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First-Order Geometrical Response Equations for State-Averaged Multiconfigurational Self-Consistent Field (SA-MCSCF) Wave Functions

KELD LARS BAK, JERRY BOATZ, AND JACK SIMONS
Chemistry Department, University of Utah, Salt Lake City, Utah 84112

Abstract

The first-order geometrical response equations for a state-averaged multiconfigurational self-consistent field (SA-MCSCF) calculation are derived. This derivation is carried through from first principles to final working equations suited for computer implementation. The final equations are expressed such that the energies and wave functions must be known only for the *internal* SA-MCSCF states. In the derivation, the special but important case where two or more *internal* states have equal weighting factors is treated in a manner fully consistent with all other cases. Except for introducing extra equations that are straightforward to solve, the case where two or more *internal* states have equal weighting factors introduces no new complications.

I. Introduction

The idea of having one set of orbitals that are optimized to minimize the weighted average energy of two or more multiconfigurational self-consistent field (MCSCF) states simultaneously was first introduced by Docken and Hinze [1]. Docken and Hinze used this concept, which now is known as *state-averaged* (SA) MCSCF, as a means to prevent the problem of rootflipping when excited states are calculated. Besides providing a means for preventing rootflipping during calculations of excited states, the SA-MCSCF approach, due to its common set of orthonormal orbitals for all states, is also used to facilitate the computation of transition properties. Earlier approaches to the problem of optimizing SA-MCSCF energies are described in Refs. 2–7.

In the last decade, much attention in electronic structure theory has been given to the task of calculating responses arising from distortions of the nuclear framework. These responses are especially used [8–13] for evaluating the geometrical Hessian that is used to characterize potential energy surfaces and for walking toward stationary points on these surfaces.

Within the concept of SA-MCSCF, the primary work that precedes this manuscript on response equations is contained in a series of papers by Lengsfield, Saxe, Yarkony, and Jensen [14–18] on nonadiabatic couplings. In these papers, the SA-MCSCF wave functions and their responses are used to enable a convenient way for evaluating nonadiabatic couplings for SA-MCSCF wave functions, as well as for configuration interaction (CI) wave functions based on the orthonormal

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orbitals from an SA-MCSCF calculation. The theory on the response equations for SA-MCSCF calculations published in this series of papers [14–18] is rather brief. One purpose of our work is to provide a more comprehensive derivation of the first-order response equations for a set of SA-MCSCF wave functions. Our derivation is sufficiently extensive that it is self-contained with all expressions derived at a level that allows computer implementation. Moreover, the derivation does not require that any but the weighted states be calculated.

When using SA-MCSCF as a remedy for rootflipping during calculations of excited states, the weights used for the different wave functions are naturally biased such that the weight for the excited state is large and weights on other states are small. On the other hand, when the SA-MCSCF concept is used to provide transition properties, the states for which these properties are desired are naturally weighted equally. In the case where two or more states are equally weighted, a special difficulty occurs [14]. Our work provides a complete derivation allowing equal weighting of two or more states in a computationally tractable manner.

SA-MCSCF theory is closely related to usual MCSCF theory, which is described in a variety of notations. In this work, we have chosen to use a notation similar to that used by Hoffmann et al. [19]. Part of the derivation is also parallel to derivations in [19] and a previous paper of Osamura et al. [20].

Our conventions and definitions are stated in Section II. The Generalized Brillouin Theorem (GBT) valid for an SA calculation is derived in Section III. In Section IV, quantities at infinitesimally displaced geometries are expressed as power series of the quantities at the undisplaced geometries and identities arising from orthonormality constraints on the states and orbitals are derived. Also in this section, the two conditions from which the response equations are derived are explicitly stated. The first condition relies on the GBT, and the equations emerging from this are derived in Section V. Similarly, the equations arising from the second condition are derived in Section VI. Section VII describes how the response equations are naturally combined and transformed to a form that is amenable for efficient implementation. A final discussion of the equations obtained is left for Section VIII, and the conclusions are in Section IX.

II. Conventions and Definitions

Consider a system of atoms in an electronic space spanned by a set of M atomic orbital (AO), or symmetry-adapted orbital (SO), basis functions, $\{X_\mu \mid \mu = 1, 2, \ldots, M\}$. From these basis functions, a set of M orthonormal molecular orbitals (MO's) are created, $\{\varphi_i \mid i = 1, 2, \ldots, M\}$, by the relation

$$\varphi_i = \sum_{\mu}^{M} K_\mu^i X_\mu, \tag{1}$$

which defines the MO coefficients K_μ^i.

For a given symmetry, a subset of all symmetry-adapted configuration-state functions (CSF's) is created from the MO's, $\{\Phi_I \mid I = 1, 2, \ldots N\}$; that is, the number of CSF's in the subset is taken to be N. The subset of CSF's again serves as a basis for generating N orthonormal states of the given symmetry, $\{\Psi_A \mid A = 1, 2, \ldots, N\}$.

The generating relation is written as

$$\Psi_A = \sum_I^N C_I^A \Phi_I, \tag{2}$$

where the C_I^A's are the CI-coefficients.

In a state-averaged calculation, the N states are divided into two sets, one which consists of Ω so-called *internal* states and one which consists of Λ so-called *external* states. Note that $N = \Omega + \Lambda$. Each of the *internal* states is assigned a weighting factor ω_R, which has to be larger than zero but less than or equal to one. The weighting factors must sum to unity. The weighting factors are the weights of the states in the SA-MCSCF energy functional, which is defined as the weighted sum of energies E_R for the set of *internal* states:

$$E^{SA} \equiv \sum_R^\Omega \omega_R \langle \Psi_R | \mathrm{H} | \Psi_R \rangle = \sum_R^\Omega \omega_R E_R . \tag{3}$$

In this work, we assume that states and orbitals are real and that the orbitals and *internal*-state CI-coefficients are variationally optimized for the functional in Eq. (3), which also can be written as

$$E^{SA} = \sum_R^\Omega \omega_R \sum_{IJ} C_I^R C_J^R H_{IJ}, \tag{4}$$

where

$$H_{IJ} = \sum_{ij} \gamma_{ij}^{IJ} h_{ij} + \sum_{ijkl} \Gamma_{ijkl}^{IJ} (ij \,|\, kl). \tag{5}$$

The symbols γ_{ij}^{IJ} and Γ_{ijkl}^{IJ} denote the one- and two-particle coupling coefficients, respectively, and h_{ij} and $(ij \,|\, kl)$ denote the one- and two-electron integrals; the $(ij \,|\, kl)$ are written in Mulliken notation.

In line with the notation used in this section, throughout this paper we will use

ν, μ, ρ, σ	to denote	AO's or SO's,
i, j, k, l, m, n, o, p	" "	MO's,
I, J, K, L	" "	CSF's,
A, B, D	" "	states in general,
R, S, T, U	" "	*internal* states,
P, Q	" "	*external* states.

III. The Generalized Brillouin Theorem (GBT) for an SA-MCSCF Calculation

The purpose of this section is to derive the GBT for an SA calculation, such that this theorem can be utilized in deriving the response equations.

An infinitesimal variation of the orbital φ_i will lead to a new orbital $\varphi_i + \delta\varphi_i$, which can be described in the space spanned by all of the orbitals:

$$\varphi_i + \delta\varphi_i = \sum_j O_{ij} \varphi_j . \tag{6}$$

Now considering a simultaneous change of all orbitals and requiring that they remain orthonormal, we find that the elements O_{ij} must define a unitary matrix; that is, we can write O_{ij} as

$$\begin{aligned} O_{ij} &= [\exp(\mathbf{X})]_{ij}, \\ &= \delta_{ij} + X_{ij} + \frac{1}{2}\sum_k X_{ik}X_{kj} + \ldots, \end{aligned} \tag{7}$$

where

$$X_{ij} = -X_{ji}. \tag{8}$$

According to Eqs. (4)–(6), the SA energy for the set of infinitesimally varied orbitals then reads

$$E^{SA} = \sum_{ij}\left(\gamma_{ij}^{SA}\sum_{kl} h_{kl}O_{ik}O_{jl}\right) + \sum_{ijkl}\left(\Gamma_{ijkl}^{SA}\sum_{mnop}(mn\,|\,op)O_{im}O_{jn}O_{ko}O_{lp}\right), \tag{9}$$

where we have defined the one- and two-particle SA density matrices as

$$\gamma_{ij}^{SA} \equiv \sum_R^{\Omega} \omega_R \gamma_{ij}^R, \tag{10a}$$

$$\Gamma_{ijkl}^{SA} \equiv \sum_R^{\Omega} \omega_R \Gamma_{ijkl}^R, \tag{10b}$$

and the one- and two-particle density matrices for each of the *internal* states as

$$\gamma_{ij}^R \equiv \sum_{IJ} \gamma_{ij}^{IJ} C_I^R C_J^R, \tag{11a}$$

$$\Gamma_{ijkl}^R \equiv \sum_{IJ} \Gamma_{ijkl}^{IJ} C_I^R C_J^R. \tag{11b}$$

Stationary points in the orbital space (energy minima and saddle points) are characterized by the condition

$$\frac{\partial E^{SA}}{\partial X_{mn}} = 0, \tag{12}$$

where $m \neq n$. Using Eq. (8) to reduce the number of variables to the $(M(M-1)/2)$ independent variables (remember that M denotes the number of orbitals), the differentiation of Eq. (9) with respect to an arbitrary X_{mn} for $m \neq n$ gives:

$$\frac{\partial E^{SA}}{\partial X_{mn}} = 2\sum_j (\gamma_{mj}^{SA}h_{nj} - \gamma_{nj}^{SA}h_{mj}) + 4\sum_{jkl}(\Gamma_{mjkl}^{SA}(nj\,|\,kl) - \Gamma_{njkl}^{SA}(mj\,|\,kl)). \tag{13}$$

To derive Eq. (13), we have exploited the following symmetries:

$$\gamma_{ij}^{IJ} = \gamma_{ji}^{JI}, \tag{14a}$$

$$\Gamma_{ijkl}^{IJ} = \Gamma_{jilk}^{JI} = \Gamma_{klij}^{IJ}, \tag{14b}$$

$$h_{ij} = h_{ji}, \tag{14c}$$

$$(ij\,|\,kl) = (ji\,|\,kl) = (kl\,|\,ji). \tag{14d}$$

Now defining the SA Lagrangian as

$$\varepsilon_{ij}^{SA} \equiv \sum_{k} \gamma_{jk}^{SA} h_{ik} + 2 \sum_{klm} \Gamma_{jklm}^{SA} (ik\,|\,lm), \tag{15}$$

Eqs. (12) and (13) give

$$\varepsilon_{ij}^{SA} - \varepsilon_{ji}^{SA} = 0, \tag{16}$$

which is the Generalized Brillouin Theorem for an SA calculation, which must be fulfilled for all stationary points in the orbital space.

IV. Quantities at an Infinitesimally Displaced Geometry

We consider a situation where the *internal* SA-MCSCF wave functions have been converged for a chosen nuclear configuration, specified by the coordinates of each nucleus. Then, one of these coordinates, say the α coordinate, is infinitesimally distorted from x to $x + \lambda$. At this distorted geometry, the quantities are expressed as power series expansions around the same quantities of the original nuclear configuration. Denoting the coordinates at the displaced geometry by $x + \lambda$, and using the convention of not explicitly writing the geometry dependence for quantities that are evaluated at the undisplaced geometry, we find to first order in λ:

$$\mathrm{H}(x + \lambda)_{IJ} = \mathrm{H}_{IJ} + \lambda \frac{\partial \mathrm{H}_{IJ}}{\partial \alpha} + \ldots, \tag{17a}$$

$$E(x + \lambda)_R = E_R + \lambda \frac{\partial E_R}{\partial \alpha} + \ldots, \tag{17b}$$

$$C(x + \lambda)_I^A = C_I^A + \lambda \frac{\partial C_I^A}{\partial \alpha} + \ldots, \tag{17c}$$

$$h(x + \lambda)_{ij} = h_{ij} + \lambda \frac{\partial h_{ij}}{\partial \alpha} + \ldots, \tag{17d}$$

$$(ij\,|\,kl)_{(x+\lambda)} = (ij\,|\,kl) + \lambda \frac{\partial (ij\,|\,kl)}{\partial \alpha} + \ldots. \tag{17e}$$

Using Eq. (1) and the orthonormality of the MO's gives the following identity:

$$0 = \sum_{\mu} \frac{\partial K_{\mu}^{i}}{\partial \alpha} \langle \mathrm{X}_{\mu} | \varphi_{j} \rangle + \sum_{\nu} \frac{\partial K_{\nu}^{j}}{\partial \alpha} \langle \varphi_{i} | \mathrm{X}_{\nu} \rangle + S_{ij}^{\alpha}, \tag{18}$$

where we have defined

$$S_{ij}^{\alpha} \equiv \sum_{\mu\nu} K_{\mu}^{i} K_{\nu}^{j} \frac{\partial \langle \mathrm{X}_{\mu} | \mathrm{X}_{\nu} \rangle}{\partial \alpha}. \tag{19}$$

The term

$$\sum_{\mu} \frac{\partial K_{\mu}^{i}}{\partial \alpha} \mathrm{X}_{\mu}$$

can, of course, be expressed as a linear combination of MO's

$$\sum_{\mu} \frac{\partial K_{\mu}^{i}}{\partial \alpha} \mathrm{X}_{\mu} = \sum_{j} U_{ji}^{\alpha} \varphi_{j}, \tag{20}$$

which, for real orbitals, defines

$$U_{ji}^{\alpha} = \sum_{\mu} \frac{\partial K_{\mu}^{i}}{\partial \alpha} \langle \mathrm{X}_{\mu} | \varphi_{j} \rangle. \tag{21}$$

Equation (18) can then be compactly expressed as

$$0 = U_{ij}^{\alpha} + U_{ji}^{\alpha} + S_{ij}^{\alpha}. \tag{22}$$

Using this notation, we can rewrite $(\partial h_{ij})/(\partial \alpha)$ and $[\partial (ij \,|\, kl)]/(\partial \alpha)$ as

$$\frac{\partial h_{ij}}{\partial \alpha} = h_{ij}^{\alpha} + \sum_{k} (U_{ki}^{\alpha} h_{kj} + U_{kj}^{\alpha} h_{ik}), \tag{23a}$$

and

$$\begin{aligned} \frac{\partial (ij \,|\, kl)}{\partial \alpha} = (ij \,|\, kl)^{\alpha} + \sum_{m} (&U_{mi}^{\alpha} (mj \,|\, kl) + U_{mj}^{\alpha} (im \,|\, kl) \\ &+ U_{mk}^{\alpha} (ij \,|\, ml) + U_{ml}^{\alpha} (ij \,|\, km)), \end{aligned} \tag{23b}$$

where

$$h_{ij}^{\alpha} \equiv \sum_{\mu\nu} K_{\mu}^{i} K_{\nu}^{j} \frac{\partial h_{\mu\nu}}{\partial \alpha}, \tag{24a}$$

$$(ij \,|\, kl)^{\alpha} \equiv \sum_{\mu\nu\rho\sigma} K_{\mu}^{i} K_{\nu}^{j} K_{\rho}^{k} K_{\sigma}^{l} \frac{\partial (\mu\nu \,|\, \rho\sigma)}{\partial \alpha}. \tag{24b}$$

Similarly, using Eq. (2) and the orthonormality of states gives

$$0 = \sum_{I} \frac{\partial C_{I}^{A}}{\partial \alpha} C_{I}^{B} + \sum_{I} C_{I}^{A} \frac{\partial C_{I}^{B}}{\partial \alpha}. \tag{25}$$

Since a change of a CI vector must be expressible in the space of all CI vectors, we have

$$\frac{\partial C_I^A}{\partial \alpha} = \sum_D^N V_{AD}^\alpha C_I^D , \tag{26}$$

which can be inserted in Eq. (25) to give

$$0 = V_{AB}^\alpha + V_{BA}^\alpha . \tag{27}$$

Since the one- and two-particle coupling coefficients both are independent of nuclear geometry (as long as the nuclear framework belongs to the point group chosen for the calculation), using Eqs. (17c) and (26), the density matrices at the displaced geometry are given to first order in λ as

$$\gamma(x + \lambda)_{ij}^R = \gamma_{ij}^R + \lambda \sum_A^N V_{RA}^\alpha \sum_{IJ} C_I^R C_J^A (\gamma_{ij}^{IJ} + \gamma_{ij}^{JI}) + \ldots , \tag{28a}$$

$$\Gamma(x + \lambda)_{ijkl}^R = \Gamma_{ijkl}^R + \lambda \sum_A^N V_{RA}^\alpha \sum_{IJ} C_I^R C_J^A (\Gamma_{ijkl}^{IJ} + \Gamma_{ijkl}^{JI}) + \ldots . \tag{28b}$$

Notice that if one wishes to include distortions that reduce the symmetry of the nuclear framework, one has to evaluate the coupling coefficients in the lower symmetry group. In general, if all possible distortions are required, the calculation has to be carried out without use of point-group symmetry.

Now that we have evaluated how different quantities at an infinitesimally displaced geometry are expressed to first order in λ, and have shown in Eqs. (22) and (27) how the orthonormality conditions of the orbitals and states reduce the number of independent variables, we are ready to derive the response equations for the set of SA wave functions. To obtain these equations, one has to take advantage of the two conditions that must be fulfilled for converged SA-MCSCF wave functions at *all* nuclear geometries:

(A) the SA-GBT condition expressed in Eq. (16) that states that the orbitals are optimized in a weighted SA manner, and

(B) the CI coefficients for each of the SA-MCSCF *internal* states have to be variationally optimized in the chosen space of CSF's; that is,

$$\delta_{RB} E_R = \sum_{IJ} C_I^R C_J^B H_{IJ} , \tag{29}$$

has to be valid for all CI coefficients of the *internal* states.

In the next section, we derive the equations that arise from the GBT condition; the equations that arise from Eq. (29) will be evaluated in Section VI.

V. First-Order Responses Arising from the GBT

Imposing the SA-GBT to be fulfilled at the infinitesimally displaced geometry, we can use Eqs. (10), (14), (15), (17d), (17e), (23), and (28) in Eq. (16) to give us this GBT condition in powers of λ. Collecting first-order terms generates the

equation

$$0 = \varepsilon_{ij}^{SA\alpha} - \varepsilon_{ji}^{SA\alpha} + \sum_{R}^{\Omega} \omega_R \sum_{A}^{N} V_{RA}^{\alpha} \sum_{J} C_J^A (T_{ij}^{JR} - T_{ji}^{JR})$$

$$+ \sum_{nk} U_{nk}^{\alpha} [\delta_{ik}\varepsilon_{nj}^{SA} - \delta_{jk}\varepsilon_{ni}^{SA} + Y_{ijnk}^{SA} - Y_{jink}^{SA}], \tag{30}$$

with the new quantities defined as

$$\varepsilon_{ij}^{SA\alpha} \equiv \sum_{k} h_{ik}^{\alpha} \gamma_{jk}^{SA} + 2 \sum_{klm} (ik \,|\, lm)^{\alpha} \Gamma_{jklm}^{SA}, \tag{31a}$$

$$T_{ij}^{JR} \equiv \sum_{I} C_I^R \left[\sum_{k} (\gamma_{jk}^{IJ} + \gamma_{jk}^{JI}) h_{ik} + 2 \sum_{klm} (\Gamma_{jklm}^{IJ} + \Gamma_{jklm}^{JI}) (ik \,|\, lm) \right], \tag{31b}$$

$$Y_{ijnk}^{SA} \equiv h_{in}\gamma_{jk}^{SA} + 2 \sum_{lm} \{(in \,|\, lm)\Gamma_{jklm}^{SA} + (il \,|\, nm)(\Gamma_{jlkm}^{SA} + \Gamma_{jlmk}^{SA})\}. \tag{31c}$$

The unknown variables in Eq. (30) are the sets of V_{RA}^{α} and U_{nk}^{α}. To eliminate redundant variables, and at the same time guarantee that the orbitals and states at the infinitesimally displaced geometry are orthonormal, we use Eqs. (22) and (27) to rewrite Eq. (30) as

$$0 = \varepsilon_{ij}^{SA\alpha} - \varepsilon_{ji}^{SA\alpha} + \sum_{R}^{\Omega} \sum_{P}^{\Lambda} V_{RP}^{\alpha} \omega_R \sum_{J} C_J^P (T_{ij}^{JR} - T_{ji}^{JR})$$

$$+ \sum_{R}^{\Omega} \sum_{S>R}^{\Omega} V_{RS}^{\alpha} \left[\omega_R \sum_{J} C_J^S (T_{ij}^{JR} - T_{ji}^{JR}) - \omega_S \sum_{J} C_J^R (T_{ij}^{JS} - T_{ji}^{JS}) \right]$$

$$+ \sum_{n} \sum_{k<n} U_{nk}^{\alpha} [Y_{ijnk}^{SA} - Y_{jink}^{SA} - Y_{ijkn}^{SA} + Y_{jikn}^{SA} + \delta_{ik}\varepsilon_{nj}^{SA} - \delta_{jk}\varepsilon_{ni}^{SA} - \delta_{in}\varepsilon_{kj}^{SA} + \delta_{jn}\varepsilon_{ki}^{SA}]$$

$$- \sum_{n} \sum_{k<n} S_{nk}^{\alpha} [Y_{ijkn}^{SA} - Y_{jikn}^{SA} + \delta_{in}\varepsilon_{kj}^{SA} - \delta_{jn}\varepsilon_{ki}^{SA}]$$

$$- \frac{1}{2} \sum_{n} S_{nn}^{\alpha} [Y_{ijnn}^{SA} - Y_{jinn}^{SA} + \delta_{in}\varepsilon_{nj}^{SA} - \delta_{jn}\varepsilon_{ni}^{SA}]. \tag{32}$$

By making the matrix definitions of Eqs. (33), Eq. (32) can be expressed as a set of linear equations for the unknowns U_{nk}^{α} and V_{RS}^{α}:

$$\tilde{A}_{ij,nk}^{11} \equiv Y_{ijnk}^{SA} - Y_{jink}^{SA} - Y_{ijkn}^{SA} + Y_{jikn}^{SA} + \delta_{ik}\varepsilon_{nj}^{SA} - \delta_{jk}\varepsilon_{ni}^{SA} - \delta_{in}\varepsilon_{kj}^{SA} + \delta_{jn}\varepsilon_{ki}^{SA}, \tag{33a}$$

$$\tilde{A}_{ij,RP}^{12} \equiv \omega_R \sum_{J} C_J^P (T_{ij}^{JR} - T_{ji}^{JR}); \tag{33b}$$

$$\tilde{A}_{ij,RS}^{13} \equiv (\omega_R - \omega_S) \sum_{J} C_J^S (T_{ij}^{JR} - T_{ji}^{JR}), \tag{33c}$$

$$\tilde{B}_{ij}^{1} \equiv \sum_{n} \sum_{k<n} S_{nk}^{\alpha} [Y_{ijkn}^{SA} - Y_{jikn}^{SA} + \delta_{in}\varepsilon_{kj}^{SA} - \delta_{jn}\varepsilon_{ki}^{SA}]$$

$$+ \frac{1}{2} \sum_{n} S_{nn}^{\alpha} [Y_{ijnn}^{SA} - Y_{jinn}^{SA} + \delta_{in}\varepsilon_{nj}^{SA} - \delta_{jn}\varepsilon_{ni}^{SA}] - \varepsilon_{ij}^{SA\alpha} + \varepsilon_{ji}^{SA\alpha}. \tag{33d}$$

The linear equations that result from Eq. (32) can be written in shorthand notation as

$$\sum_{n}\sum_{k<n}\tilde{A}^{11}_{ij,nk}U^{\alpha}_{nk} + \sum_{R}^{\Omega}\sum_{P}^{\Lambda}\tilde{A}^{12}_{ij,RP}V^{\alpha}_{RP} + \sum_{R}^{\Omega}\sum_{S>R}^{\Omega\neq\Delta}\tilde{A}^{13}_{ij,RS}V^{\alpha}_{RS} = \tilde{B}^{1}_{ij}. \tag{34}$$

In accordance with the definitions in Section II, Ω is the number of *internal* states, and Λ, the number of *external* states. The Δ is defined as the number of pairs of *different internal* states with *equal* weighting factors, and the notation $\Omega \neq \Delta$, appearing in the limit for the last sum in Eq. (34), is used to denote the sum $S > R$ running only over S and R being *internal* states with *unequal* weighting factors.

In principle, Eq. (34) represents M^2 equations for i and j forming all possible combinations of orbital indices. However, from the definitions in Eqs. (33), we see that

$$\tilde{A}^{11}_{ij,nk} = -\tilde{A}^{11}_{ji,nk}, \tag{35a}$$

$$\tilde{A}^{12}_{ij,RP} = -\tilde{A}^{12}_{ji,RP}, \tag{35b}$$

$$\tilde{A}^{13}_{ij,RS} = -\tilde{A}^{13}_{ji,RS}, \tag{35c}$$

$$\tilde{B}^{1}_{ij} = -\tilde{B}^{1}_{ji}; \tag{35d}$$

that is, the number of nonredundant and nonzero equations is $(M(M-1)/2)$. These equations, which can be labeled $i > j$, represent the first-order response equations arising from the SA-GBT.

VI. First-Order Responses from Requiring the *Internal* States to be Variationally Optimized

Equation (29) represents the requirement that the *internal* SA-MCSCF states be variationally optimized within the chosen CSF space. Using $\delta_{RB} = \Sigma_I C^R_I C^B_I$ in Eq. (29) together with Eqs. (17a), (17b), (17c), and (26), this condition can be expressed at the infinitesimally displaced geometry in powers of λ. Defining the molecular gradient elements,

$$E^{\alpha}_{R} \equiv \frac{\partial E_R}{\partial \alpha}, \tag{36}$$

and collecting first-order terms in λ, gives the following equation:

$$E^{\alpha}_{R}\delta_{RB} + (E_R - E_B)V^{\alpha}_{RB} - \sum_{IJ} C^R_I C^B_J \frac{\partial H_{IJ}}{\partial \alpha} = 0. \tag{37}$$

Using Eqs. (14a), (14b), (23a), and (23b) and the definition of H_{IJ} in Eq. (5) to evaluate $(\partial H_{IJ})/(\partial\alpha)$, we obtain

$$\frac{\partial H_{IJ}}{\partial \alpha} = H^{\alpha}_{IJ} + \sum_{ij} U^{\alpha}_{ij}\left\{\sum_{k}(\gamma^{IJ}_{jk} + \gamma^{JI}_{jk})h_{ik} + 2\sum_{klm}(\Gamma^{IJ}_{jklm} + \Gamma^{JI}_{jklm})(ik\,|\,lm)\right\}, \tag{38}$$

with the so-called *derivative Hamiltonian* defined as

$$H_{IJ}^{\alpha} \equiv \sum_{ij} \gamma_{ij}^{IJ} h_{ij}^{\alpha} + \sum_{ijkl} \Gamma_{ijkl}^{IJ} (ij \,|\, kl)^{\alpha}. \tag{39}$$

When Eq. (38) is inserted into Eq. (37), we obtain

$$E_R^{\alpha} \delta_{RB} + (E_R - E_B) V_{RB}^{\alpha} - \sum_{IJ} C_I^R C_J^B H_{IJ}^{\alpha} - \sum_{nk} U_{nk}^{\alpha} \sum_J C_J^B T_{nk}^{JR} = 0. \tag{40}$$

As in Eq. (30), the variables in Eq. (40) are the sets U_{nk}^{α} and V_{RB}^{α}. According to Eqs. (22) and (27), some of these variables are redundant. By using Eq. (22), we can exploit the redundancies in the U_{nk}^{α} set to reduce the sum over n and k to a sum for which $k < n$. This will also guarantee the orbitals at the displaced geometry to be orthonormal. Equation (40) then reads:

$$\begin{aligned} E_R^{\alpha} \delta_{RB} + (E_R - E_B) V_{RB}^{\alpha} - \sum_{IJ} C_I^R C_J^B H_{IJ}^{\alpha} - \\ \sum_n \sum_{k<n} U_{nk}^{\alpha} \sum_J C_J^B (T_{nk}^{JR} - T_{kn}^{JR}) + \\ \sum_n \sum_{k<n} S_{nk}^{\alpha} \sum_J C_J^B T_{kn}^{JR} + \frac{1}{2} \sum_n S_{nn}^{\alpha} \sum_J C_J^B T_{nn}^{JR} = 0. \end{aligned} \tag{41}$$

In Eq. (41), R can take all Ω values, and B, all N values; that is, Eq. (41) represents, in principle, ΩN equations. However, for B belonging to the *internal* states, it can be seen that the individual terms in the sum on the left-hand side of Eq. (41) are unaltered when the R and B indices are interchanged. That means that we have $(\Omega(\Omega - 1)/2)$ redundant equations that can be removed by only considering the equations for which $B \geq R$.

To be able to conveniently couple these nonredundant equations to the equations in Eq. (34), we split the equations represented in Eq. (41) into three sets that are slightly modified.

The first equation set is chosen to involve the $\Omega\Lambda$ equations for which the B index refers to *external* states, and these equations are subsequently multiplied by the weighting factor ω_R of the *internal* R state. The second set involves equations where the B index refers to *internal* states with weighting factors, ω_B's, *different* from the weighting factor ω_R of the *internal* R state. This set of equations is subsequently multiplied by $(\omega_R - \omega_B)$, which is unambiguous since $\omega_R \neq \omega_B$. With the number of pairs of *different internal* states with *equal* weighting factors previously defined as Δ, the number of equations in the second set is $(\Omega(\Omega - 1)/2 - \Delta)$. The third equation set consists of the remaining equations. For these, the B index refers to *internal* states for which the weighting factor ω_B *equals* the weighting factor ω_R of the *internal* R state. This last set of $(\Omega + \Delta)$ equations includes the equations for which $B = R$.

For the first set of equations, the B designation is changed to the P designation, since B is in the *external* space. The first set of equations obtained from

Eq. (41) then reads:

$$\sum_n \sum_{k<n} \tilde{A}^{21}_{RP,nk} U^\alpha_{nk} + \sum_S^\Omega \sum_Q^\Lambda \tilde{A}^{22}_{RP,SQ} V^\alpha_{SQ} = \tilde{B}^2_{RP}, \tag{42}$$

with the definitions:

$$\tilde{A}^{21}_{RP,nk} \equiv \omega_R \sum_J C^P_J (T^{JR}_{nk} - T^{JR}_{kn}), \tag{43a}$$

$$\tilde{A}^{22}_{RP,SQ} \equiv \delta_{RS}\delta_{PQ}\omega_R (E_P - E_R), \tag{43b}$$

$$\tilde{B}^2_{RP} \equiv \omega_R \sum_J C^P_J \left(-\sum_I C^R_I H^\alpha_{IJ} + \sum_n \sum_{k<n} S^\alpha_{nk} T^{JR}_{kn} + \frac{1}{2} \sum_n S^\alpha_{nn} T^{JR}_{nn} \right). \tag{43c}$$

For the second set of equations, B belongs to the *internal* states, and, hence, the B designation is changed to an S designation. The second set of equations derived from Eq. (41) then reads:

$$\sum_n \sum_{k<n} \tilde{A}^{31}_{RS,nk} U^\alpha_{nk} + \sum_T^\Omega \sum_{U>T}^{\Omega \neq \Delta} \tilde{A}^{33}_{RS,TU} V^\alpha_{TU} = \tilde{B}^3_{RS}, \tag{44}$$

where

$$\tilde{A}^{31}_{RS,nk} \equiv (\omega_R - \omega_S) \sum_J C^S_J (T^{JR}_{nk} - T^{JR}_{kn}), \tag{45a}$$

$$\tilde{A}^{33}_{RS,TU} \equiv \delta_{RT}\delta_{SU}(\omega_R - \omega_S)(E_S - E_R), \tag{45b}$$

$$\tilde{B}^3_{RS} \equiv (\omega_R - \omega_S) \sum_J C^S_J \left(-\sum_I C^R_I H^\alpha_{IJ} + \sum_n \sum_{k<n} S^\alpha_{nk} T^{JR}_{kn} + \frac{1}{2} \sum_n S^\alpha_{nn} T^{JR}_{nn} \right). \tag{45c}$$

In Eq. (44), the limit $\Omega \neq \Delta$ is used consistent with the definition stated in connection with Eq. (34).

In the last set of equations obtained from Eq. (41), B belongs to the *internal* states. Hence, the B designation is changed to an S designation and the equations are written as

$$\sum_n \sum_{k<n} \tilde{A}^{41}_{RS,nk} U^\alpha_{nk} + (E_S - E_R) V^\alpha_{RS} = \tilde{B}^4_{RS}, \tag{46}$$

with

$$\tilde{A}^{41}_{RS,nk} \equiv \sum_J C^S_J (T^{JR}_{nk} - T^{JR}_{kn}), \tag{47a}$$

$$\tilde{B}^4_{RS} \equiv E^\alpha_R \delta_{RS} + \sum_J C^S_J \left(-\sum_I C^R_I H^\alpha_{IJ} + \sum_n \sum_{k<n} S^\alpha_{nk} T^{JR}_{kn} + \frac{1}{2} \sum_n S^\alpha_{nn} T^{JR}_{nn} \right). \tag{47b}$$

In summary, the response equations arising from requiring the *internal* SA-MCSCF states to be variationally optimized are written in Eqs. (42), (44), and (46) and they represent in their totality $(\Omega\Lambda + \Omega(\Omega + 1)/2)$ equations.

VII. Strategy for Solving the Response Equations in the CSF Basis

The response equations derived in the previous sections consist of the four sets of linear equations given in Eqs. (34), (42), (44), and (46). The purpose of this section is to rewrite these equations in a more compact form and to transform parts of the equations such that the CI-vectors for the *external* states do not need to be calculated.

The first three sets of equations [Eqs. (34), (42), and (44)] are already derived such that they are easily combined to form one set of linear equations with as many variables as equations. However, since the last set [eq. (46)] is the only set that contains the V^a_{RS} elements for which the weighting factors of the *internal* R and S states are equal, this set of equations also has to be solved. In the following treatment, we first consider the equations that arise from combining Eqs. (34), (42), and (44). Then, assuming that these equations have been solved, we go on and show how to solve the remaining part of the problem by treating the equations arising from Eq. (46).

A. First Part of the Response Equations

We begin by defining the following matrices and vectors:

$$\tilde{\mathbf{A}} \equiv \begin{pmatrix} \tilde{\mathbf{A}}^{11} & \tilde{\mathbf{A}}^{21+} & \tilde{\mathbf{A}}^{31+} \\ \tilde{\mathbf{A}}^{21} & \tilde{\mathbf{A}}^{22} & 0 \\ \tilde{\mathbf{A}}^{31} & 0 & \tilde{\mathbf{A}}^{33} \end{pmatrix}, \tag{48a}$$

$$\tilde{\mathbf{V}} \equiv \begin{pmatrix} \mathbf{U}^{a} \\ \mathbf{V}^{aex} \\ \mathbf{V}^{ain} \end{pmatrix}, \tag{48b}$$

$$\tilde{\mathbf{B}} \equiv \begin{pmatrix} \tilde{\mathbf{B}}^{1} \\ \tilde{\mathbf{B}}^{2} \\ \tilde{\mathbf{B}}^{3} \end{pmatrix}, \tag{48c}$$

where $\mathbf{V}^{aex}$ and $\mathbf{V}^{ain}$ are the vectors of the V^a_{RP} elements and the V^a_{RS} elements, respectively. Whereas R and P in V^a_{RP}, respectively, denote *internal* and *external* states, the R and S in V^a_{RS} denote *internal* states with *different* weighting factors. The response equations represented in Eqs. (34), (42), and (44) can then compactly be written as

$$\tilde{\mathbf{A}}\tilde{\mathbf{V}} = \tilde{\mathbf{B}}. \tag{49}$$

To evaluate the $\tilde{\mathbf{A}}^{21}$, $\tilde{\mathbf{A}}^{22}$, and $\tilde{\mathbf{B}}^{2}$ blocks, it appears [see Eqs. (43a–c)] to be necessary to know both the CI vectors and energies for *all external* states. This requirement, however, can be removed by making a suitable unitary transformation with a matrix constructed from the CI vectors. Before performing the trans-

formation, Eq. (49) has to be modified by introducing extra "dummy" equations, such that the dimension of the $\tilde{\mathbf{A}}^{22}$ block is extended to $\Omega N \times \Omega N$ and the row dimensions of $\tilde{\mathbf{A}}^{21}$, $\mathbf{V}^{\alpha ex}$, and $\tilde{\mathbf{B}}^{2}$ are extended to ΩN. In particular, by defining the following elements:

$$\tilde{\tilde{\mathbf{A}}}^{21}_{RA,nk} \equiv \begin{cases} \tilde{\mathbf{A}}^{21}_{RA,nk} & \text{for } A \text{ within the } \textit{external} \text{ states,} \\ 0 & \text{for } A \text{ within the } \textit{internal} \text{ states,} \end{cases} \tag{50a}$$

$$\tilde{\tilde{\mathbf{A}}}^{22}_{RA,SB} \equiv \begin{cases} \tilde{\mathbf{A}}^{22}_{RA,SB} & \text{for } A \text{ and } B \text{ both within the } \textit{external} \text{ states,} \\ \delta_{RS}\delta_{AB}\omega_R z & \text{otherwise } (z \text{ is an arbitrary but nonzero constant}), \end{cases} \tag{50b}$$

$$\tilde{\tilde{\mathbf{B}}}^{2}_{RA} \equiv \begin{cases} \tilde{\mathbf{B}}^{2}_{RA} & \text{for } A \text{ within the } \textit{external} \text{ states,} \\ 0 & \text{for } A \text{ within the } \textit{internal} \text{ states,} \end{cases} \tag{50c}$$

and the matrices:

$$\tilde{\tilde{\mathbf{A}}} \equiv \begin{pmatrix} \tilde{\mathbf{A}}^{11} & \tilde{\tilde{\mathbf{A}}}^{21+} & \tilde{\mathbf{A}}^{31+} \\ \tilde{\tilde{\mathbf{A}}}^{21} & \tilde{\tilde{\mathbf{A}}}^{22} & 0 \\ \tilde{\mathbf{A}}^{31} & 0 & \tilde{\mathbf{A}}^{33} \end{pmatrix}, \tag{51a}$$

$$\tilde{\tilde{\mathbf{V}}} \equiv \begin{pmatrix} \tilde{\tilde{\mathbf{U}}}^{\alpha} \\ \tilde{\tilde{\mathbf{V}}}^{\alpha ex} \\ \tilde{\tilde{\mathbf{V}}}^{\alpha in} \end{pmatrix}, \tag{51b}$$

$$\tilde{\tilde{\mathbf{B}}} \equiv \begin{pmatrix} \tilde{\mathbf{B}}^{1} \\ \tilde{\tilde{\mathbf{B}}}^{2} \\ \tilde{\mathbf{B}}^{3} \end{pmatrix}, \tag{51c}$$

the extended set of response equations can be written as

$$\tilde{\tilde{\mathbf{A}}}\tilde{\tilde{\mathbf{V}}} = \tilde{\tilde{\mathbf{B}}}. \tag{52}$$

The solution vector $\tilde{\tilde{\mathbf{V}}}$ arising from this new matrix equation can be shown to contain the original responses of Eq. (49) as well as additional elements *that identically vanish:*

$$\tilde{\tilde{\mathbf{U}}}^{\alpha} = \mathbf{U}^{\alpha}, \tag{53a}$$

$$\tilde{\tilde{V}}^{\alpha ex}_{SA} = \begin{cases} V^{\alpha}_{SA} & \text{for } A \text{ within the } \textit{external} \text{ states,} \\ 0 & \text{for } A \text{ within the } \textit{internal} \text{ states,} \end{cases} \tag{53b}$$

$$\tilde{\tilde{\mathbf{V}}}^{\alpha in} = \mathbf{V}^{\alpha in}. \tag{53c}$$

Equation (52) can be subjected to a unitary transformation that eliminates the need to know the CI vectors of any but the *internal* states. To do so, we first define a matrix with elements

$$\tilde{U}_{RI,SA} \equiv \delta_{RS} C^{A}_{I}. \tag{54}$$

This matrix is easily shown to be unitary:

$$\tilde{\mathbf{U}}^{+}\tilde{\mathbf{U}} = \mathbf{1}, \tag{55}$$

and the larger matrix defined as

$$\tilde{\tilde{\mathbf{U}}} \equiv \begin{pmatrix} \mathbf{1}_{\text{mol}} & 0 & 0 \\ 0 & \tilde{\mathbf{U}} & 0 \\ 0 & 0 & \mathbf{1}_{\text{in}} \end{pmatrix}, \tag{56}$$

with $\mathbf{1}_{\text{mol}}$ and $\mathbf{1}_{\text{in}}$ being identity matrices with the dimensions of $\tilde{\mathbf{A}}^{11}$ and $\tilde{\mathbf{A}}^{33}$, respectively, and, therefore, also unitary. Note that this unitary matrix has earlier been used by Lengsfield [5] in deriving second-order MCSCF theory for SA wave functions. Using the matrix to perform a unitary transformation on Eq. (52) gives

$$\tilde{\tilde{\mathbf{U}}}\tilde{\tilde{\mathbf{A}}}\tilde{\tilde{\mathbf{U}}}^{+}\tilde{\tilde{\mathbf{U}}}\tilde{\tilde{\mathbf{V}}} = \tilde{\tilde{\mathbf{U}}}\tilde{\tilde{\mathbf{B}}}. \tag{57}$$

Defining

$$\mathbf{A} \equiv \tilde{\tilde{\mathbf{U}}}\tilde{\tilde{\mathbf{A}}}\tilde{\tilde{\mathbf{U}}}^{+}, \tag{58a}$$

$$\mathbf{V} \equiv \tilde{\tilde{\mathbf{U}}}\tilde{\tilde{\mathbf{V}}}, \tag{58b}$$

$$\mathbf{B} \equiv \tilde{\tilde{\mathbf{U}}}\tilde{\tilde{\mathbf{B}}}, \tag{58c}$$

Eq. (57) reads

$$\mathbf{AV} = \mathbf{B}. \tag{59}$$

The **A** matrix and the **V** and **B** vectors are naturally written in subblocks:

$$\mathbf{A} = \begin{pmatrix} \mathbf{A}^{11} & \mathbf{A}^{21^{+}} & \mathbf{A}^{31^{+}} \\ \mathbf{A}^{21} & \mathbf{A}^{22} & 0 \\ \mathbf{A}^{31} & 0 & \mathbf{A}^{33} \end{pmatrix}, \tag{60a}$$

$$\mathbf{V} = \begin{pmatrix} \mathbf{V}^{1} \\ \mathbf{V}^{2} \\ \mathbf{V}^{3} \end{pmatrix}, \tag{60b}$$

$$\mathbf{B} = \begin{pmatrix} \mathbf{B}^{1} \\ \mathbf{B}^{2} \\ \mathbf{B}^{3} \end{pmatrix}, \tag{60c}$$

where the elements of the blocks are easily evaluated. Using the following two definitions,

$$L_{IJ} \equiv \sum_{R}^{\Omega} C_I^R C_J^R, \tag{61a}$$

$$M_{IJ} \equiv \delta_{IJ} - L_{IJ}, \tag{61b}$$

which also result in the following equation:

$$M_{IJ} = \sum_{P}^{\Lambda} C_I^P C_J^P, \tag{62}$$

the final working expressions for the elements obtained are

$$\mathrm{A}^{11}_{ij,nk} = Y^{\mathrm{SA}}_{ijnk} - Y^{\mathrm{SA}}_{jink} - Y^{\mathrm{SA}}_{ijkn} + Y^{\mathrm{SA}}_{jikn} + \delta_{ik}\varepsilon^{\mathrm{SA}}_{nj} - \delta_{jk}\varepsilon^{\mathrm{SA}}_{ni} - \delta_{in}\varepsilon^{\mathrm{SA}}_{kj} + \delta_{jn}\varepsilon^{\mathrm{SA}}_{ki}, \tag{63a}$$

$$\mathrm{A}^{21}_{RK,nk} = \omega_R \sum_J M_{KJ}(T^{JR}_{nk} - T^{JR}_{kn}), \tag{63b}$$

$$\mathrm{A}^{22}_{RK,SL} = \omega_R \delta_{SR}\left(\sum_{IJ} M_{KI} M_{JL} H_{IJ} - M_{KL} E_R + z L_{KL} \right), \tag{63c}$$

$$\mathrm{A}^{31}_{RS,nk} = (\omega_R - \omega_S) \sum_J C_J^S (T^{JR}_{nk} - T^{JR}_{kn}), \tag{63d}$$

$$\mathrm{A}^{33}_{RS,TU} = \delta_{RT}\delta_{SU}(\omega_R - \omega_S)(E_S - E_R), \tag{63e}$$

$$\begin{aligned} \mathrm{B}^1_{ij} = {} & \sum_n \sum_{k<n} S^{\alpha}_{nk}[Y^{\mathrm{SA}}_{ijkn} - Y^{\mathrm{SA}}_{jikn} + \delta_{in}\varepsilon^{\mathrm{SA}}_{kj} - \delta_{jn}\varepsilon^{\mathrm{SA}}_{ki}] \\ & + \frac{1}{2} \sum_n S^{\alpha}_{nn}[Y^{\mathrm{SA}}_{ijnn} - Y^{\mathrm{SA}}_{jinn} + \delta_{in}\varepsilon^{\mathrm{SA}}_{nj} - \delta_{jn}\varepsilon^{\mathrm{SA}}_{ni}] - \varepsilon^{\mathrm{SA}\alpha}_{ij} + \varepsilon^{\mathrm{SA}\alpha}_{ji}, \end{aligned} \tag{63f}$$

$$\mathrm{B}^2_{RI} = \omega_R \sum_J M_{IJ}\left(-\sum_K C^R_K H^{\alpha}_{KJ} + \sum_n \sum_{k<n} S^{\alpha}_{kn} T^{JR}_{kn} + \frac{1}{2} \sum_n S^{\alpha}_{nn} T^{JR}_{nn} \right), \tag{63g}$$

$$\begin{aligned} \mathrm{B}^3_{RS} = {} & (\omega_R - \omega_S) \sum_J C_J^S \left(-\sum_I C^R_I H^{\alpha}_{IJ} + \sum_n \sum_{k<n} S^{\alpha}_{kn} T^{JR}_{kn} \right. \\ & \left. + \frac{1}{2} \sum_n S^{\alpha}_{nn} T^{JR}_{nn} \right), \end{aligned} \tag{63h}$$

$$V^1_{nk} = U^{\alpha}_{nk}, \tag{63i}$$

$$V^2_{RI} = \frac{\partial C^R_I}{\partial \alpha} - \sum_S^{\Omega} V^{\alpha}_{RS} C^S_I, \tag{63j}$$

$$V^3_{RS} = V^{\alpha}_{RS}. \tag{63k}$$

Solving the first part of the response equations [i.e., Eq. (59)] gives the solution vector **V**, which consists of the three parts $\mathbf{V}^1$, $\mathbf{V}^2$, and $\mathbf{V}^3$. As shown in Eqs. (63), $\mathbf{V}^1$ gives the set of U^{α}_{nk}'s [i.e., all responses concerning orbitals are recovered from solving Eq. (59)]. The $\mathbf{V}^2$ gives the set of

$$\left(\frac{\partial C^R_I}{\partial \alpha} - \sum_S^{\Omega} V^{\alpha}_{RS} C^S_I \right)$$

elements for R belonging to the *internal* states and I belonging to the set of active CSF's; that is, $\mathbf{V}^2$ contains information about CI responses arising from *internal-external* rotations. The last part, $\mathbf{V}^3$, gives the set of V^{α}_{RS}'s for R and S both be-

longing to *internal* states with *different* weighting factors. This is the CI response information for *internal-internal* rotations, but only for *internal* states with different weighting factors. The only remaining response information concerns the CI-response arising from rotations among pairs of *internal* states that have *equal* weighting factors. This remaining information is gained from the second part of the response equations, which we now detail.

B. Second Part of the Response Equations

For nondegenerate states, Eq. (46) can be rewritten such that the responses for *different internal* states R and S with *equal* weighting factors reads

$$V_{RS}^{\alpha} = (E_S - E_R)^{-1} \sum_J C_J^S \Bigg\{ -\sum_I C_I^R H_{IJ}^{\alpha} + \frac{1}{2} \sum_n S_{nn}^{\alpha} T_{nn}^{JR} + \sum_n \sum_{k<n} [T_{kn}^{JR} S_{nk}^{\alpha} + (T_{kn}^{JR} - T_{nk}^{JR}) U_{nk}^{\alpha}] \Bigg\} \tag{64}$$

(this result can be inferred from eq. (2.13a) in Ref. 14).

Assuming that Eq. (59) has been solved, the orbital responses U_{nk}^{α}'s are known and the response information about *internal-internal* CI rotations for all pairs of *different* states that have *equal* weighting factors are easily resolved from Eq. (64). Notice that the case in which two *degenerate* states occur with equal weighting is not resolved by our derivation; it will be the subject of future work.

When both response Eqs. (59) and (64) have been solved, all first-order response information is contained in the two vectors $\mathbf{V}$ and $\mathbf{V}^4$, where $\mathbf{V}^4$ is defined as the vector of the solutions V_{RS}^{α} in Eq. (64). The CI responses contained in the $\mathbf{V}^2$ and $\mathbf{V}^3$ parts of $\mathbf{V}$ can then be used with $\mathbf{V}^4$ to evaluate the responses of the CI coefficients for *internal* states as

$$\frac{\partial C_I^R}{\partial \alpha} = V_{RI}^2 + \sum_S^{\Omega} V_{RS}^{\alpha} C_I^S . \tag{65}$$

The results of solving the response equations thus give us the vector $\mathbf{V}^1$ of orbital responses U_{nk}^{α} and the set of CI responses $(\partial C_I^R)/(\partial \alpha)$ for *all internal* states.

VIII. Discussion

In the previous section, we have shown that first-order responses, for all *internal* SA wave functions, are analytically evaluated by solving the two sets of equations in Eqs. (59) and (64). The matrix $\mathbf{A}$ appearing in Eq. (59) is seen to be symmetric.

With the earlier definitions of M, N, Ω, and Δ in Sections II and V, the number of linear equations in Eq. (59) is $(M(M-1)/2) + (\Omega N) + (\Omega(\Omega - 1)/2 - \Delta)$. If the calculation is carried out with the use of point-group symmetry, this number is reduced because only rotations among orbitals, or, respectively, CSF's, of the same symmetries have to be considered. However, except where the active CSF space consists of one CSF, this potentially reduced set of equations will still contain a number of redundancies. These redundancies arise because some of

the orbital rotations result in a new set of CSF's that is a unitary transformation of the original set of CSF's. In the case of a complete active space (CAS) calculation, only rotations among core orbitals and valence orbitals, among core orbitals and virtual orbitals, and among valence orbitals and virtual orbitals are nonredundant; that is, in a CAS SA-MCSCF calculation with no use of spatial symmetry, if the number of core orbitals is *MCo*, the number of valence orbitals is *MVa*, and the number of virtual orbitals is *MVi*, the linear set of nonredundant equations represented in Eq. (59) has the dimension $(MCoMVa + MCoMVi + MVaMVi) + (\Omega N) + (\Omega(\Omega - 1)/2 - \Delta)$.

Note that for an SA calculation where all *internal* states have been assigned *different* weighting factors, Eq. (64) vanishes and only Eq. (59) has to be solved. This situation occurs in the special case where the SA-MCSCF calculation is a usual MCSCF calculation (i.e., in the case where we have only one *internal* state). In this case, the linear response equations in Eq. (59) are similar, but not identical, to the response equations derived for MCSCF wave functions by Osamura et al. [20] and Hoffmann et al. [19]. The difference is due to the way we extend the $\tilde{\mathbf{A}}$ and $\tilde{\mathbf{B}}$ matrices to the $\tilde{\tilde{\mathbf{A}}}$ and $\tilde{\tilde{\mathbf{B}}}$ matrices, which is different from the equivalent extension made in Refs. 19 and 20. The most pronounced difference between the resulting sets of equations is that the molecular gradient elements E_R^α appear in the equations of Refs. 19 and 20, but does not appear in the equations derived in this work. However, it should be mentioned that the molecular gradient elements for each *internal* state can be evaluated if desired, in our approach, from the following equation derived from Eq. (41):

$$E_R^\alpha = \sum_J C_J^R \left\{ \sum_I C_I^R H_{IJ}^\alpha - \frac{1}{2} \sum_n S_{nn}^\alpha T_{nn}^{JR} + \sum_n \sum_{k<n} [(T_{nk}^{JR} - T_{kn}^{JR}) U_{nk}^\alpha - T_{kn}^{JR} S_{nk}^\alpha] \right\}, \tag{66}$$

which contains only terms that also are needed for the response equations.

We end this discussion by mentioning that the responses for SA wave functions, obtained as described in this work, can be used for the calculation of nonadiabatic coupling elements between the *internal* SA wave functions, as shown by Lengsfield et al. [14, 16].

IX. Conclusions

In this work, we have derived first-order geometrical response equations valid for an SA-MCSCF calculation. The derivation is carried through from first principles, and the terms in the resulting working equations are expressed such that computer implementation from the formulas is straightforward. The energy gradients of each of the states involved in the SA-MCSCF energy functional are also given in computationally tractable form. The final results are given such that only the energies and wave functions for the *internal* states must be known.

The case in which the weighting factors for two or more nondegenerate *internal* states are chosen to be equal is treated in a fashion consistent with situations

where this is not true. This treatment of *internal* states with equal weighting factors results in an extra set of equations that has to be solved after the first set of response equations has been solved.

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