87) can be reduced to Hamiltonian average values involving modified integrals and modified density matrices. We note that if the computational effort in evaluating ${}^{\text{CI}} \hat{\mathbf{S}}^{(1)}$ is prohibitively large, ${}^{\text{CI}} \hat{\mathbf{S}}^{(1)}$ may in most of the expressions of Eq. (87), be approximated reasonably well by ${}^{\text{MC}} \hat{\mathbf{S}}^{(1)}$ of Eq. (46).

We point out that, in the limit where the orbitals are determined in the MCSCF calculation which only contains one configuration, the expressions for the molecular gradient and Hessian in Eqs. (85) and (87) reduce to those in Eqs. (76) and (80), respectively.

VII. GRADIENT AND HESSIAN FOR A COUPLED-CLUSTER WAVE FUNCTION

A. The coupled-cluster energy

At an internuclear distance, \mathbf{R}^0 we assume that we have carried out a Hartree-Fock calculation and used the orbitals to determine a coupled cluster²³ (CC) wave function which we denote $|\text{CC}\rangle$,

$$|\text{CC}\rangle = \exp(T)|\text{HF}\rangle. \quad (88)$$

The so-called cluster operator T is

$$T = T_1 + T_2 + \dots + T_N, \quad (89)$$

where, for example, the low-order cluster contributions are

$$T_1 = \sum_{m\alpha} t_{\alpha}^m a_m^{\dagger} a_{\alpha}, \quad (90)$$

$$T_2 = \sum_{\substack{m,n \\ \alpha,\beta}} t_{\alpha\beta}^{mn} a_m^{\dagger} a_n^{\dagger} a_{\alpha} a_{\beta}. \quad (91)$$

The indices $\alpha\beta\gamma\delta$ ($mnpq$) denote (un)occupied orbitals in the HF reference determinant $|\text{HF}\rangle$ and indices ijk and l refer to unspecified orbital occupation.

The CC total energy is determined by projecting the CC Schrödinger equation

$$\exp(-T)H\exp(T)|\text{HF}\rangle = E|\text{HF}\rangle \quad (92)$$

from the left against $\langle\text{HF}|$,

$$E = \langle\text{HF}|\exp(-T)H\exp(T)|\text{HF}\rangle. \quad (93)$$

The CC amplitudes t can be evaluated by projecting Eq. (92) from the left by singly, doubly, through N -fold excited determinants $\{|\bar{m}\bar{n}\dots\rangle\}$

$$\langle\bar{m}\bar{n}\dots|\exp(-T)H\exp(T)|\text{HF}\rangle = 0 \quad (94)$$

and then solving the resulting set of nonlinear equations for t . It is common in practical calculations to limit consideration to the case in which T is approximated by $T_1 + T_2$, although in the following we have made no such restriction.

The CC state $|\bar{\text{CC}}\rangle$ at a displaced geometry $\mathbf{R}^0 + \mu$ may be written as

$$|\bar{\text{CC}}\rangle = \exp(\bar{T})|\bar{\text{HF}}\rangle, \quad (95)$$

$$\bar{T} = \bar{T}_1 + \bar{T}_2 + \dots + \bar{T}_N, \quad (96)$$

where

$$\bar{T}_1 = \sum_{m\alpha} \bar{t}_{\alpha}^m \bar{a}_m^{\dagger} \bar{a}_{\alpha}, \quad (97)$$

$$\bar{T}_2 = \sum_{\substack{m,n \\ \alpha,\beta}} \bar{t}_{\alpha\beta}^{mn} \bar{a}_m^{\dagger} \bar{a}_n^{\dagger} \bar{a}_{\alpha} \bar{a}_{\beta}, \quad (98)$$

and the $\bar{}$ symbol indicates that the calculation is carried out using the HF orbitals at the displaced geometry. The CC state $|\bar{\text{CC}}\rangle$ has an implicit dependence on the nuclear displacement μ in the orbitals and in the CC amplitudes \bar{t} . The HF orbital dependence has been determined explicitly through second order in Sec. II [see Eqs. (45) and (47)]. The CC amplitude dependence may be established from the equations determining the

CC amplitudes \bar{t} ,

$$\langle\bar{m}\bar{n}\dots|\exp(-\bar{T})H(\mathbf{R}^0 + \mu)\exp(\bar{T})|\bar{\text{HF}}\rangle = 0. \quad (99)$$

To do this, the \bar{t} amplitudes are expanded in power series in μ ,

$$\bar{t} = t^{(0)} + \mu t^{(1)} + \frac{1}{2}\mu^2 t^{(2)} + \dots \quad (100)$$

Because the HF orbitals and CC amplitudes are determined separately (in independent calculations) we are interested in determining the $t^{(1)}$, $t^{(2)}$, etc. responses under the assumption that the orbitals stay fixed during the nuclear displacement. The $t^{(1)}$, $t^{(2)}$, etc. may then be determined by requiring Eq. (99) to be satisfied through each power in μ . To achieve such an order-by-order analysis, we transform Eq. (99) to the basis of the undisplaced Hartree-Fock orbitals

$$\langle\bar{m}\bar{n}\dots|\exp(-\bar{T})\exp(-i^{\text{HF}}\hat{\kappa})(H_0 + \mu\mathbf{H}_1 + \frac{1}{2}\mu\mathbf{H}_2\mu) \times \exp(i^{\text{HF}}\hat{\kappa})\exp(\bar{T})|\text{HF}\rangle = 0, \quad (101)$$

and introduce the transformed \bar{H}_0 , \bar{H}_1 , and \bar{H}_2 operators of Eqs. (49) (the $\bar{}$ symbol over the T operators denotes that the operator contains the CC amplitudes \bar{t} at the displaced geometry)

$$\langle\bar{m}\bar{n}\dots|\exp(-\bar{T})(\bar{H}_0 + \mu\bar{H}_1 + \frac{1}{2}\mu\bar{H}_2\mu)\exp(\bar{T})|\text{HF}\rangle = 0. \quad (102)$$

Solving Eq. (102) through each order in μ gives $t^{(0)}$, $t^{(1)}$, $t^{(2)}$, etc. for the case in which the Hartree-Fock calculation and the CC calculation are carried out independently (i.e., in a noncoupled manner). The zeroth-order equations that result from Eq. (102) are easily seen to reduce to the CC equations at the undisplaced geometry [Eq. (94)]. The first-order equations read

$$\langle\bar{m}\bar{n}\dots|\exp(-T^{(0)})\{\bar{H}_1 - [\mathbf{T}^{(1)}, \bar{H}_0]\}\exp(T^{(0)})|\text{HF}\rangle = 0 \quad (103)$$

which is a set of linear equations²¹ that determines the amplitudes $t^{(1)}$. The second-order equation reads

$$\langle\bar{m}\bar{n}\dots|\exp(-T^{(0)})\{\bar{H}_2 - [\mathbf{T}_0^{(1)}, \bar{H}_1] + \frac{1}{2}[\mathbf{T}^{(1)}, [\mathbf{T}^{(1)}, \bar{H}_0]] - [\mathbf{T}^{(2)}, \bar{H}_0]\}\exp(T^{(0)})|\text{HF}\rangle = 0. \quad (104)$$

Equation (104) is a set of linear equations which may be used to determine $t^{(2)}$ once $t^{(1)}$ is determined via Eq. (103).

After having described the response of the CC amplitudes to a nuclear displacement μ we turn to consider how the CC energy varies as a function of nuclear displacement μ . The total CC energy at $\mathbf{R}^0 + \mu$ may be written as

$$E(\mathbf{R}^0 + \mu) = \langle\bar{\text{HF}}|\exp(-\bar{T})H(\mathbf{R}^0 + \mu)\exp(\bar{T})|\bar{\text{HF}}\rangle \quad (105)$$

or, expressed in terms of the HF orbitals calculated at the undisplaced geometry,

$$E(\mathbf{R}^0 + \mu) = \langle\text{HF}|\exp(-\bar{T})\exp(-i^{\text{HF}}\hat{\kappa})(H_0 + \mu\mathbf{H}_1 + \frac{1}{2}\mu\mathbf{H}_2\mu)\exp(i^{\text{HF}}\hat{\kappa})\exp(\bar{T})|\text{HF}\rangle. \quad (106)$$

The total CC energy contains an implicit dependence on μ in $i^{\text{HF}}\hat{\kappa}$ and \bar{T} and explicit dependence on μ in the Hamiltonian.

B. The CC molecular gradient

The molecular gradient is determined as the first derivative of the total energy in Eq. (106) with respect

to μ ,

$$\frac{dE(\mathbf{R}^0 + \mu)}{d\mu} = \frac{\partial E}{\partial \kappa} \mathbf{H}^{\mathbf{F}} \mathbf{K}^{(1)} + \frac{\partial E}{\partial t} \mathbf{t}^{(1)} + \langle \text{HF} | \exp(-T^{(0)}) \mathbf{H}_1 \exp(T^{(0)}) | \text{HF} \rangle. \quad (107)$$

The partial derivatives of the total energy with respect to an orbital variation may be evaluated as

$$\frac{\partial E^{(0)}}{\partial \kappa_{m\alpha}} = \langle \text{HF} | \exp(-T^{(0)}) \times [a_m^\dagger a_\alpha - a_\alpha^\dagger a_m, H_0] \exp(T^{(0)}) | \text{HF} \rangle, \quad (108)$$

where we have introduced the notation

$$E^{(i)} = \langle \text{HF} | \exp(-T^{(0)}) \exp(-i \mathbf{H}^{\mathbf{F}} \hat{\mathbf{K}}) \times H_i \exp(i \mathbf{H}^{\mathbf{F}} \hat{\mathbf{K}}) \exp(T^{(0)}) | \text{HF} \rangle, \quad i = 0, 1, 2. \quad (109)$$

Equation (108) does not vanish even though it is of the Brillouin matrix element form since it involves $\exp(T^{(0)}) | \text{HF} \rangle$ rather than $| \text{HF} \rangle$. Likewise,

$$\frac{\partial E^{(0)}}{\partial t_{\alpha\beta\cdots}} = \langle \text{HF} | \exp(-T^{(0)}) \times [H_0, a_m^\dagger a_n^\dagger \cdots a_\alpha a_\beta \cdots] \exp(T^{(0)}) | \text{HF} \rangle, \quad (110)$$

and Eq. (107) therefore becomes

$$\frac{dE(\mathbf{R}^0 + \mu)}{d\mu} = \langle \text{HF} | \exp(-T^{(0)}) \{ -i [\mathbf{H}^{\mathbf{F}} \hat{\mathbf{K}}^{(1)}, H_0] + [H_0, \mathbf{T}^{(1)}] + \mathbf{H}_1 \} \exp(T^{(0)}) | \text{HF} \rangle, \quad (111)$$

where the $\mathbf{T}^{(1)}$ operator contains the parameters $\mathbf{t}^{(1)}$ of Eq. (103). The first term in the CC molecular gradient [Eq. (111)] describes how the Hartree-Fock orbitals polarize in the field of a nuclear displacement. The second term contains the CC amplitude response, while

the third term contains the Hellmann-Feynmann force and finite basis terms. The first term in Eq. (111) may efficiently be evaluated using the technique described in Appendix B.

C. The CC molecular Hessian

The CC molecular Hessian is the second derivative of the total energy in Eq. (106) with respect to μ . Using the chain rule for obtaining total derivatives we obtain

$$\begin{aligned} \frac{d^2 E(\mathbf{R}^0 + \mu)}{d\mu d\mu} &= (\mathbf{H}^{\mathbf{F}} \mathbf{K}^{(2)} \mathbf{t}^{(2)}) \left(\frac{\partial E^{(0)}}{\partial \kappa} \right) + (\mathbf{H}^{\mathbf{F}} \mathbf{K}^{(1)} \mathbf{t}^{(1)}) \\ &\times \left(\frac{\partial^2 E^{(0)}}{\partial \kappa \partial \kappa} \quad \frac{\partial^2 E^{(0)}}{\partial \kappa \partial t} \right) \begin{pmatrix} \mathbf{H}^{\mathbf{F}} \mathbf{K}^{(1)} \\ \mathbf{t}^{(1)} \end{pmatrix} + 2(\mathbf{H}^{\mathbf{F}} \mathbf{K}^{(1)} \mathbf{t}^{(1)}) \\ &\times \left(\frac{\partial E^{(1)}}{\partial \kappa} \right) + \langle \text{HF} | \exp(-T^{(0)}) \mathbf{H}_2 \exp(T^{(0)}) | \text{HF} \rangle. \quad (112) \end{aligned}$$

Unlike the case for variational calculations, none of the terms in Eq. (112) vanish and both $\mathbf{t}^{(2)}$ and $\mathbf{H}^{\mathbf{F}} \mathbf{K}^{(2)}$ are required for evaluating Eq. (112). When expansions of the exponential operators are carried out, Eq. (112) may easily be rewritten as

$$\begin{aligned} \frac{d^2 E(\mathbf{R}^0 + \mu)}{d\mu d\mu} &= \langle \text{HF} | \exp(-T^{(0)}) \{ -i [\mathbf{H}^{\mathbf{F}} \hat{\mathbf{K}}^{(2)}, H_0] - [\mathbf{T}^{(2)}, H_0] + [\mathbf{H}^{\mathbf{F}} \hat{\mathbf{K}}^{(1)}, [\mathbf{H}^{\mathbf{F}} \hat{\mathbf{K}}^{(1)}, H_0]] \\ &+ i [\mathbf{T}^{(1)}, [\mathbf{H}^{\mathbf{F}} \hat{\mathbf{K}}^{(1)}, H_0]] + [\mathbf{T}^{(1)}, [\mathbf{T}^{(1)}, H_0]] - 2i [\mathbf{H}^{\mathbf{F}} \hat{\mathbf{K}}^{(1)}, \mathbf{H}_1] - 2[\mathbf{T}^{(1)}, \mathbf{H}_1] + \mathbf{H}_2 \} \exp(T^{(0)}) | \text{HF} \rangle. \quad (113) \end{aligned}$$

Equation (113) represents the molecular Hessian for a coupled cluster wave function. The evaluation of the terms in Eq. (113) involving the orbital operators $\mathbf{H}^{\mathbf{F}} \hat{\mathbf{K}}^{(1)}$ and $\mathbf{H}^{\mathbf{F}} \hat{\mathbf{K}}^{(2)}$ may be greatly simplified using the techniques of Appendix B. If the CC calculation is carried out using a set of MCSCF orbitals in place of the HF orbitals discussed above, the CC molecular gradient and Hessian of Eqs. (111) and (113) may be straightforwardly generalized by replacing the $\mathbf{H}^{\mathbf{F}} \hat{\mathbf{K}}^{(1)}$ and $\mathbf{H}^{\mathbf{F}} \hat{\mathbf{K}}^{(2)}$ operator with the corresponding ${}^{\text{MC}} \hat{\mathbf{K}}^{(1)}$ and ${}^{\text{MC}} \hat{\mathbf{K}}^{(2)}$ operators.

VIII. MOLECULAR GRADIENTS AND HESSIANS FOR THE MØLLER-PLESSET ENERGY

A. The Fock operator

We begin by assuming that a Hartree-Fock Roothaan (HFR) calculation has been carried out at a geometry \mathbf{R}^0 . The Hartree-Fock orbitals and orbital energies are then determined as eigenvectors and eigenvalues of the

Fock matrix

$$\langle \text{HF} | [a_i, [H, a_j^\dagger]] | \text{HF} \rangle = \delta_{ij} \epsilon_j, \quad (114)$$

the orbital energies being

$$\epsilon_i = h_{ii} + \sum_{\alpha} (\langle i\alpha | i\alpha \rangle - \langle i\alpha | \alpha i \rangle), \quad (115)$$

where h_{rr} is defined in Eq. (5) and the integrals $\langle ij | kl \rangle$ refer to the HF basis. The indices $\alpha\beta\gamma\delta$ ($mnpq$) denote (un)occupied orbitals in the Hartree-Fock determinant $| \text{HF} \rangle$ and indices i, j, k , and l refer to unspecified orbital occupation. In Møller-Plesset perturbation theory^{7,24} the Fock operator

$$F = \sum_k \epsilon_k a_k^\dagger a_k \quad (116)$$

is used as the zeroth-order Hamiltonian and all of the Slater determinants $| \tau \rangle$ consisting of all determinants formed from the HF orbital basis other than the HF zeroth-order wave function $| \text{HF} \rangle$ constitute the other

zeroth-order complement states. The fluctuation potential

$$U = \frac{1}{2} \sum_{ijkl} \langle \phi_i \phi_j | \phi_k \phi_l \rangle a_i^\dagger a_j^\dagger a_l a_k - \sum_{i,j,\alpha} C_{\alpha k} C_{\alpha i} (\langle \phi_i \phi_k | \phi_j \phi_l \rangle - \langle \phi_i \phi_k | \phi_i \phi_j \rangle) a_i^\dagger a_j \quad (117)$$

is the perturbation operator. Here $C_{\alpha k}$ is the expansion coefficient of the α th occupied HF orbital in the symmetrically orthogonalized $\{\phi_k\}$ AO basis.

The total energy of a MPPT calculation can be expressed in terms of the HF orbitals and orbital energies of Eq. (114). In MPPT molecular gradient and Hessian calculations we therefore need to determine the linear and quadratic responses of the HF orbitals and orbital energies in Eq. (114). In the next subsection we derive these responses. The simplest nontrivial MPPT total energy expression is obtained in second order. The following subsections show how molecular gradients and Hessians may be obtained for the second-order MPPT energy. We then derive the molecular gradient and show how the Hessian can be obtained for the third-order MPPT energy to demonstrate that the complications involved in obtaining higher MPPT expressions for molecular gradients and Hessians increase no more than do the conventional perturbation theory energy expressions themselves.

B. Orbital and orbital energy responses

At a displaced geometry $\mathbf{R}^0 + \boldsymbol{\mu}$ the orbitals and orbital energies of a Hartree-Fock-Roothaan calculation satisfy

$$\langle \tilde{\mathbf{H}}\mathbf{F} | [\tilde{a}_i, [H, \tilde{a}_j^\dagger]]_+ | \tilde{\mathbf{H}}\mathbf{F} \rangle = \delta_{ij} \tilde{\epsilon}_j, \quad (118)$$

where the symbol $\tilde{}$ denotes orbitals and orbital energies at the displaced geometry. The orbitals at the displaced geometry may be expressed in terms of the original orbitals

$$\tilde{a}_j^\dagger = \exp(-i^{\text{CH}}\hat{\kappa}) a_j^\dagger \exp(i^{\text{CH}}\hat{\kappa}), \quad (119)$$

where the orbital rotation operator

$$i^{\text{CH}}\hat{\kappa} = i \sum_{i>j} c_{\text{H}\kappa_{ij}} (a_i^\dagger a_j - a_j^\dagger a_i) \quad (120)$$

contains both the redundant and nonredundant operators of a Hartree-Fock calculation. It is essential to maintain even the redundant operators ($a_\beta^\dagger a_\alpha - a_\alpha^\dagger a_\beta$) because the nonredundant part of the rotation can only make the unoccupied-occupied and occupied-unoccupied blocks of the Fock matrix equal to zero (i.e., to fulfill the Brillouin theorem),

$$\langle \tilde{\mathbf{H}}\mathbf{F} | [\tilde{a}_m, [H, \tilde{a}_\alpha^\dagger]]_+ | \tilde{\mathbf{H}}\mathbf{F} \rangle = - \langle \tilde{\mathbf{H}}\mathbf{F} | \tilde{a}_m \tilde{a}_\alpha^\dagger H | \tilde{\mathbf{H}}\mathbf{F} \rangle = \langle \tilde{\mathbf{H}}\mathbf{F} | [\tilde{a}_\alpha^\dagger \tilde{a}_m, H] | \tilde{\mathbf{H}}\mathbf{F} \rangle. \quad (121)$$

Rotations carried out within the nonredundant space cannot simultaneously assure that the occupied-occupied

$$\langle \tilde{\mathbf{H}}\mathbf{F} | [\tilde{a}_\alpha, [H, \tilde{a}_\beta^\dagger]]_+ | \tilde{\mathbf{H}}\mathbf{F} \rangle = - \langle \tilde{\mathbf{H}}\mathbf{F} | \tilde{a}_\beta^\dagger H \tilde{a}_\alpha | \tilde{\mathbf{H}}\mathbf{F} \rangle \quad (122)$$

and unoccupied-unoccupied

$$\langle \tilde{\mathbf{H}}\mathbf{F} | [\tilde{a}_m, [H, \tilde{a}_n^\dagger]]_+ | \tilde{\mathbf{H}}\mathbf{F} \rangle = \langle \tilde{\mathbf{H}}\mathbf{F} | \tilde{a}_m H \tilde{a}_n^\dagger | \tilde{\mathbf{H}}\mathbf{F} \rangle \quad (123)$$

blocks of the Fock matrix will also be diagonalized. The occupied-occupied and unoccupied-unoccupied blocks of a Fock matrix are undefined in a total energy optimization procedure but are introduced into the Hartree-Fock Roothaan calculation defined above so as to give the orbital energies a physical interpretation (via Koopmann's theorem).

If we wish to use the HF state response of Sec. II in a Hartree-Fock Roothaan calculation, we may do so by parametrizing the unitary transformation of Eq. (119) such that the unoccupied-occupied block of the Fock matrix is first diagonalized by the HF response of Sec. II and then the occupied-occupied and unoccupied-unoccupied blocks of Fock matrix can be diagonalized by a unitary transformation containing the redundant optimization operators of the HF calculation. The unitary transformation which relates the displaced and undisplaced orbitals then reads

$$\tilde{a}_j^\dagger = \exp(-i^{\text{RD}}\hat{\kappa}) \exp(-i^{\text{HF}}\hat{\kappa}) a_j^\dagger \times \exp(i^{\text{HF}}\hat{\kappa}) \exp(i^{\text{RD}}\hat{\kappa}), \quad (124)$$

where $^{\text{HF}}\hat{\kappa}$ contains the nonredundant rotational parameters of the HF calculation and $^{\text{RD}}\hat{\kappa}$ contains the redundant set of rotational parameters. The linear and quadratic responses of $^{\text{HF}}\hat{\kappa}$ are then given through Eqs. (46) and (47), while the linear and quadratic responses of $^{\text{RD}}\hat{\kappa}$ can be determined from the requirement that the occupied-occupied and unoccupied-unoccupied blocks of the Fock matrix be diagonal through first and second order (in the nuclear displacement), respectively.

In the present communication we choose, however, to determine the orbital and orbital energy responses using the parametrization of Eq. (119) where the redundant and nonredundant parameters of the HF calculation are determined simultaneously. Such a determination is completely analogous to the one carried out in a coupled Hartree-Fock (CH) calculation.^{7,22} The orbital energies and the orbital rotational parameters may then be expanded in power series in $\boldsymbol{\mu}$,

$$\tilde{\epsilon} = \epsilon^{(0)} + \boldsymbol{\mu} \boldsymbol{\epsilon}^{(1)} + \frac{1}{2} \boldsymbol{\mu} \boldsymbol{\epsilon}^{(2)} \boldsymbol{\mu} + \dots, \quad (125)$$

$$i^{\text{CH}}\hat{\kappa} = i^{\text{CH}}\hat{\kappa}^{(0)} + \boldsymbol{\mu} i^{\text{CH}}\hat{\kappa}^{(1)} + \frac{1}{2} \boldsymbol{\mu} i^{\text{CH}}\hat{\kappa}^{(2)} \boldsymbol{\mu} + \dots, \quad (126)$$

where the individual responses are determined by requiring Eq. (118) to be satisfied through each power in $\boldsymbol{\mu}$. We initially rewrite Eq. (118) as

$$\tilde{\epsilon}_r = \langle \mathbf{H}\mathbf{F} | [a_r, [\tilde{H}(\mathbf{R}^0 + \boldsymbol{\mu}), a_r^\dagger]]_+ | \mathbf{H}\mathbf{F} \rangle, \quad (127)$$

where $\tilde{H}(\mathbf{R}^0 + \boldsymbol{\mu}) = \exp(-i^{\text{CH}}\hat{\kappa}) H(\mathbf{R}^0 + \boldsymbol{\mu}) \exp(i^{\text{CH}}\hat{\kappa})$. Using exponential operator expansions we readily see that the zeroth-order equation reduces to the Fock matrix equation at undisplaced geometry [Eq. (114)]. $i^{\text{CH}}\hat{\kappa}^{(0)}$ therefore is zero and $\epsilon^{(0)}$ is the orbital energy of the undisplaced calculation. The first-order equation reads

$$\delta_{ki} \epsilon_k^{(1)} = \langle \mathbf{H}\mathbf{F} | [a_k, [H_1, a_i^\dagger]]_+ | \mathbf{H}\mathbf{F} \rangle - i \langle \mathbf{H}\mathbf{F} | [a_k, [[i^{\text{CH}}\hat{\kappa}^{(1)}, H_0], a_i^\dagger]]_+ | \mathbf{H}\mathbf{F} \rangle. \quad (128)$$

The off-diagonal elements of Eq. (128) constitute a set of coupled linear equations in $i^{\text{CH}}\hat{\kappa}_{ki}^{(1)}$ which determine $i^{\text{CH}}\hat{\kappa}^{(1)}$. Inserting $i^{\text{CH}}\hat{\kappa}^{(1)}$ into the diagonal elements of Eq. (128) then determines $\epsilon_k^{(1)}$.

The second-order response equation reads

$$\delta_{kl} \epsilon_k^{(2)} = 2 \langle \text{HF} | [a_k, [\mathbf{H}_2, a_l^\dagger]] | \text{HF} \rangle - 2i \langle \text{HF} | [a_k, [[\text{CH}\hat{\mathbf{K}}^{(1)}, \mathbf{H}_1], a_l^\dagger]] | \text{HF} \rangle \\ - 2i \langle \text{HF} | [a_k, [[\text{CH}\hat{\mathbf{K}}^{(2)}, H_0], a_l^\dagger]] | \text{HF} \rangle - \langle \text{HF} | [a_k, [[\text{CH}\hat{\mathbf{K}}^{(1)}, [\text{CH}\hat{\mathbf{K}}^{(1)}, H_0]], a_l^\dagger]] | \text{HF} \rangle. \quad (129)$$

The off-diagonal elements of Eq. (129) give a set of linear equations that determine $\text{CH}\hat{\mathbf{K}}^{(2)}$ once $\text{CH}\hat{\mathbf{K}}^{(1)}$ is determined via Eq. (128). The diagonal elements of Eq. (129) determine $\epsilon^{(2)}$ once a $\text{CH}\hat{\mathbf{K}}^{(2)}$ has been determined. The actual evaluation of the $\epsilon^{(1)}$, $\text{CH}\hat{\mathbf{K}}^{(2)}$, and $\text{CH}\hat{\mathbf{K}}^{(2)}$ responses may be simplified using the techniques of Appendix B.

Now that it has been demonstrated how the orbital and orbital energy responses can be evaluated, let us turn to how the second- and third-order MPPT energies depend on μ so that we can extract the desired molecular gradients and Hessians.

C. Second-order Møller-Plesset energy

The second order MPPT energy is given as

$$E(\mathbf{R}^0) = \langle \text{HF} | H | \text{HF} \rangle + \sum_r \frac{\langle \text{HF} | H | r \rangle \langle r | U | \text{HF} \rangle}{E_{\text{HF}}^0 - E_r^0}, \quad (130)$$

where E_{HF}^0 and E_r^0 are the zeroth order energies of $|\text{HF}\rangle$ and $|r\rangle$, respectively. At a displaced geometry $\mathbf{R}^0 + \mu$, it becomes

$$E(\mathbf{R}^0 + \mu) = \langle \tilde{\text{HF}} | H(\mathbf{R}^0 + \mu) | \tilde{\text{HF}} \rangle \\ + \sum_r \frac{\langle \tilde{\text{HF}} | H(\mathbf{R}^0 + \mu) | \tilde{r} \rangle \langle \tilde{r} | U(\mathbf{R}^0 + \mu) | \tilde{\text{HF}} \rangle}{\tilde{E}_{\text{HF}}^0 - \tilde{E}_r^0}, \quad (131)$$

where the $\tilde{}$ symbol denotes orbitals and states at the displaced geometry. The first term in Eq. (131) is the Hartree-Fock total energy expression at $\mathbf{R}^0 + \mu$; its linear and quadratic dependence on μ is determined by the Hartree-Fock molecular gradient and Hessian given previously in Eqs. (55) and (61), respectively. We therefore concentrate on determining the linear and quadratic μ dependence of the correlation (last) term in Eq. (131). The Hamiltonian dependence $H(\mathbf{R}^0 + \mu)$ on μ is written out explicitly through second order in Eq. (9). The fluctuation potential (μ) dependence may be determined in a manner similar to that used to express the Hamiltonian's dependence:

$$U(\mathbf{R}^0 + \mu) = U_0 + \mu \mathbf{U}_1 + \frac{1}{2} \mu \mathbf{U}_2 \mu + \dots, \quad (132)$$

where U_0 is the fluctuation potential at undisplaced geometry and \mathbf{U}_1 and \mathbf{U}_2 are defined as

$$\mathbf{U}_1 = \frac{1}{2} \sum_{rs} \nabla \langle \langle \phi_r \phi_s | \phi_t \phi_u \rangle \rangle a_r^\dagger a_s^\dagger a_u a_t \\ - \sum_{rs} C_{\alpha t} C_{\alpha u} \nabla \langle \langle \phi_r \phi_t | \phi_s \phi_u \rangle - \langle \phi_r \phi_t | \phi_u \phi_s \rangle \rangle a_r^\dagger a_s, \quad (133)$$

and

$$\mathbf{U}_2 = \frac{1}{2} \sum_{rs} \nabla \nabla \langle \langle \phi_r \phi_s | \phi_t \phi_u \rangle \rangle a_r^\dagger a_s^\dagger a_u a_t \\ - \sum_{rs} C_{\alpha t} C_{\alpha u} \nabla \nabla \langle \langle \phi_r \phi_t | \phi_s \phi_u \rangle - \langle \phi_r \phi_t | \phi_u \phi_s \rangle \rangle a_r^\dagger a_s, \quad (134)$$

where we have used the definitions of Eqs. (15) and (18). Equations (133) and (134) express the μ dependence of U in the symmetrically orthogonalized basis. It is, of course, possible and probably wise to transform \mathbf{U}_1 and \mathbf{U}_2 to the HF molecular orbital basis before evaluating their average or transition values among $|\text{HF}\rangle$ and $|r\rangle$.

From Eq. (131) it is clear that only doubly excited determinants with respect to $|\tilde{\text{HF}}\rangle$ contribute in the sum over states. These doubly excited states may be expressed in terms of the orbitals at \mathbf{R}^0 as

$$|\tilde{r}\rangle = \tilde{a}_m^\dagger \tilde{a}_n^\dagger \tilde{a}_\alpha \tilde{a}_\beta |\tilde{\text{HF}}\rangle = \exp(i \text{CH}\hat{\mathbf{K}}) a_m^\dagger a_n^\dagger a_\alpha a_\beta |\text{HF}\rangle, \quad (135)$$

where Eqs. (24) and (51) are used and $m > n$, $\alpha > \beta$. The orbital energy denominator corresponding to the doubly excited state in Eq. (131) becomes

$$\tilde{\Delta} \epsilon_r = \tilde{E}_{\text{HF}}^0 - \tilde{E}_r^0 = -\tilde{\epsilon}_m - \tilde{\epsilon}_n + \tilde{\epsilon}_\alpha + \tilde{\epsilon}_\beta, \quad (136)$$

where the $\tilde{\epsilon}_i$ are Hartree-Fock orbital energies at the displaced geometry. Inserting the power series expansion of the orbital energies in Eq. (125) into Eq. (136) gives

$$\Delta \tilde{\epsilon}_r = \Delta \epsilon_r^{(0)} + \mu \Delta \epsilon_r^{(1)} + \frac{1}{2} \mu \Delta \epsilon_r^{(2)} \mu, \quad (137)$$

where

$$\Delta \epsilon_r^{(i)} = +\epsilon_\alpha^{(i)} + \epsilon_\beta^{(i)} - \epsilon_m^{(i)} - \epsilon_n^{(i)}, \quad i = 0, 1, 2, \dots \quad (138)$$

The dependence on nuclear displacement has now been described for the individual components in the second term of Eq. (131). Introducing this dependence explicitly displays more clearly the μ dependence of the second-order MPPT energy

$$\Delta E_2(\mathbf{R}^0 + \mu) = \sum_r \frac{\langle \text{HF} | \exp(-i \text{CH}\hat{\mathbf{K}}) (H_0 + \mu \mathbf{H}_1 + \frac{1}{2} \mu \mathbf{H}_2 \mu) \exp(i \text{CH}\hat{\mathbf{K}}) | r \rangle \langle r | \exp(-i \text{CH}\hat{\mathbf{K}}) (U_0 + \mu \mathbf{U}_1 + \frac{1}{2} \mu \mathbf{U}_2 \mu) \exp(i \text{CH}\hat{\mathbf{K}}) | \text{HF} \rangle}{\Delta \tilde{\epsilon}_r}. \quad (139)$$

An expansion may now be carried out on the exponential operators

$$\exp(-i \text{CH}\hat{\mathbf{K}}) H(\mathbf{R}^0 + \mu) \exp(i \text{CH}\hat{\mathbf{K}}) = H(\mathbf{R}^0 + \mu) - i [\text{CH}\hat{\mathbf{K}}, H(\mathbf{R}^0 + \mu)] - \frac{1}{2} [\text{CH}\hat{\mathbf{K}}, [\text{CH}\hat{\mathbf{K}}, H(\mathbf{R}^0 + \mu)]] + \dots \quad (140)$$

and the denominators in Eq. (139) may be expanded as

$$\frac{1}{\Delta \tilde{\epsilon}} = \frac{1}{\Delta \epsilon^{(0)}} - \frac{\mu \Delta \epsilon^{(1)}}{(\Delta \epsilon^{(0)})^2} - \frac{1}{2} \frac{\mu \Delta \epsilon^{(2)} \mu}{(\Delta \epsilon^{(0)})^3} + \frac{\mu \Delta \epsilon^{(1)} \Delta \epsilon^{(1)} \mu}{(\Delta \epsilon^{(0)})^3} + \dots \quad (141)$$

Using Eqs. (140) and (141) we may identify the terms in Eq. (139) that are linear and quadratic in μ . These terms

represent the correlation contributions to the desired MPPT molecular gradients and Hessians. The linear terms become

$$\frac{d[\Delta E_2(\mathbf{R}^0 + \boldsymbol{\mu})]}{d\boldsymbol{\mu}} = \sum_r \frac{\langle \text{HF} | H_0 | r \rangle}{\Delta \epsilon_r^{(0)}} \mathbf{T}_r, \quad (142)$$

where

$$\mathbf{T}_r = \langle r | 2\mathbf{U}_1 - i[\text{CH}\hat{\mathbf{K}}^{(1)}, H_0 + U_0] - \frac{\Delta \epsilon_r^{(1)}}{\Delta \epsilon_r^{(0)}} H_0 | \text{HF} \rangle. \quad (143)$$

To obtain Eq. (143) we have used

$$\langle r | H_i | \text{HF} \rangle = \langle r | U_i | \text{HF} \rangle, \quad i = 0, 1, 2. \quad (144)$$

The quadratic term may similarly be identified as

$$\frac{d^2 \Delta E_2(\mathbf{R}^0 + \boldsymbol{\mu})}{d\boldsymbol{\mu} d\boldsymbol{\mu}} = \sum_r \left(\frac{\langle \text{HF} | H_0 | r \rangle}{\Delta \epsilon_r^{(0)}} \mathbf{V}_r + \frac{\langle 0 | H_1 | r \rangle}{\Delta \epsilon_r^{(0)}} \mathbf{X}_r + \frac{\langle \text{HF} | [\text{CH}\hat{\mathbf{K}}^{(1)} H_0] | r \rangle}{\Delta \epsilon_r^{(0)}} \mathbf{Y}_r \right), \quad (145)$$

where

$$\begin{aligned} \mathbf{V}_r = & \langle r | 2\mathbf{H}_2 - i2[\text{CH}\hat{\mathbf{K}}^{(1)}, \mathbf{H}_1 + \mathbf{U}_1] - [\text{CH}\hat{\mathbf{K}}^{(1)}, [\text{CH}\hat{\mathbf{K}}^{(1)}, H_0 + U_0]] - 2i[\text{CH}\hat{\mathbf{K}}^{(2)}, H_0 + U_0] | \text{HF} \rangle \\ & + \frac{2(\Delta \epsilon_r^{(1)})^2}{(\Delta \epsilon_r^{(0)})^2} \frac{\Delta \epsilon_r^{(2)}}{\Delta \epsilon_r^{(0)}} \langle r | H_0 | \text{HF} \rangle - 2\langle \text{HF} | \mathbf{H}_1 | r \rangle \frac{\Delta \epsilon_r^{(1)}}{\Delta \epsilon_r^{(0)}} + 4i\langle \text{HF} | [\text{CH}\hat{\mathbf{K}}^{(1)}, H_0] | r \rangle \frac{\Delta \epsilon_r^{(1)}}{\Delta \epsilon_r^{(0)}}, \end{aligned} \quad (146)$$

$$\mathbf{X}_r = -2i\langle r | [\text{CH}\hat{\mathbf{K}}^{(1)}, H_0 + U_0] + \mathbf{U}_1 | \text{HF} \rangle - \frac{2\Delta \epsilon_r^{(1)}}{\Delta \epsilon_r^{(0)}} \langle r | H_0 | \text{HF} \rangle, \quad (147)$$

and

$$\mathbf{Y}_r = -2\langle r | [\text{CH}\hat{\mathbf{K}}^{(1)}, U_0] | \text{HF} \rangle. \quad (148)$$

Equations (142) and (145) thus give the second-order correlation contribution to the Møller–Plesset molecular gradient and Hessian, respectively. We should point out that most of the terms in Eqs. (142) and (145) may be efficiently evaluated using the techniques described in Appendix B.

D. Third-order Møller–Plesset energy

The third-order contribution to the correlation energy may, at a displaced nuclear geometry, be written as

$$\begin{aligned} \Delta E_3(\mathbf{R}^0 + \boldsymbol{\mu}) = & \sum_{r,s} \frac{\langle \tilde{\text{HF}} | U(\mathbf{R}^0 + \boldsymbol{\mu}) | \tilde{r} \rangle \langle \tilde{r} | U(\mathbf{R}^0 + \boldsymbol{\mu}) | \tilde{s} \rangle \langle \tilde{s} | U(\mathbf{R}^0 + \boldsymbol{\mu}) | \tilde{\text{HF}} \rangle}{(\tilde{E}_{\text{HF}}^0 - \tilde{E}_r^0)(\tilde{E}_{\text{HF}}^0 - E_s^0)} \\ & - \langle \tilde{\text{HF}} | U(\mathbf{R}^0 + \boldsymbol{\mu}) | \tilde{\text{HF}} \rangle \sum_r \frac{\langle \tilde{\text{HF}} | U(\mathbf{R}^0 + \boldsymbol{\mu}) | \tilde{r} \rangle \langle \tilde{r} | U(\mathbf{R}^0 + \boldsymbol{\mu}) | \tilde{\text{HF}} \rangle}{(\tilde{E}_{\text{HF}}^0 - \tilde{E}_r^0)^2}. \end{aligned} \quad (149)$$

It is clear from Eq. (149) that only doubly excited determinants with respect to $|\tilde{\text{HF}}\rangle$ contribute in the sums over the states (r and s). Expressing these doubly excited states in terms of the orbitals appropriate to \mathbf{R}^0 [see Eq. (135)] and using Eqs. (132), (137), (140), and (141) allows us to identify the terms that are linear in $\boldsymbol{\mu}$ in Eq. (149) as

$$\begin{aligned} \frac{d\Delta E_3(\mathbf{R}^0 + \boldsymbol{\mu})}{d\boldsymbol{\mu}} = & \sum_{rs} \frac{\langle \text{HF} | 2\mathbf{U}_1 - 2i[\text{CH}\hat{\mathbf{K}}^{(1)}, U_0] - \frac{2\Delta \epsilon_r^{(1)}}{\Delta \epsilon_r^{(0)}} U_0 | r \rangle \langle r | U_0 | s \rangle \langle s | U_0 | \text{HF} \rangle}{\Delta \epsilon_r^{(0)} \Delta \epsilon_s^{(0)}} \\ & + \sum_{rs} \frac{\langle \text{HF} | U_0 | r \rangle \langle r | \mathbf{U}_1 - i[\text{CH}\hat{\mathbf{K}}^{(1)}, U_0] | s \rangle \langle s | U_0 | \text{HF} \rangle}{\Delta \epsilon_r^{(0)} \Delta \epsilon_s^{(0)}} - 2\langle \text{HF} | U_0 | \text{HF} \rangle \\ & \times \sum_r \frac{\langle \text{HF} | \mathbf{U}_1 - i[\text{CH}\hat{\mathbf{K}}^{(1)}, H_0] + \frac{\Delta \epsilon_r^{(1)}}{\Delta \epsilon_r^{(0)}} U_0 | r \rangle \langle r | U_0 | \text{HF} \rangle}{(\Delta \epsilon_r^{(0)})^2} - \langle \text{HF} | \mathbf{U}_1 - i[\text{CH}\hat{\mathbf{K}}^{(1)}, U_0] | \text{HF} \rangle \sum_r \frac{\langle \text{HF} | U_0 | r \rangle \langle r | U_0 | \text{HF} \rangle}{(\Delta \epsilon_r^{(0)})^2}, \end{aligned} \quad (150)$$

where $\Delta \epsilon_r^{(1)}$ denotes the orbital energy differences $\mathbf{E}_{\text{HF}}^{(1)} - \mathbf{E}_r^{(1)}$. Equation (150) gives the third-order correlation contribution to the Møller–Plesset molecular gradient. It is worth noticing that evaluation of Eq. (150) requires one to set up an integral list containing \mathbf{H}_1 and $[\text{CH}\hat{\mathbf{K}}^{(1)}, U_0]$ and further to evaluate $\Delta \epsilon_r^{(1)}$. As soon as these quantities have been determined, the evaluation of Eq. (150) reduces to an evaluation of a modified third-order correlation energy. Since the quantities \mathbf{H}_1 ,

$[\text{CH}\hat{\mathbf{K}}^{(1)}, U_0]$, and $\Delta \epsilon_r^{(1)}$ also were required for evaluating the second-order correlation contribution to the MPPT molecular gradient, it is easily seen that the complication involved in evaluating the correlation contributions to the MPPT molecular gradient are in direct proportion to those arising in the order-by-order energy calculations. These same observations also hold when evaluating higher-order correlation contribution to the MPPT molecular gradient.

The third-order correlation contribution to the MPPT molecular Hessian is identified as the terms in Eq. (149) that are quadratic in μ . We will not write out an explicit expression for the Hessian but we do point out that the basic quantities necessary for evaluating the Hessian are the same as those required for evaluating the second-order MPPT molecular Hessian.

IX. COMPARISON WITH RESULTS OF OTHERS AND CONCLUDING REMARKS

Previous attempts¹⁻¹³ to derive analytical expressions for molecular gradients and Hessians use the configuration mixing coefficients $\{C_g\}$, the molecular orbital expansion coefficients $\{C_{ia}\}$ and the *nonorthogonal* atomic basis orbitals $\{\chi_a\}$ as parameters which depend implicitly on the nuclear positions $\{\mathbf{R}\}$. The gradient is then, for example, determined as

$$\frac{dE}{d\mu} = \sum_g \frac{\partial F}{\partial C_g} \frac{\partial C_g}{\partial \mu} + \sum_{ia} \frac{\partial F}{\partial C_{ia}} \frac{\partial C_{ia}}{\partial \mu} + \sum_a \frac{\partial F}{\partial \chi_a} \frac{\partial \chi_a}{\partial \mu} + \left\langle 0 \left| \frac{\partial H}{\partial \mu} \right| 0 \right\rangle, \quad (151)$$

where F is the Lagrangian function which combines the variational energy E with the relevant constraints:

$$F = E - \sum_{ij} \epsilon_{ij} \left(\sum_{ab} C_{ia} S_{ab} C_{jb} - \delta_{ij} \right) - \eta \left(\sum_g C_g^2 - 1 \right). \quad (152)$$

The Lagrange multipliers ϵ_{ij} are introduced to assure that the molecular orbital expansion coefficients $\{C_{ia}\}$ describe a set of orthonormal molecular orbitals. The Lagrange multiplier η assures that the configuration amplitudes are normalized. In forming the partial derivatives in Eq. (151) all parameters but the one appearing in the derivative are held fixed. The last term in Eq. (151) is the Hellmann-Feynman force term. In SCF or MCSCF theories the orbital and configuration expansion coefficients are determined such that both

$$\frac{\partial F}{\partial C_{ia}} = 0 \quad (153)$$

and

$$\frac{\partial F}{\partial C_g} = 0. \quad (154)$$

The contributions to the molecular gradient from the first two terms in Eq. (151) therefore vanish in SCF and MCSCF theory, and the molecular gradient then becomes

$$\frac{dE}{d\mu} = \sum_a \frac{\partial E}{\partial \chi_a} \frac{\partial \chi_a}{\partial \mu} - \sum_{ij} \epsilon_{ij} C_{ia} C_{jb} \frac{\partial S_{ab}}{\partial \mu} + \left\langle 0 \left| \frac{\partial H}{\partial \mu} \right| 0 \right\rangle. \quad (155)$$

The next to the last term in Eq. (155) is referred to by Pulay as the density force term. It has its origin in the third term (the basis function derivative term) of Eq. (151) and its effect is to assure that the molecular orbital normalization condition (which contains an overlap matrix) is fulfilled when the basis function variations are carried out.

If, alternatively, one had chosen to use an orthonormal set of atomic orbitals $\{\phi_i\}$ as variational parameters, the energy gradient would be determined from the equation

$$\frac{dE}{d\mu} = \sum_g \frac{\partial F}{\partial C_g} \frac{\partial C_g}{\partial \mu} + \sum_{ia} \frac{\partial F}{\partial C_{ia}} \frac{\partial C_{ia}}{\partial \mu} + \sum_i \frac{\partial F}{\partial \phi_i} \frac{\partial \phi_i}{\partial \mu} + \left\langle 0 \left| \frac{\partial H}{\partial \mu} \right| 0 \right\rangle, \quad (156)$$

where the Lagrangian function now is

$$F = E - \sum_{ij} \left(\epsilon_{ij} \sum_a C_{ia} C_{ja} - \delta_{ij} \right) - \eta \left(\sum_g C_g^2 - 1 \right). \quad (157)$$

Notice that the atomic overlap matrix does not appear in the constrained equations since the molecular orbital expansion coefficients are now expressed in terms of *orthonormal* atomic orbitals. Since Eqs. (153) and (154) also hold for the variable choice in Eq. (157), for either an SCF or MCSCF wave function the molecular gradient may, for an orthonormal set of atomic orbitals, be rewritten as

$$\frac{dE}{d\mu} = \sum_i \frac{\partial E}{\partial \phi_i} \frac{\partial \phi_i}{\partial \mu} + \left\langle 0 \left| \frac{\partial H}{\partial \mu} \right| 0 \right\rangle. \quad (158)$$

Equation (158) contains no density force term. However, the derivatives in Eq. (157) refer to orthogonalized atomic orbitals. The derivatives in Eq. (155) which contained a density force term referred to primitive (nonorthogonal) atomic orbitals. Using the fact that the orthogonalized atomic orbitals are linear combinations of primitive atomic orbitals with geometry dependent expansion coefficients, it is shown in Appendix A4 how Eq. (155) may be reduced to Eq. (158) in the SCF and MCSCF case and thus how the density force term is actually included in the basis set derivative when an orthogonalized atomic basis is used. It is also clear from the previous analysis that terms analogous to the density force term, which may appear in other wave function cases if the gradients are expressed in a non-orthogonal atomic basis, would not show up if the results were expressed in terms of orthogonalized atomic orbitals. In addition, the use of nonorthogonal orbitals would require, in calculating the molecular Hessian, knowledge of Lagrangian multiplier derivatives.

In the approach advocated in the present paper, we use the configuration (S_{n0}) and orbital ($\kappa_{rs}, r > s$) rotation amplitudes and a set of *orthonormal* atomic basis functions $\{\phi_i\}$ as our parameters in terms of which the nuclear-displacement response of the energy is computed. This allows us to avoid constraint equations and Lagrange multipliers as in Eq. (152) and (157).

Analytical gradients of HF or CI wave functions have previously always been derived in terms of a set of canonical Hartree-Fock orbitals whose responses were determined from coupled Hartree-Fock theory in a manner paralleling Sec. VII B. The canonical Hartree-Fock equations constrain the form of the occupied-occupied and unoccupied-unoccupied blocks of the Fock matrix to be the same as the form of the unoccupied-occupied block, which is determined from the Brillouin theorem.¹⁴ This particular choice of the occupied-occupied and unoccupied-unoccupied blocks of the Fock matrix assures that the orbital energies have a physical interpretation via Koopmans' theorem although it also introduces additional geometry dependent parameters (the redundant orbital rotational parameters $\kappa_{\alpha\beta}$ and κ_{mn} of

Eq. (124) that are not present in our earlier analysis). The Hartree-Fock molecular gradient and Hessian are however, invariant to the introduction of this additional set of geometry dependent parameters. To clarify this point, consider at a displaced geometry ($\mathbf{R}^0 + \boldsymbol{\mu}$) the Hartree-Fock energy described in terms of canonical Hartree-Fock orbitals as

$$E(\mathbf{R}^0 + \boldsymbol{\mu}) = \langle \text{HF} | \exp(-i^{\text{CH}}\hat{\kappa}) H(\mathbf{R}^0 + \boldsymbol{\mu}) \exp(i^{\text{CH}}\hat{\kappa}) | \text{HF} \rangle, \quad (159)$$

where the $^{\text{CH}}\hat{\kappa}$ are defined in Eq. (120) and the response of $^{\text{CH}}\kappa$ to a nuclear displacement is determined from Eqs. (126)–(129). Using Eq. (124) we may, alternatively and without loss of generality, write Eq. (159) as

$$\begin{aligned} E(\mathbf{R}^0 + \boldsymbol{\mu}) &= \langle \text{HF} | \exp(-i^{\text{RD}}\hat{\kappa}) \exp(-i^{\text{HF}}\hat{\kappa}) H(\mathbf{R}^0 + \boldsymbol{\mu}) \\ &\times \exp(i^{\text{HF}}\hat{\kappa}) \exp(i^{\text{RD}}\hat{\kappa}) | \text{HF} \rangle \\ &= \langle \text{HF} | \exp(-i^{\text{HF}}\hat{\kappa}) H(\mathbf{R}^0 + \boldsymbol{\mu}) \exp(i^{\text{HF}}\hat{\kappa}) | \text{HF} \rangle \end{aligned} \quad (160)$$

which is the Hartree-Fock total energy expression used in our earlier development. The total energy expressions of Eqs. (159) and (160) are identical even though the orbital rotations are parametrized differently. Hence, nuclear displacement derivatives of the two expressions are identical.

To derive Eq. (160) we used the fact that the redundant rotations have no effect on the total Hartree-Fock wave function

$$\exp(i^{\text{RD}}\hat{\kappa}) | \text{HF} \rangle = | \text{HF} \rangle. \quad (161)$$

When the action of these same redundant rotations on a correlated wave function as $| \text{CI} \rangle$ is considered, $\exp(i^{\text{RD}}\hat{\kappa}) | \text{CI} \rangle$ is easily seen not to be identical to $| \text{CI} \rangle$. As a result, the analytical expressions for the molecular gradient and Hessian of a CI wave function will differ depending on whether canonical Hartree-Fock orbitals or noncanonical Hartree-Fock orbitals are used to construct the $| \text{CI} \rangle$ wave function. If one desires to determine the CI molecular gradient and Hessian using a set of canonical Hartree-Fock orbitals one may simply replace $^{\text{HF}}\hat{\kappa}^{(1)}$ and $^{\text{HF}}\hat{\kappa}^{(2)}$ with $^{\text{CH}}\hat{\kappa}^{(1)}$ and $^{\text{CH}}\hat{\kappa}^{(2)}$ in the expressions for the CI molecular gradient and Hessian given in Eqs. (76), (79), and (80), after determining $^{\text{CH}}\kappa^{(1)}$ and $^{\text{CH}}\kappa^{(2)}$ as in Sec. VII B.

Because the fully occupied and virtual orbitals are not uniquely determined in an exponential unitary MCSCF calculation, CI calculations performed using these MCSCF orbitals with a fixed configuration list at two neighboring geometries will not be consistent. In particular, if the two geometries are only infinitesimally displaced, the resultant CI energy change may not be infinitesimally small. One can, however, uniquely determine all MCSCF orbitals and solve this problem by diagonalizing the redundant part of a Fock potential¹⁴ using $\exp(i^{\text{RD}}\hat{\kappa})$. An analogous difficulty arises in performing a CC calculation using nonuniquely defined orbitals; this problem can also be solved by the above outlined procedure.

In addition to what we consider to be a more straightforward treatment of atomic orbital basis effects, we have obtained several gradient and Hessian expressions for the first time. To clarify this point, it is appropriate

at this time to provide a brief comparison of how our results compare with those obtained by other workers. To this end, let us now consider each wave function case treated in this paper.

A. The Hartree-Fock wave function

Equations (55) and (61) give our expressions for the HF gradient and Hessian, respectively. The gradient result already exists in the literature, for example, in the review by Pulay¹ and in Pople's 1979 MPPT article.⁷ Both of these previous results contain the density force terms [Eq. (14) of Ref. 1] which arise via the application of the constraints on the C_{ia} amplitudes given in Eq. (152). As described earlier, the density force term does not arise in our treatment because a set of orthogonalized atomic orbitals was used.

The HF Hessian has been given by Pople⁷ in his MPPT paper and earlier by Thomsen and Swanström and by Bratoz.³ As was the case for the HF gradient discussed above, these earlier HF Hessian results seem to agree with our expression except for the presence of derivatives of the so-called density force terms which would not have arisen if orthonormal atomic orbitals had been used (i.e., the ∇S_{ab} term mentioned above would vanish). Note that our HF molecular gradient and Hessian cover all open-shell cases. In contrast, Fock operator based molecular gradients and Hessians have conventionally been derived for each individual open shell case.

B. The MCSCF wave function

The gradient for the MCSCF case has been given explicitly by Schaefer *et al.*⁹ and implicitly by Pulay in Ref. 1 and for the complete active space SCF method in Ref. 26. We do not know of any previous MCSCF Hessian expressions in the open literature, hence our result [Eq. (70)] is new. The gradient results of Refs. 1 and 9 seem to agree with our Eq. (64) except that they contain the density-force terms discussed earlier.

C. The CI wave function

Both Schaefer⁹ and Pople⁷ have given explicit treatments of the CI gradient, and Pulay's treatment¹ can be viewed as also giving implicitly the CI gradient. Pople's treatment⁷ was limited to CI wave functions of the double excitation form, whereas Schaefer's⁹ was rather general. To our knowledge, no one else has obtained an analytical result for the molecular Hessian in this case.²⁵

The gradient expressions of Pople and of Schaefer have the same elements as we find in Eq. (76) but they also contain factors which arise from the density force terms mentioned earlier because they are expressed in terms of nonorthogonal atomic orbital basis sets.

D. The MPPT wave function

The gradient corresponding to the second-order MPPT energy has been given explicitly by Pople *et al.*⁷ We do not know of any previous second-order Hessian or third-order gradient expressions with which to compare our results [Eqs. (145) and (150)]. The second-

order gradient expression of Pople in Ref. 7 Eq. (62) seems to agree with our Eq. (142) except for terms similar to the density force term arising in the HF case. These density force terms occur because the coupled Hartree-Fock equations in Ref. 7 had the imposed constraint that the resultant orbitals be orthonormal through each power in the nuclear displacement. We do not have such terms because we have solved the coupled Hartree-Fock equations by carrying out an exponential unitary transformation of the orbitals thereby guaranteeing the orbitals to be orthonormal.

E. The coupled-cluster wave function

Gradient and Hessian expressions for the CC wave function do not, to our knowledge, exist in the literature. The linear and quadratic responses of the CC amplitudes (neglecting orbital response) have previously been derived by Monkhorst.²¹ The combination of t amplitude and orbital responses such as we described in Sec. VII have not previously been derived. As a result, our gradient and Hessian expressions [Eqs. (111) and (113)] are new and there are no other CC results with which to compare them.

X. SUMMARY

In summary, we have obtained gradient and Hessian expressions for several classes of wave functions (SCF, MCSCF, CI, MPPT, and CC). Most of these results do not exist elsewhere in the literature. We made use of exponential unitary operator methods because they allow us to express the wave function's configuration and orbital responses in terms of the minimum number of parameters; no constraint equations are needed. We have further incorporated all basis set effects within the finite-basis Hamiltonian. This turns out to be very useful when deriving the orbital and wave function responses.

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APPENDIX A: FINITE-BASIS EFFECTS

1. Derivatives of atomic basis orbitals

A single primitive Gaussian type orbital (PGTO) centered at $R_A = X_A, Y_A, Z_A$ has a functional form

$$G_A(r) = N_A^{-1/2} (x - X_A)^l (y - Y_A)^m \times (z - Z_A)^n \exp[-\alpha(r - R_A)^2], \quad (\text{A1})$$

where the integers l, m , and n define the nature of the Cartesian PGTO, α is the orbital exponent, and $N_A^{-1/2}$ is a normalization constant whose value is independent of R_A . The first and second derivatives of such a basis orbital with respect to X_A, Y_A , or Z_A are needed to form \mathbf{H}_1 and \mathbf{H}_2 as outlined in Sec. II:

$$\frac{dG_A}{dX_A} = -N_A^{-1/2} (y - Y_A)^m (z - Z_A)^n [l(x - X_A)^{l-1} - 2\alpha(x - X_A)^{l+1}] \exp[-\alpha(r - R_A)^2], \quad (\text{A2})$$

$$\frac{d^2 G_A}{dX_A^2} = N_A^{-1/2} (y - Y_A)^m (z - Z_A)^n [l(l-1)(x - X_A)^{l-2} - (4l+2)\alpha(x - X_A)^l + 4\alpha^2(x - X_A)^{l+2}] \exp[-\alpha(r - R_A)^2], \quad (\text{A3})$$

$$\frac{d^2 G_A}{dX_A dY_A} = N_A^{-1/2} (z - Z_A)^n [l(x - X_A)^{l-1} - 2\alpha(x - X_A)^{l+1}] \times [m(y - Y_A)^{m-1} - 2\alpha(y - Y_A)^{m+1}] \exp[-\alpha(r - R_A)^2]. \quad (\text{A4})$$

All other first and second derivatives can be obtained in like fashion by simply permuting X_A, Y_A, Z_A and l, m, n .

Given the derivatives of the PGTO's it is now possible to obtain expressions for the derivatives of the contracted GTO's (G_A^c) and point-group symmetry adapted GTO's (G_A^s) which form the final nonorthogonal orbital bases used in most *ab initio* calculations. Because the atomic orbital contraction coefficients $D_{A,A'}$ combine PGTO's which reside on the same center (R_A), their numerical values are independent of R_A . Similarly, the point-group symmetry expansion coefficients $M_{A',A''}^s$ (s labels the irreducible representation) are independent of the geometrical parameters (R_A, R_B , etc.) which describe where the PGTO's and contracted GTO's sit. As a result, the derivatives of the symmetry adapted orbitals

$$G_{A'}^s = \sum_{A'} M_{A',A''}^s G_{A''}^c = \sum_{A',A} M_{A',A''}^s D_{A,A'} G_A \quad (\text{A5})$$

are simply combinations of derivatives of the PGTO orbitals, which were given above. For example,

$$\frac{d^2 G_{A'}^s}{dX_C dY_C} = \sum_{A',A} M_{A',A''}^s D_{A,A'} \frac{d^2 G_A}{dX_C dY_C}. \quad (\text{A6})$$

Notice that the PGTO's and their contractions, sit at R_A , so that $dG_A/dY_C = 0$ unless $C = A$. Likewise $d^2 G_{A'}^s / dX_C dY_D = 0$ if $C \neq D$.

As was described in Sec. II, we chose to utilize a symmetrically orthogonalized¹⁸ atomic orbital basis $\{\phi_i\}$ for expressing the one and two electron components of the electron Hamiltonian H . Hence, to evaluate the first and second derivatives of H with respect to nuclear displacement (μ) along any direction $X_A, Y_A, Z_A, X_B, Y_B, Z_B$, etc. derivatives of the symmetrically orthogonalized orbitals are needed. Let us assume that the symmetry adapted orbitals G_j^s are combined to form the ϕ_i ,

$$\phi_i = \sum_j S_{ji}^{-1/2} G_j^s, \quad (\text{A7})$$

where the overlap matrix S involves the $\{G_k^s\}$:

$$S_{ji} = \langle G_j^s | G_i^s \rangle. \quad (\text{A8})$$

Because the orbitals G_i^s are symmetry adapted, the overlap matrix S is block diagonal

$$\langle G_j^s | G_i^s \rangle = S_{ji}^s \delta_{ss'} \quad (\text{A9})$$

and, as a result, each ϕ_i can be labeled by a symmetry quantum number (s),

$$\phi_i = \sum_j (S_{ji}^s)^{-1/2} G_j^s. \quad (\text{A10})$$

In what follows, the symmetry label s will be dropped but it should be kept in mind that this label allows us to deal with only those orbitals belonging to the irreducible representation labeled by s .

To evaluate the first and second derivatives of each ϕ_i with respect to nuclear displacements is now relatively straightforward

$$\frac{d\phi_i}{dX_A} = \sum_j \left[S_j^{-1/2} \frac{dG_j^s}{dX_A} + G_j^s \frac{dS_j^{-1/2}}{dX_A} \right], \quad (\text{A11})$$

$$\begin{aligned} \frac{d^2\phi_i}{dX_A dY_C} = & \sum_j \left[\frac{dS_j^{-1/2}}{dY_C} \frac{dG_j^s}{dX_A} + \frac{dS_j^{-1/2}}{dX_A} \frac{dG_j^s}{dY_C} \right. \\ & \left. + S_j^{-1/2} \frac{d^2G_j^s}{dX_A dY_C} + G_j^s \frac{d^2S_j^{-1/2}}{dX_A dY_C} \right]. \quad (\text{A12}) \end{aligned}$$

Although the derivatives of G_j^s appearing in Eqs. (A11) and (A12) are displayed above, we have yet to give expressions for the derivatives of the $S^{-1/2}$ matrix elements.

To obtain an expression for $(d/dX)S^{-1/2}$, we first differentiate the identity $S^{-1/2}S = S^{1/2}$ and right multiply by $S^{-1/2}$ to obtain

$$\left(\frac{d}{dX} S^{-1/2} \right) S^{1/2} + S^{-1/2} \frac{dS}{dX} S^{-1/2} = \left(\frac{d}{dX} S^{1/2} \right) S^{-1/2}. \quad (\text{A13})$$

Now using the derivatives of the identity $S^{1/2}S^{-1/2} = 1$,

$$\left(\frac{dS^{1/2}}{dX} \right) S^{-1/2} = -S^{1/2} \frac{dS^{-1/2}}{dX} \quad (\text{A14})$$

in the right-hand side of Eq. (A13), we obtain

$$\left(\frac{d}{dX} S^{-1/2} \right) S^{1/2} + S^{1/2} \left(\frac{d}{dX} S^{-1/2} \right) = -S^{-1/2} \frac{dS}{dX} S^{-1/2}. \quad (\text{A15})$$

If we write Eq. (A15) out in the basis which diagonalizes S (and $S^{1/2}$), we obtain the desired expression for the elements of the $(d/dX)S^{-1/2}$ matrix (in this eigenvector basis):

$$\left(\frac{d}{dX} S^{-1/2} \right)_{ij} = - \left(\frac{dS}{dX} \right)_{ij} S_i^{-1/2} S_j^{-1/2} (S_i^{1/2} + S_j^{1/2})^{-1}, \quad (\text{A16})$$

where the $\{s_i\}$ are the eigenvalues of S and dS/dX is the derivative of the overlap matrix appearing in Eq. (A8). Note that dS/dX is straightforward to evaluate because it involves derivatives of the G_i^s which are easily expressed in terms of the PGTO derivatives of Eqs. (A2)–(A4).

The second derivatives of $S^{-1/2}$ can be obtained by taking the second derivative with respect to X and Y of the identity $S^{-1/2}S^{-1/2} = S^{-1}$ and rearranging to obtain

$$\begin{aligned} \left(\frac{d^2}{dY dX} S^{-1/2} \right) S^{-1/2} + S^{-1/2} \left(\frac{d^2}{dY dX} S^{-1/2} \right) \\ = \frac{d^2}{dY dX} S^{-1} - \left(\frac{dS^{-1/2}}{dY} \right) \left(\frac{dS^{-1/2}}{dX} \right) - \left(\frac{dS^{-1/2}}{dX} \right) \left(\frac{dS^{-1/2}}{dY} \right). \quad (\text{A17}) \end{aligned}$$

The derivative of S^{-1} which appears as the first term on the right-hand side of Eq. (A17) can be evaluated by taking the first and second derivatives of the identity $S^{-1}S = 1$ to obtain, respectively,

$$\frac{dS^{-1}}{dX} = -S^{-1} \frac{dS}{dX} S^{-1} \quad (\text{A18})$$

and

$$\frac{d^2S^{-1}}{dY dX} = -S^{-1} \left[\frac{d^2S}{dY dX} - \frac{dS}{dY} S^{-1} \frac{dS}{dX} - \frac{dS}{dX} S^{-1} \frac{dS}{dY} \right] S^{-1}. \quad (\text{A19})$$

Putting the pieces back together, we can now obtain the desired expression for $d^2S^{-1/2}/dY dX$ by evaluating

Eq. (A17) in the basis which diagonalizes S :

$$\begin{aligned} \left(\frac{d^2S^{-1/2}}{dY dX} \right)_{ji} = & - (S_j^{-1/2} + S_i^{-1/2})^{-1} \left\{ S_i^{-1} S_j^{-1} \left[\left(\frac{dS}{dY dX} \right)_{ji} \right. \right. \\ & - \sum_k \left(\frac{dS}{dY} \right)_{jk} S_k^{-1} \left(\frac{dS}{dX} \right)_{ki} - \sum_k \left(\frac{dS}{dX} \right)_{jk} S_k^{-1} \left(\frac{dS}{dY} \right)_{ki} \left. \right] \\ & \left. + \sum_k \left(\frac{dS^{-1/2}}{dY} \right)_{jk} \left(\frac{dS^{-1/2}}{dX} \right)_{ki} + \sum_k \left(\frac{dS^{-1/2}}{dX} \right)_{jk} \left(\frac{dS^{-1/2}}{dY} \right)_{ki} \right\}. \quad (\text{A20}) \end{aligned}$$

Equations (A16) and (A20) provide the derivatives which are needed in Eqs. (A11) and (A12) for evaluating $d\phi_i/dX$ and $d^2\phi_i/dY dX$. However, as expressed above, these matrix derivatives were obtained in the basis $V_i = \{V_{i,1} \cdots V_{i,n}\}$ which diagonalizes S ,

$$S V_i = S_i V_i. \quad (\text{A21})$$

In Eqs. (A11) and (A12), we need the derivative matrices in the basis of the G_i^s . In practice then, we first obtain the matrix derivatives from Eqs. (A16) and (A20) and we subsequently transform the matrices back to the original G_i^s basis via

$$\left(\frac{dS^{-1/2}}{dX} \right)_{ji} \Big|_{G^s \text{ basis}} = \sum_{k,l} V_{k,j} \left(\frac{dS^{-1/2}}{dX} \right)_{k,l} V_{l,i} \quad (\text{A22})$$

and

$$\left(\frac{d^2S^{-1/2}}{dY dX} \right)_{ji} \Big|_{G^s \text{ basis}} = \sum_{k,l} V_{k,j} \left(\frac{d^2S^{-1/2}}{dY dX} \right)_{k,l} V_{l,i}. \quad (\text{A23})$$

This provides us with a prescription for evaluating the first and second derivatives of our symmetrically orthogonalized orbital basis. These derivatives then allow us to evaluate the geometry dependence of the Hamiltonian (i.e., H_1 and H_2) as described in Sec. II.

2. Creation and annihilation operator dependence on μ

In developing expressions [Eqs. (13) and (16)] for the linear and quadratic μ dependence of $H(R^0 + \mu)$, we explicitly considered the μ dependence of the orthonormal $\{\phi_s\}$ basis orbitals which appeared in the Hamiltonian of Eq. (3). However we did not allow for any μ dependence in the creation $\{a_s^\dagger\}$ and annihilation $\{a_s\}$ operators occurring in H . To understand why it is permissible to neglect the μ dependence of the $\{a_s^\dagger\}$ and $\{a_s\}$ let us recall how the operators a_s^\dagger and a_s enter into the electronic energy expression whose molecular gradient and Hessian we seek.

All of the energy expressions treated in this paper (MCSCF, HF, CI, MPPT, CC) involve products of one- and two-electron integrals over the $\{\phi_s\}$ basis and one- and two-electron density matrices, e.g., $\langle 0 | a_s^\dagger a_r^\dagger a_t a_u | k \rangle$. These density matrices can be evaluated once $|0\rangle$ and $|k\rangle$, which might be identical to $|0\rangle$, are expressed in terms of products of creation operators operating on the vacuum ket $|vac\rangle$. The evaluation of the density matrices reduces to the evaluation of sums of vacuum expectation values of operator strings such as

$$\langle vac | a_{v_1} a_{v_2} \cdots a_{v_N} a_s^\dagger a_r^\dagger a_t a_u a_{w_N}^\dagger \cdots a_{w_2}^\dagger a_{w_1}^\dagger | vac \rangle. \quad (\text{A24})$$

Using Wick's theorem,¹⁹ such vacuum expectation values reduce to the sum over all totally contracted terms, one typical term of which is

$$\begin{aligned}
& \langle \text{vac} | a_{v_1} a_{v_2} \cdots a_{v_N} a_s^\dagger a_t^\dagger a_u a_{w_N}^\dagger \cdots a_{w_2}^\dagger a_{w_1}^\dagger | \text{vac} \rangle \\
&= (-1)^4 \langle \text{vac} | a_{v_1} a_{w_N}^\dagger | \text{vac} \rangle \langle \text{vac} | a_{v_2} a_s^\dagger | \text{vac} \rangle \\
&\quad \times \langle \text{vac} | a_{v_N} a_t^\dagger | \text{vac} \rangle \langle \text{vac} | a_t a_{w_2}^\dagger | \text{vac} \rangle \langle \text{vac} | a_u a_{w_1}^\dagger | \text{vac} \rangle \cdots
\end{aligned}
\quad (\text{A25})$$

The contractions $\underline{a_i a_j^\dagger}$ are defined as¹⁹

$$\underline{a_i a_j^\dagger} \equiv a_i a_j^\dagger + a_j^\dagger a_i = [a_j^\dagger, a_i]_+ . \quad (\text{A25a})$$

Because creation and annihilation operators corresponding to orthonormal orbitals such as $\{\phi_s\}$ obey

$$[a_j^\dagger, a_i]_+ = \delta_{ij} , \quad (\text{A26})$$

the gradient of the (contraction) anticommutator vanishes

$$\nabla([a_j^\dagger, a_i]_+) = [(\nabla a_j^\dagger), a_i]_+ + [a_j^\dagger, (\nabla a_i)]_+ = 0 . \quad (\text{A27})$$

Similarly the second derivative with respect to μ of any contraction $\underline{a_i a_j^\dagger}$ vanishes. If the orbitals $\{\phi_s\}$ were not orthonormal, the contraction would be

$$\underline{a_i a_j^\dagger} \equiv a_i a_j^\dagger + a_j^\dagger a_i = S_{ij}(\mathbf{R}) \quad (\text{A28})$$

and the derivative of $\underline{a_i a_j^\dagger}$ would become

$$\nabla \underline{a_i a_j^\dagger} = \nabla[a_i^\dagger, a_j]_+ = \nabla S_{ji}(\mathbf{R}) \quad (\text{A29})$$

which does not vanish.

When an orthonormal basis is used for evaluating molecular gradients and Hessians, the gradient of any density matrix element therefore is zero and considerations of how the creation and annihilation operators depend on μ need not be addressed. On the contrary, if the basis has a nonunit overlap matrix the gradient of a density matrix element is nonvanishing and explicit consideration of the creation and annihilation operator dependence on μ is required. Since the one- and two-electron density matrices dependence on μ is an unnecessary complication in evaluating the molecular gradients and Hessians, we have chosen to express the Hamiltonian in the symmetry orthonormalized atomic orbital basis.

3. The complete-basis limit

The contributions to \mathbf{H}_1 and \mathbf{H}_2 arising from the use of finite basis sets involve the derivatives appearing above in Eqs. (A11) and (A12). These contributions vanish as the AO basis approaches completeness. To demonstrate this fact, we first note that the electronic Hamiltonian at any molecular geometry \mathbf{R} can be written [see Eq. (3)] as sums of products of so-called field operators²⁰

$$\psi(r) = \sum_s \phi_s(r) a_s , \quad (\text{A30})$$

which destroy $[\psi(r)]$ or create $[\psi^*(r)]$ an electron at the spatial point r . The exact operator $\psi(r)$ and its creation-operator adjoint are geometry independent since their defining equations contain no reference to molecular geometry. It is only when one attempts to expand $\psi(r)$ or $\psi^*(r)$ in the AO basis $\{\phi_s\}$ that one introduces reference to molecular geometry and potential basis incompleteness. Hence, we must view Eq. (A30) as holding only when the $\{\phi_s\}$ basis is complete. For this

reason, our finite-basis Hamiltonian [Eq. (3)], which is expressed in terms of products of finite sums $\sum_s \phi_s(r) a_s$ is \mathbf{R} dependent. This \mathbf{R} dependence may be explicitly determined by differentiating the finite-basis field operator with respect to the nuclear displacement μ . The first derivative is, for example,

$$\frac{d\psi^*(r)}{d\mu} = \sum_s \left(\frac{d\phi_s^*(r)}{d\mu} a_s^\dagger + \phi_s^* \frac{da_s^\dagger}{d\mu} \right) . \quad (\text{A31})$$

The creation and annihilation operator dependence on nuclear displacement can be disregarded when an orthonormal basis is used to expand the field operators (see previous subsection) and Eq. (A31) then becomes

$$\frac{d\psi^*(r)}{d\mu} = \sum_s \frac{d\phi_s^*(r)}{d\mu} a_s^\dagger . \quad (\text{A32})$$

As the basis set $\{\phi_i\}$ becomes complete, the field operator becomes independent of μ ; i.e.,

$$\frac{d\psi^*(r)}{d\mu} = 0 . \quad (\text{A33})$$

In the complete basis limits we therefore have

$$\sum_s \frac{d\phi_s^*(r)}{d\mu} a_s^\dagger = 0 . \quad (\text{A34})$$

Introducing Eq. (A34) into \mathbf{H}_1 of Eq. (13) shows that, in the limit of complete basis, only the Hellmann–Feynman force term of \mathbf{H}_1 survives. Equation (13) also shows that if the basis set derivative terms in \mathbf{H}_1 are included in a complete-basis calculation, additional and unnecessary complications are introduced into the calculation of the molecular gradient.

In \mathbf{H}_2 it may similarly be shown that the only term that survives when a complete basis is used is the electric field gradient term induced by the movement of the nuclei.

4. The origin of density forces

To make the connection between our SCF and MCSCF gradients and those given by Pulay,¹ Pople,⁷ and Schaefer⁹ (in terms of the original nonorthogonal basis $\{\chi_i\}$), we first note that our gradient in each of these two cases [Eqs. (55) and (64)] is of the form

$$\langle 0 | \mathbf{H}_1 | 0 \rangle = \left\langle 0 \left| \frac{\partial H}{\partial \mu} \right| 0 \right\rangle = \left(\frac{\partial}{\partial \mu} \langle 0 | H | 0 \rangle \right)_{C_{ia}, C_g} , \quad (\text{A35})$$

where $|0\rangle$ is either $|\text{HF}\rangle$ or $|\text{MC}\rangle$. In the last identity, we simply stress that the derivative with respect to μ is to be applied only to the symmetrically orthogonalized basis functions occurring in H [see Eq. (3)]. The molecular orbital expansion coefficients $\{C_{ia}\}$ in this basis and the configuration amplitudes $\{C_g\}$ are not to be differentiated.

The one- and two-electron operator components of $\langle 0 | H | 0 \rangle$ can be written in terms of the molecular-orbital density matrices $\langle 0 | a_i^\dagger a_j | 0 \rangle$ and $\langle 0 | a_i^\dagger a_j^\dagger a_l a_k | 0 \rangle$, the molecular-orbital expansion coefficients $\{C_{ia}\}$ and one- and two-electron integrals over the symmetrically orthogonalized basis. For example, the one-electron component E_1 is

$$E_1 \equiv \sum_{i,j} \langle 0 | a_i^\dagger a_j | 0 \rangle C_{ia} C_{jb} \langle \phi_a | h_1 | \phi_b \rangle$$

$$= \sum_{i,j} \langle 0 | a_i^\dagger a_j | 0 \rangle C_{ia} C_{jb} A_{aa'} A_{bb'} \langle \chi_{a'} | h_1 | \chi_{b'} \rangle, \quad (\text{A36})$$

where $A_{aa'} = S_{aa'}^{-1/2}$ if the basis orbitals $\{\phi_a\}$ are symmetrically orthogonalized. The μ derivative of Eq. (A36) in which the C_{ia} and C_{jb} (hence $\langle 0 | a_i^\dagger a_j | 0 \rangle$) are fixed is a sum of two terms

$$\left(\frac{dE_1}{d\mu} \right)_{C_{ia}, C_{jb}} = \sum_{i,j} \langle 0 | a_i^\dagger a_j | 0 \rangle C_{ia} C_{jb} \left[A_{aa'} A_{bb'} \frac{\partial}{\partial \mu} \right. \\ \left. \times \langle \chi_{a'} | h_1 | \chi_{b'} \rangle + \langle \chi_{a'} | h_1 | \chi_{b'} \rangle 2A_{bb'} \frac{\partial A_{aa'}}{\partial \mu} \right]. \quad (\text{A37})$$

The first term is exactly the primitive atomic orbital integral derivative given by Pulay, Pople, and Schaefer since the $\sum_a C_{ia} A_{aa'} \equiv \bar{C}_{ia'}$ are just the expansion coefficients of the molecular orbitals in the primitive basis.

To reexpress the second term in Eq. (A37) in the same form as other workers have used, it is useful to notice that the combination $\sum_{j,b} 2\langle 0 | a_i^\dagger a_j | 0 \rangle C_{jb} A_{bb'} \times \langle \chi_{a'} | h_1 | \chi_{b'} \rangle$ is equal to the derivative of the one-electron part of $\langle 0 | H | 0 \rangle$ with respect to $\bar{C}_{ia'}$, keeping the basis functions $\{\chi_{a'}\}$ and the configuration amplitudes C_{ϵ} fixed ($\partial E_1 / \partial \bar{C}_{ia'} \big|_{C_{\epsilon}, \chi_{a'}}$). In either MCSCF or SCF theory, when the energy is optimized with respect to the $\{\bar{C}_{ia'}\}$ parameters subject to constraints $\bar{C} \bar{S} \bar{C} = 1$ [see Eq. (152)] this derivative can, using Eq. (153), be re-expressed as follows¹:

$$\left(\frac{\partial E_1}{\partial \bar{C}_{ia'}} \right) = \sum_{j,b'} 2\epsilon_{ij} \bar{C}_{jb'} S_{a'b'}, \quad (\text{A38})$$

where the ϵ_{ij} are Lagrange multipliers introduced to force the molecular orbitals to be orthonormal. Introducing this result into Eq. (A37) gives

$$\left(\frac{dE_1}{d\mu} \right)_{C_{ia}, C_{jb}} = \sum_{i,j} \langle 0 | a_i^\dagger a_j | 0 \rangle \bar{C}_{ia'} \bar{C}_{jb'} \frac{\partial}{\partial \mu} \langle \chi_{a'} | h_1 | \chi_{b'} \rangle \\ + \sum_{i,j} \langle 0 | a_i^\dagger a_j | 0 \rangle C_{ia} C_{jb} 2\epsilon_{ij} S_{a'b'} A_{bb'} \frac{\partial}{\partial \mu} A_{aa'}. \quad (\text{A39})$$

Finally, differentiation of the orthonormality requirement

$$\langle \phi_a | \phi_b \rangle = \delta_{ab} = \sum_{a',b'} A_{aa'} A_{bb'} S_{a'b'}, \quad (\text{A40})$$

allows the second term in Eq. (A39) to be expressed in terms of $\partial S_{a'b'} / \partial \mu$ thereby yielding

$$\left(\frac{dE_1}{d\mu} \right)_{C_{ia}, C_{jb}} = \sum_{i,j} \left[\langle 0 | a_i^\dagger a_j | 0 \rangle \bar{C}_{ia'} \bar{C}_{jb'} \frac{\partial}{\partial \mu} \langle \chi_{a'} | h_1 | \chi_{b'} \rangle \right. \\ \left. - \epsilon_{ij} \langle 0 | a_i^\dagger a_j | 0 \rangle \bar{C}_{ia'} \bar{C}_{jb'} \frac{\partial S_{a'b'}}{\partial \mu} \right]. \quad (\text{A41})$$

The second term in Eq. (A41) is exactly the density-force term contained in Pulay's and Pople's gradient expression. In deriving Eq. (A41) we have for simplicity only considered the one-electron part of the Hamiltonian. It is tedious but straightforward to show that

Eq. (A41) is also satisfied when the two-electron part of the Hamiltonian is considered. It may further easily be seen that Schaefer's Lagrangian terms [Eq. (18) of Ref. 9 from 1982] can also be identified as the second factor in Eq. (A41).

In summary, our SCF and MCSCF gradient expressions do indeed agree with the earlier results of Pulay, Pople, and Schaefer once our expressions are reformulated in terms of the original nonorthogonal basis. Although it may be possible to derive, within a nonorthogonal basis, gradient expressions for the other cases treated here as well as Hessians for all of these cases, it is our feeling that by using orthogonalized basis orbitals, we have simplified the derivations.

APPENDIX B: EFFICIENT EVALUATION OF RESPONSE MATRIX ELEMENTS

In this Appendix we introduce two devices which prove to be very useful for evaluating certain matrix products which enter into the molecular gradient and Hessian expression occurring throughout this paper.¹⁷ The first "trick" allows us to replace any commutator $[Y, H]$, where Y is a one-electron operator such as $\hat{\kappa}^{(1)}$ or $\hat{\kappa}^{(2)}$ [see Eqs. (25) and (78)] and H is H_0 , H_1 , or H_2 [see Eq. (9)], by a new one- and two-electron Hamiltonian \tilde{H} in which one-index transformed integrals occur.¹⁷ The second device allows the expectation value of a commutator $\langle 0 | [\hat{S}, X] | 0 \rangle$, where \hat{S} is $\hat{S}^{(1)}$ or $\hat{S}^{(2)}$, to be replaced by a transition value of X : $\langle 0 | X | \tilde{0} \rangle$. This means that the expectation value of $[\hat{S}, X]$ can be evaluated in terms of transition density matrices and the integrals occurring in X itself.¹⁷

Let us begin by considering the commutator of a Hamiltonian H (which can be H_0 or H_1 or H_2) in Eq. (3) and the operator $\hat{\kappa}$ of Eq. (25). The parameters κ_{rs} of Eq. (25) may, for example, have been determined in a response calculation in which case they may be $\kappa_{rs}^{(1)}$ or $\kappa_{rs}^{(2)}$. Carrying out the commutator gives what we refer to as a modified Hamiltonian \tilde{H} ,

$$\tilde{H} \equiv [\hat{\kappa}, H] = \sum_{rs} i\tilde{h}_{rs} a_r^\dagger a_s + \frac{1}{2} \sum_{rstu} i\widetilde{\langle rs | tu \rangle} a_r^\dagger a_s^\dagger a_u a_t, \quad (\text{B1})$$

where the modified one- and two-electron integrals are defined as

$$\tilde{h}_{rs} = \sum_p (h_{rp} \kappa_{sp} + h_{ps} \kappa_{rp}) \quad (\text{B2})$$

and

$$\widetilde{\langle rs | tu \rangle} = \sum_p (\kappa_{rp} \langle ps | tu \rangle + \kappa_{sp} \langle rp | tu \rangle \\ + \kappa_{tp} \langle rs | pu \rangle + \kappa_{up} \langle rs | tp \rangle), \quad (\text{B3})$$

The essential point is that the commutator generates a new Hamiltonian \tilde{H} which is itself a one- and two-electron operator expressed in the original creation and annihilation operator basis but which involves a transformed set of integrals. Note that the integral transformations in Eqs. (B2) and (B3) are simple one-index transformations which would involve very little computational effort. This replacement of the commutator of the one-electron operator ($\hat{\kappa}^{(1)}$ or $\hat{\kappa}^{(2)}$) and H_0 , H_1 , or H_2

by the modified Hamiltonian, which involves integrals having one index transformed, is used numerous times throughout this paper.

Consider next the average value of the commutator of an operator X with the operator \hat{S} (or $\hat{S}^{(1)}$ or $\hat{S}^{(2)}$) of Eq. (23),

$$\langle 0 | [\hat{S}, X] | 0 \rangle. \quad (\text{B4})$$

The transfer operators \hat{S} are constructed from the state $|0\rangle$ and its orthogonal complement set of states and the parameters S_{n0} may, for example, have been determined in a linear response calculation. Using Eq. (23) we may write the expression (B4) as a transition matrix element of the operator X :

$$\langle 0 | [\hat{S}, X] | 0 \rangle = \langle \delta 0 | X | 0 \rangle + \langle 0 | X | \delta 0 \rangle, \quad (\text{B5})$$

where

$$|\delta 0\rangle \equiv -\sum_n iS_{n0} |n\rangle. \quad (\text{B6})$$

The transition value of the operator X shown in Eq. (B5) can be evaluated just as the expectation value of X over $|0\rangle$ is computed except with all one- and two-electron density matrix elements replaced by the corresponding transition density matrix elements

$$\langle 0 | \dots | 0 \rangle - \langle 0 | \dots | \delta 0 \rangle + \langle \delta 0 | \dots | 0 \rangle.$$

To clarify the important roles played by the relations given in Eqs. (B1) and (B5) we demonstrate their use in some specific examples. Consider the evaluation of the orbital-response component of the CI molecular gradient ${}^{\text{HF}}F^{(0)} {}^{\text{HF}}K^{(1)}$ shown in Eq. (76). Using Eq. (B1) we can express this product as

$$\begin{aligned} {}^{\text{HF}}F^{(0)} {}^{\text{HF}}K^{(1)} &= \left\langle \text{CI} \left| \left[\sum_{m\alpha} {}^{\text{HF}}K_{m\alpha}^{(1)} (a_m^\dagger a_\alpha - a_\alpha^\dagger a_m), H_0 \right] \right| \text{CI} \right\rangle \\ &= -i \langle \text{CI} | [{}^{\text{HF}}\hat{K}^{(1)}, H_0] | \text{CI} \rangle \\ &= -i \langle \text{CI} | \tilde{H}_0 | \text{CI} \rangle, \end{aligned} \quad (\text{B7})$$

where ${}^{\text{HF}}\hat{K}^{(1)}$ is defined in Eq. (78). Hence the orbital polarization term in a CI gradient calculation may be straightforwardly evaluated as a modified Hamiltonian average value using integrals [see Eqs. (B2) and (B3)] whose one-index transformation involves ${}^{\text{HF}}K_{rs}^{(1)}$ as the transformation matrix.

As the next example, let us examine the evaluation of the third term in the CI molecular Hessian shown in Eq. (80). Using both of the tricks shown in Eqs. (B1)

and (B5) we write

$$\begin{aligned} {}^{\text{HF}}K^{(1)} \frac{\partial^2 E^{(0)}}{\partial S \partial K} \text{CI} S^{(1)} &= -\langle \text{CI} | [{}^{\text{CI}}\hat{S}^{(1)}, [{}^{\text{HF}}\hat{K}^{(1)}, H_0]] | \text{CI} \rangle \\ &= -\langle \delta \text{CI} | [{}^{\text{HF}}\hat{K}^{(1)}, H_0] | \text{CI} \rangle - \langle \text{CI} | [{}^{\text{HF}}\hat{K}^{(1)}, H_0] | \delta \text{CI} \rangle \\ &= -\langle \delta \text{CI} | \tilde{H}_0 | \text{CI} \rangle - \langle \text{CI} | \tilde{H}_0 | \delta \text{CI} \rangle, \end{aligned} \quad (\text{B8})$$

where δCI is defined as in Eq. (B6) with ${}^{\text{CI}}S_{n0}^{(1)}$ playing the role of S_{n0} . Equation (B8) demonstrates that the third term in Eq. (80) may be evaluated as a transition value of a modified Hamiltonian in which the one-index integral transformation needed to form \tilde{H}_0 involves $\kappa_{rs}^{(1)}$ and the transition density matrix arises via $S^{(1)}$. Provided that $\kappa^{(2)}$, $\kappa^{(1)}$, and $S^{(1)}$ have been evaluated, all molecular gradient and Hessian elements of Secs. III–VI and some of the molecular gradient and Hessian elements of Secs. VII and VIII may be evaluated using the modified integral lists and/or transition density matrix elements as outlined above.

The orbital energy derivatives, $\epsilon^{(1)}$ and $\epsilon^{(2)}$ of Eqs. (128) and (129) and the orbital response ${}^{\text{CH}}K^{(2)}$ of Eq. (128) may similarly be easily evaluated. For example, by writing $\epsilon_r^{(1)}$ as

$$\epsilon_r^{(1)} = \langle \text{HF} | [a_r, [H_1 - i\tilde{H}_0, a_r^\dagger]] | \text{HF} \rangle \quad (\text{B9})$$

with

$$\tilde{H}_0 = [{}^{\text{CH}}\hat{K}^{(1)}, H_0] \quad (\text{B10})$$

allows $\epsilon_r^{(1)}$ to be evaluated as an orbital energy $\epsilon_r^{(0)}$ [see Eqs. (114)], but with the Hamiltonian operator H_0 replaced by H_1 and \tilde{H}_0 , involving both original and modified integrals with the integral transformation arising from $\kappa_{rs}^{(1)}$.

Evaluation of the linear response in Eq. (46) requires explicit construction of $G^{(0)}$ and $F^{(1)}$. The quadratic response in Eq. (47) contains the matrices $G^{(0)}$, $F^{(2)}$, $G^{(1)}$, $\lambda^{(1)}$ and the three-index matrix $K^{(0)}$. However, explicit evaluation of $K^{(0)}$ is not required because only $K_{ijk}^{(0)} \lambda_k^{(1)}$ or $K_{ijk}^{(0)} \lambda_j^{(1)} \lambda_k^{(1)}$ appear in the response equations.¹⁷ However, before the tools of Eqs. (B1) and (B5) can be applied to $K_{ijk}^{(0)} \lambda_k^{(1)}$ or $K_{ijk}^{(0)} \lambda_j^{(1)} \lambda_k^{(1)}$, the orbital part of the excitation operators (${}^{\text{MC}}\hat{K}^{(1)}$) must be moved next to the Hamiltonian, and state transfer operators (${}^{\text{MC}}\hat{S}^{(1)}$) have to be moved to operate directly on the reference state as in Eq. (B5). Such a move introduces new Hessian and gradient elements. To clarify this part we write out in detail some of the terms which arise in evaluating $K_{ijk}^{(0)} \lambda_k^{(1)}$,

$$\begin{aligned} K_{ijk}^{(0)} \lambda_k^{(1)} &= \frac{1}{6} \langle 0 | [Q_i^\dagger - Q_i, [Q_j^\dagger - Q_j, [Q_k^\dagger - Q_k, H_0]]] | 0 \rangle \kappa_k^{(1)} + \frac{1}{6} \langle 0 | [Q_i^\dagger - Q_i, [Q_k^\dagger - Q_k, [Q_j^\dagger - Q_j, H_0]]] | 0 \rangle \kappa_k^{(1)} \\ &+ \frac{1}{6} \langle 0 | [Q_k^\dagger - Q_k, [Q_j^\dagger - Q_j, [Q_i^\dagger - Q_i, H_0]]] | 0 \rangle \kappa_k^{(1)} + \dots + \frac{1}{2} \langle 0 | [R_k^\dagger - R_k, [Q_j^\dagger - Q_j, [Q_i^\dagger - Q_i, H_0]]] | 0 \rangle S_k^{(1)} \\ &+ \dots + \frac{1}{2} \langle 0 | [R_k^\dagger - R_k, [R_j^\dagger - R_j, [Q_j^\dagger - Q_j, H_0]]] | 0 \rangle S_k^{(1)} + \frac{1}{2} \langle 0 | [R_j^\dagger - R_j, [R_k^\dagger - R_k, [Q_j^\dagger - Q_j, H_0]]] | 0 \rangle S_k^{(1)} + \dots \end{aligned} \quad (\text{B11})$$

The first term in Eq. (B11) may be straightforwardly evaluated as a Hessian matrix element with modified integrals since the sum $\kappa_k^{(1)} (Q_k^\dagger - Q_k)$ occurs in the com-

mutator involving the Hamiltonian. In the second term of Eq. (B11) $Q_k^\dagger - Q_k$ must be moved next to the Hamiltonian before Eq. (B1) can be applied. This may be done

using the commutator identity

$$[Q_k^* - Q_k, [Q_j^* - Q_j, H]] = [Q_j^* - Q_j, [Q_k^* - Q_k, H]] + [[Q_k^* - Q_k, Q_j^* - Q_j], H]. \quad (\text{B12})$$

The result of inserting the first term in Eq. (B12) gives just the first term of Eq. (11). Inserting the second term in Eq. (B12) gives a sum of MCSCF Hessian matrix elements since the commutator

$$[Q_k^* - Q_k, Q_j^* - Q_j]$$

is itself a sum of one-electron operators. In the third term, the commutator identity of Eq. (B12) can be applied two times. The fourth and fifth terms of Eq. (B11) may straightforwardly be evaluated using Eq. (B5). In the last term we need to interchange $R_k^* - R_k$ and $R_j^* - R_j$ before we can apply Eq. (B5). To do this we use an operator identity similar to the one of Eq. (B12). In Ref. 17 a more detailed description is given of how to evaluate all of these terms in $K_{ijk}^{(0)} \lambda_k^{(1)}$.

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