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Geometrical linear responses and directional energy derivatives for energetically degenerate MCSCF electronic functions

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Summary. For state-averaged multiconfigurational self consistent field (SA-MCSCF) wave functions, second-order geometrical response equations are derived that allow the determination of first-order configuration amplitude response for equally weighted, energetically degenerate states. The first-order response equations obtained in earlier work do not suffice to determine these particular responses parameters. To formulate such a derivation in a well defined manner, it is found that a specific linear combination of the degenerate states must be formed; this specific combination of states then defines how state energies and wave functions evolve as one passes through the surface intersection. The linear combination among the degenerate states is dependent upon the molecular distortion for which the responses are to be evaluated. Expressions for first- and second-order directional energy derivatives for these energetically degenerate wave functions are also derived. All the equations obtained are computationally tractable and expressed in terms of quantities that result from optimizing the SA-MCSCF wave functions and from solving the first- and part of the second-order geometrical response equations.

Key words: MCSCF – Geometrical response equations

1. Introduction

1.1. Intersections of adiabatic surfaces and non-adiabatic couplings

In quantum chemistry, adiabatic potential surfaces are defined as the energy eigenvalues of the electronic Hamiltonian obtained within some approximation scheme and taken as continuous functions of the internal nuclear coordinates. Internal coordinates are used because electronic energies are not affected by translations or rotations of the nuclear framework. The number of internal coordinates for polyatomic molecules is therefore $3N_A - 6$, with N_A being the number of nuclear centers. Each computational method implies its own particular set of adiabatic surfaces. In this work, emphasis is placed on adiabatic surfaces that result from the state-averaged multiconfigurational self-consistent field (SA-MCSCF) method.

Potential surfaces are of fundamental importance in chemistry. They form the basis underlying the concept of equilibrium molecular configurations, the study of chemical reactions and the interpretation of molecular spectra. These functions of $3N_A - 6$ variables may intersect along "seams" of various lower dimension. Within such intersections, two or more eigenstates are energetically degenerate for the corresponding nuclear configurations. The degeneracies may or may not be imposed by symmetry; in any case, the treatment of such degenerate cases requires special attention for both computational and conceptual reasons. Not surprisingly, there exist many good papers on these topics including more recent papers by Mead and Truhlar [1–4] and by Davidson and coworkers [5–7]. The very recent work of Frey and Davidson [7] presents an excellent review that focuses on symmetry-imposed crossings but also addresses general intersections. In Ref. [7] an extensive list of references is also given.

The location and characterization of geometries at which intersections of adiabatic energy surfaces occur is of considerable importance. Non-adiabatic effects (i.e., couplings among adiabatic surfaces induced by dynamic motions of the underlying nuclei) are often large in magnitude for potential surfaces that are energetically close, or for surfaces that cross. Lengsfield, Saxe, and Yarkony [8–11] have shown that state-averaged multiconfigurational self consistent field (SA-MCSCF) wave functions are advantageous to use for the analytical evaluation of non-adiabatic coupling because the orbital and configurational descriptions of the interacting states can be treated in a "balanced" manner, and because the same set of orthonormal orbitals are used for the interacting states.

The key to the evaluation of non-adiabatic couplings is the first-order orbital- and configuration-amplitude (so-called CSF) responses. These responses describe how the molecular orbitals and configuration mixing amplitudes (also known as CI-coefficients) of the interacting states respond to motions of the nuclei. Considering a nuclear distortion along the direction a, and denoting by K^i_μ the amplitude on the basis function μ for the molecular orbital i, the first-order orbital-amplitude responses are written as $(\partial K^i_\mu)/(\partial a) = \sum_j U^a_{ji} K^j_\mu$. Similarly, when for state A the amplitude on configuration I is denoted C^A_I, the first order CSF-responses are written $(\partial C^A_I)/(\partial a) = \sum_B V^a_{AB} C^B_I$. That is, the first-order orbital- and CSF-responses are specified by the expansion-coefficients, U^a_{ji} and V^a_{AB}, which multiply the orbital or configuration mixing amplitudes prior to distortion, respectively. In the following, we refer to the V^a_{AB} coefficient as the first order *state-state responses* among the A and B states.

As shown by Lengsfield and coworkers [8], and by the authors and Boatz [12], these first-order orbital- and CSF-responses, necessary for evaluation of non-adiabatic coupling, result from solving the first-order geometrical response equations obtained by making the SA-MCSCF energy function, E^{SA}, stationary and from the secular equations for each state contained in E^{SA}. In Ref. [12], these equations are derived in detail and presented in a form that works for interacting non-degenerate states and for degenerate states that do *not* appear with equal weighting in E^{SA}.

1.2. The case involving equally weighted degenerate states presents special difficulties

To treat energetically degenerate states in a "balanced" manner, it is generally most reasonable to weight them equally in the SA-MCSCF E^{SA}. Particularly, if

the energy degeneracy is imposed by symmetry, different weighting of the degenerate states in E^{SA} is inappropriate, and may lead to non-credible CSF-responses. Since first-order CSF-responses for *equally weighted, energetically degenerate* states can not be obtained from the equations of Ref. [12], an additional theory that accomplishes this is needed.

In this work, we show how second-order geometrical response equations can be used to reach this goal. In our derivation, for a nuclear configuration where two or more states are energetically degenerate *and* equally weighted, we assume that the first-order geometrical response equations of Ref. [12] have been solved for a molecular deformation lying along a chosen direction denoted a in the $3N_A$ dimensional space that includes translations and rotations. These first-order equations are shown here to determine the orbital and certain of the CSF-responses; the remainder of the CSF-responses involve only the energetically degenerate states and are subsequently determined using the tools detailed in this work.

The parts of the CSF-responses that can *not* be computed from the first-order response equations of Ref. [12] are the first order state-state responses among states that belong to the degenerate, equally weighted states. It is shown here that solving the part of the second-order geometrical response equations that arise from taking second derivatives of the SA-MCSCF equations with respect to the a direction gives these state-state responses among the energetically degenerate states. Combined with responses obtained from the first-order equations, these responses then completely specify the first-order CSF-responses of each of the degenerate states.

An essential aspect of our deviation involves taking a particular linear combination of the energetically degenerate wave functions in a manner that makes the resulting eigenfunctions evolve continuously through the crossing points. This particular combination of states is defined in terms of the direction a in which the crossing is approached. For this reason, the resulting wave function and energy responses are given as *directional derivatives* rather than conventional analytic derivatives. Formulas for obtaining first- and second-order directional energy derivatives also result from this work and remain valid whether or not the degeneracy is symmetry imposed.

In Sect. 2, we detail different situations under which two states can be degenerate, and we discuss considerations appropriate to these different situations. Section 3 contains the derivation of the response equations that allow the determination of first-order CSF-responses as well as directional first- and second-order energy derivatives for a set of energetically degenerate, equally weighted SA-MCSCF wave functions. In Sect. 4 we summarize and give our concluding remarks.

2. General considerations for two energetically degenerate states

2.1. Degenerate states at the reference geometry – three special cases

When considering symmetry properties of states that are energetically degenerate, different situations can be observed. Generally two or more states may be energetically degenerate for a given nuclear configuration. However, the main features of these different situations can be understood by considering two degenerate states only. The discussion in this section therefore focuses on two degenerate functions, although it should be stressed that the subsequent analysis

and hence the primary results of this paper apply equally well to triple and higher degeneracies.

At a so-called reference geometry, we denote the set of nuclear coordinates as x, and we assume that the two electronic states $\Psi_T(x)$ and $\Psi_U(x)$ are energetically degenerate and diagonalize the electronic Hamiltonian $H(x)$ at x:

$$\langle \Psi_T(x) | H(x) | \Psi_T(x) \rangle = E_T(x) = E_U(x) = \langle \Psi_U(x) | H(x) | \Psi_U(x) \rangle, \quad (1a)$$

$$\langle \Psi_U(x) | H(x) | \Psi_T(x) \rangle = 0. \quad (1b)$$

In Eqs. (1), $E_T(x)$ is the electronic energy for state T at the reference geometry.

The electronic Hamiltonian at the reference geometry has a specific point group symmetry, and all states are labeled according to which irreducible representations of that point group they belong as well as with their spin multiplicity. In this work, the symmetry of an eigenstate is therefore defined as the combined spatial and spin symmetry. Since the two states $\Psi_T(x)$ and $\Psi_U(x)$ are *energetically* degenerate, but may or may not be symmetry degenerate, three different situations need to be delineated:

(a) The two states have different symmetry.
(b) The two states have the same, symmetry-degenerate E-symmetry.
(c) The two states have the same, non-symmetry-degenerate symmetry.

Case (a) is usually described as a symmetry allowed crossing which can happen in a space of dimension $3N_A - 7$ (recall that the dimension of the general potential surface is $3N_A - 6$). An example of case (a) is provided by the BeH_2 species in C_{2v} geometry where the lowest $^1A_1$ and $^1B_2$ potential surfaces intersect [13]. The space within which C_{2v} symmetry is preserved is two-dimensional; hence, the seam within which the $^1A_1$ and $^1B_2$ surfaces intersect is one-dimensional.

Case (b) is described as a symmetry imposed crossing, and the Jahn–Teller theorem [14] applies to this case if the molecule is nonlinear. An example of case (b) is provided by the $^2E'$ states of B_3 at D_{3h} geometry [15]. Case (c) is called an accidental crossing. The three-dimensional potential energy surfaces belonging to the two lowest $^1A_1$ states of O_3 at the specific C_{2v} geometry described by Xantheas, Elbert, and Ruedenberg [16], where these surfaces intersect serves as an example of case (c).

Teller [17] and, after a dispute on the topic, Mead [18] showed that for nonrelativistic Hamiltonians and for triatomic or larger systems, energetic degeneracies for states that globally belong to the same spin and space symmetry, can appear in $3N_A - 8$ dimensional spaces. For the triatomic systems that serves as examples of cases (b) and (c), we therefore expect the degeneracies to appear in one dimension. For the B_3 example it is obvious that the one-dimensional degeneracy preserving seam is specified by the "breathing" coordinate which preserves the D_{3h} geometry. For O_3, the described point of intersection appears for C_{2v} symmetry. However, this point belongs to a one-dimensional seam of intersection that elsewhere correspond to molecular C_s symmetry [16].

2.2. *Infinitesimal distortion away from the reference geometry*

Now consider an infinitesimal displacement away from the reference geometry from x to $x + \lambda$ along the distortion direction denoted a. The functions $\Psi_T(x)$ and $\Psi_U(x)$, whose CI coefficients diagonalize the Hamiltonian at x, will evolve into new functions $\Psi_T(x + \lambda)$ and $\Psi_U(x + \lambda)$ which may not diagonalize the

Hamiltonian at this infinitesimally displaced geometry. However, there always exists a unitary transformation to combine $\Psi_T(x+\lambda)$ and $\Psi_U(x+\lambda)$ into two states, $\Psi_R(x+\lambda)$ and $\Psi_S(x+\lambda)$ that do diagonalize H at the infinitesimally displaced geometry. The criteria defining this unitary transformation are to be found later in Eq. (30). For now, it suffices to note that this transformation is dependent upon the coordinate a along which the distortion is to be made. For this reason, the derivatives obtained in this paper should be viewed as "directional derivatives" rather than as analytic derivatives.

Assuming that such a unitary transformation has already been performed, we continue our analysis with the two eigenstates $\Psi_R(x)$ and $\Psi_S(x)$. At the infinitesimally distorted geometry we consider the point group that applies to the Hamiltonian at both the reference and the infinitesimally displaced geometry (notice, if *no* rotation or translation is involved in the distortion, this point group is the one that also applies to the Hamiltonian at the displaced geometry). According to this definition, the infinitesimal distortion of the nuclear framework can either preserve or lower the point group symmetry. Contingent upon either of these outcomes, several resulting symmetries of the eigenstates at the displaced geometry are possible, and the three cases (a), (b), and (c) can accordingly be split into subcases which are important to distinguish among.

Two subcases appear under case (a) when distortions occur:

(a1) The two states have different symmetries at the displaced geometry.

(a2) The two states have the same, non-symmetry-degenerate symmetry at the displaced geometry.

To illustrate, consider again the BeH_2 molecule in C_{2v} geometries at which the lowest $^1A_1$ and $^1B_2$ potential surfaces intersect [13]. A C_{2v} symmetry-preserving distortion of this system provides an example of case (a1). Case (a2) appears for a non-symmetry preserving distortion that lowers the symmetry to either C_s or C_1 symmetry, in which case, at the displaced geometry, both states are $^1A'$ states if of C_s symmetry and ^1A states if of C_1 symmetry. Notice that for the BeH_2 example, although C_1 can never become the point group of the stationary molecule, if rotational motion is considered as a source of non-adiabatic coupling, it could become the point group appropriate for handling such couplings.

Under the same class of distortions, case (b) splits into three subcases:

(b1) The two states have the same E-symmetry at the displaced geometry.

(b2) The two states have different symmetries at the displaced geometry.

(b3) The two states have the same, non-symmetry-degenerate symmetry at the displaced geometry.

Let us again take the example of two $^2E'$ states of the B_3 molecule at D_{3h} geometry [15]. A D_{3h} symmetry-preserving distortion such as the totally symmetric breathing mode leads to case (b1). If the distortion lowers the symmetry to C_{2v}, the states at the displaced geometry have $^2A_1$ and $^2B_2$ symmetry and case (b2) is obtained. For distortions that leads to C_s symmetry, both states become $^2A'$ states and we realize an example of case (b3).

For case (c) there is only one possible subcase:

(c1) The two states have the same, non-symmetry-degenerate symmetry at the displaced geometry.

We illustrate this by again considering the special C_{2v} geometries where the lowest $^1A_1$ states of O_3 intersect [16]. If the distortion preserves C_{2v} symmetry, the states will still have $^1A_1$ symmetry, and if it lowers the symmetry to C_s, then the states both become $^1A'$ states.

In cases (a1) and (b2), symmetry forbids mixing of the R and S states, and therefore the first-order as well as higher-order state-state responses that could mix Ψ_R and Ψ_S, are zero. In case (b1) the Ψ_R and Ψ_S states remain energetically degenerate as the system is distorted. Therefore, the first-order state-state response among Ψ_R and Ψ_S is not well defined (i.e., is arbitrary), but can be chosen as zero.

For the three remaining cases, the first-order geometrical state-state response is not so trivially defined by symmetry; as specified earlier, these responses are likewise not provided through the equations of Ref. [12]. Response equations for SA-MCSCF wave functions which allow the determination of the state-state responses in these cases, and in more complex cases where more than two states are degenerate at the reference geometry, are derived in the next section. Since responses of wave functions and of energies are both determined via the SA-MCSCF approximation to the Schrödinger equation, they are closely related. That is, the derivations in the next section also provide equations needed for evaluating first- and second-order directional energy derivatives for equally weighted energetically degenerate SA-MCSCF wave functions.

3. Theoretical approach

3.1. Basic definitions

This subsection introduces the notation and basic definitions needed for the evaluation of the response equations that allow the determination of *all geometrical linear responses and directional first- and second-order energy derivatives* for SA-MCSCF wave functions.

Consider a molecular system in a specific configuration defined by the positions of the nuclei. The set of normalized electronic SA-MCSCF wave functions is denoted $\{\Psi_A \mid A = 1, 2, \ldots, N\}$. These wave functions are expanded in a subset of all symmetry adapted orthonormal configuration state functions (CSF's), $\{\Phi_I \mid I = 1, 2, \ldots, N\}$, as:

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

where the C_I^A's are the CI-coefficients of Ψ_A. Since the electronic wave functions are taken to be normalized, the CI-coefficients must obey the condition:

$$\sum_I C_I^{B+} C_I^A = \delta_{BA}. \tag{3}$$

The CSFs are created from a set of orthonormal molecular orbitals (MOs), $\{\varphi_i \mid i = 1, 2, \ldots, M\}$, which again are created as linear combinations of a chosen set of atomic orbital (AO), or symmetry adapted orbital (SO), basis functions, $\{X_\mu \mid \mu = 1, 2, \ldots, M\}$:

$$\varphi_i = \sum_\mu^M K_\mu^i X_\mu, \tag{4}$$

where the K_μ^i's are the MO coefficients.

Assuming that the states and orbitals are real and taking the set of electronic state functions to diagonalize the electronic Hamiltonian in the space they span, the following equations for the CI-coefficients must be fulfilled:

$$\sum_{IJ} C_I^B C_J^A (\delta_{IJ} E_B - H_{IJ}) = 0. \tag{5}$$

E_B is the energy for state B and the Hamiltonian matrix elements that appear in this equation and elsewhere are defined as:

$$H_{IJ} \equiv \sum_{ij} h_{ij} \gamma_{ij}^{IJ} + \sum_{ijkl} (ij \mid kl) \Gamma_{ijkl}^{IJ}, \tag{6}$$

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

The molecular orbitals are assumed to variationally optimize the SA energy functional:

$$E^{SA} \equiv \sum_{R}^{\Omega} \omega_R \langle \Psi_R | H | \Psi_R \rangle = \sum_{R}^{\Omega} \omega_R E_R, \tag{7}$$

which only involves a subset of all N electronic states. The number of states in this subset is denoted Ω and these states are called *internal* states and labeled R, S, T, U. Accordingly, the states not in this subset are termed *externals*. The number of *external* wave functions is denoted Λ, and $\Omega + \Lambda = N$. The ω_R in Eq. (7) is the weight factor assigned to the internal state R.

In the SA energy functional, only the Ω *internal* states appear, and these states are assumed to diagonalize the Hamiltonian as in Eq. (5). For purposes of derivation, all the *external* plus *internal* states are assumed to obey Eq. (5). However, as demonstrated explicitly later in this paper, the precise nature of the *external* states (in particular that they obey Eq. (5)) disappears in the final working equations.

The condition that E^{SA} be stationary with respect to variations in the molecular orbitals in the Ψ_R's results in having the SA-Generalized Brillouin Theorem (GBT):

$$\varepsilon_{ij}^{SA} - \varepsilon_{ji}^{SA} = 0, \tag{8}$$

fulfilled.

The SA Lagrangian in Eq. (8) is defined as:

$$\varepsilon_{ij}^{SA} \equiv \sum_{k} h_{ik} \gamma_{ji}^{SA} + 2 \sum_{klm} (ik \mid lm) \Gamma_{jklm}^{SA}, \tag{9}$$

with the one and two particle SA density matrices defined as the weighted sum of one- and two-particle density matrices involving only the *internal* states:

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

$$\Gamma_{ijkl}^{SA} \equiv \sum_{R}^{\Omega} \omega_R \Gamma_{ijkl}^{R}. \tag{10b}$$

The density matrices for each of the *internal* states are given as:

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

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

To maximize understanding of the equations obtained in this section, in agreement with the above notation and the notation in Ref. [12], we adopte the following conventions:

$\nu, \mu, \varrho, \sigma$	denote AO's or SO's,
i, j, k, l, m, n, p	denote MO's,
I, J, K, L	denote CSF's,
A, B	denote states in general,
R, S, T, U	denote *internal* states,
P, Q	denote *external* states.

In order to derive geometrical response equations, one can directly differentiate Eqs. (5) and (8) with respect to the coordinates that define the distortion to be considered. To determine the geometrical first-order CSF-responses for energetically degenerate *and* equally weighted *internal* SA states, we need to take first- and second-order derivatives with respect to the distortion coordinate a. These differentiations and the resulting equations are treated in the next two subsections; before doing so, we define a few quantities and introduce identities that will be used for these derivations.

The geometrical first- and second-order state-state responses among the states A and B, V_{AB}^{a} and V_{AB}^{aa}, respectively, are defined from the first- and second-order CSF-responses for state A with respect to the coordinate a:

$$\frac{\partial C_I^A}{\partial a} = \sum_{B}^{N} V_{AB}^{a} C_I^B, \tag{12}$$

$$\frac{\partial^2 C_I^A}{\partial a^2} = \sum_{B}^{N} V_{AB}^{aa} C_I^B. \tag{13}$$

These definitions lead to the following identities:

$$0 = V_{AB}^{a} + V_{BA}^{a}, \tag{14a}$$

$$0 = V_{AB}^{aa} + V_{BA}^{aa} + 2\sum_{I} \frac{\partial C_I^A}{\partial a} \frac{\partial C_I^B}{\partial a}, \tag{14b}$$

$$\frac{\partial V_{AB}^{a}}{\partial a} = V_{AB}^{aa} + \sum_{I} \frac{\partial C_I^A}{\partial a} \frac{\partial C_I^B}{\partial a}, \tag{14c}$$

$$\sum_{I} \frac{\partial C_I^A}{\partial a} \frac{\partial C_I^b}{\partial a} = \sum_{D} V_{AD}^{a} V_{BD}^{a}. \tag{14d}$$

Similarly, the geometrical first- and second-order orbital responses among orbitals i and j, U_{ij}^{a} and U_{ij}^{aa}, respectively, are defined in terms of responses of the MO-coefficients:

$$\frac{\partial K_\mu^i}{\partial a} = \sum_j U_{ji}^a K_\mu^j, \tag{15}$$

$$\frac{\partial^2 K_\mu^i}{\partial a^2} = \sum_j U_{ji}^{aa} K_\mu^j. \tag{16}$$

These definitions imply the following identities:

$$0 = U_{ij}^a + U_{ji}^a + S_{ij}^a, \tag{17a}$$

$$0 = U_{ij}^{aa} + U_{ji}^{aa} + S_{ij}^{aa} + 2\sum_k (U_{ik}^a U_{jk}^a - S_{ik}^a S_{jk}^a), \tag{17b}$$

$$\frac{\partial U_{ij}^a}{\partial a} = U_{ij}^{aa} - \sum_k U_{ik}^a U_{kj}^a, \tag{17c}$$

with S_{ij}^a and S_{ij}^{aa} defined as:

$$S_{ij}^a \equiv \sum_{\mu\nu} K_\mu^i K_\nu^j \frac{\partial \langle X_\mu \mid X_\nu \rangle}{\partial a}, \tag{18a}$$

$$S_{ij}^{aa} \equiv \sum_{\mu\nu} K_\mu^i K_\nu^j \frac{\partial^2 \langle X_\mu \mid X_\nu \rangle}{\partial a^2}. \tag{18b}$$

As stated above, these identities will be of considerable use in the derivations carried out below.

3.2. Linear geometrical response equations and first-order directional energy derivatives

3.2.1. The response equations. Just as Eqs. (5) and (8) constitute the fundamental working equations of SA-MCSCF theory, their derivatives form the basis on which the desired wave function and energy responses can be determined. With the first-order energy derivative along the coordinate a, E_B^a, defined as:

$$E_B^a \equiv \frac{\partial E_B}{\partial a}, \tag{19}$$

first order differentiation of Eq. (5) with respect to the coordinate a, gives the set of equations:

$$0 = \delta_{BA} E_B^a + (E_B - E_A) V_{BA}^a - \sum_{IJ} C_I^B C_J^A \frac{\partial H_{IJ}}{\partial a}. \tag{20}$$

The derivative of the Hamiltonian matrix with respect to the coordinate a appearing above is given in terms of quantities defined earlier and the so-called *derivative Hamiltonian*, as:

$$\frac{\partial H_{IJ}}{\partial a} = H_{IJ}^a + \sum_{ij} U_{ij}^a \left\{ \sum_k h_{ik} (\gamma_{jk}^{IJ} + \gamma_{jk}^{JI}) + 2 \sum_{klm} (ik \mid lm)(\Gamma_{jklm}^{IJ} + \Gamma_{jklm}^{JI}) \right\}. \tag{21}$$

The *derivative Hamiltonian* is:

$$H_{IJ}^a \equiv \sum_{ij} h_{ij}^a \gamma_{ij}^{IJ} + \sum_{ijkl} (ij \mid kl)^a \Gamma_{ijkl}^{IJ}, \tag{22}$$

where:

$$h_{ij}^{a} \equiv \sum_{\mu\nu} K_{\mu}^{i} K_{\nu}^{j} \frac{\partial h_{\mu\nu}}{\partial a}, \tag{23a}$$

$$(ij \mid kl)^{a} \equiv \sum_{\mu\nu\varrho\sigma} K_{\mu}^{i} K_{\nu}^{j} K_{\varrho}^{k} K_{\sigma}^{l} \frac{\partial(\mu\nu \mid \varrho\sigma)}{\partial a}. \tag{23b}$$

Similarly, first-order differentiation of Eq. (8) with respect to the coordinate a gives the equation:

$$\begin{aligned} 0 = {} & \varepsilon_{ij}^{\mathrm{SA}a} - \varepsilon_{ji}^{\mathrm{SA}a} + \sum_{R}^{\Omega} \sum_{P}^{\Lambda} V_{RP}^{a} \omega_{R} \sum_{J} C_{J}^{P} (T_{ij}^{JR} - T_{ji}^{JR}) \\ & + \sum_{S>R}^{\Omega} V_{RS}^{a} (\omega_{R} - \omega_{S}) \sum_{J} C_{J}^{R} (T_{ij}^{JS} - T_{ji}^{JS}) \\ & + \sum_{n>k} U_{nk}^{a} [Y_{ijnk}^{\mathrm{SA}} - Y_{jink}^{\mathrm{SA}} - Y_{ijkn}^{\mathrm{SA}} + Y_{jikn}^{\mathrm{SA}} + \delta_{ik} \varepsilon_{nj}^{\mathrm{SA}} - \delta_{jk} \varepsilon_{ni}^{\mathrm{SA}} - \delta_{in} \varepsilon_{kj}^{\mathrm{SA}} + \delta_{jn} \varepsilon_{ki}^{\mathrm{SA}}] \\ & - \sum_{n>k} S_{nk}^{a} [Y_{ijkn}^{\mathrm{SA}} - Y_{jikn}^{\mathrm{SA}} + \delta_{in} \varepsilon_{kj}^{\mathrm{SA}} - \delta_{jn} \varepsilon_{ki}^{\mathrm{SA}}] \\ & - \tfrac{1}{2} \sum_{n} S_{nn}^{a} [Y_{ijnn}^{\mathrm{SA}} - Y_{jinn}^{\mathrm{SA}} + \delta_{in} \varepsilon_{nj}^{\mathrm{SA}} - \delta_{jn} \varepsilon_{ni}^{\mathrm{SA}}], \end{aligned} \tag{24}$$

where we have used the definitions:

$$\varepsilon_{ij}^{\mathrm{SA}a} \equiv \sum_{k} h_{ik}^{a} \gamma_{jk}^{\mathrm{SA}} + 2 \sum_{klm} (ik \mid lm)^{a} \Gamma_{jklm}^{\mathrm{SA}}, \tag{25}$$

$$T_{ij}^{JR} \equiv \sum_{I} C_{I}^{R} \left[\sum_{k} h_{ik} (\gamma_{jk}^{IJ} + \gamma_{jk}^{JI}) + 2 \sum_{klm} (ik \mid lm)(\Gamma_{jklm}^{IJ} + \Gamma_{jklm}^{JI}) \right], \tag{26}$$

$$Y_{ijnk}^{\mathrm{SA}} \equiv h_{in} \gamma_{jk}^{\mathrm{SA}} + 2 \sum_{lm} \{(in \mid lm) \Gamma_{jklm}^{\mathrm{SA}} + (il \mid nm)(\Gamma_{jlkm}^{\mathrm{SA}} + \Gamma_{jlmk}^{\mathrm{SA}})\}. \tag{27}$$

3.2.2. Problems that arise when degenerate states have equal weighting. As shown in Ref. [12], the fundamental results of Eq. (20) and of Eq. (24) for B referring to *internal* states only (i.e. $B = R$), can be combined to give the geometrical first-order response equations that determine most, but not all, of the desired orbital responses and state-state responses that involve *internal* states. If two or more of the *internal* states are energetically degenerate and equally weighted, it is seen from Eqs. (20) and (24) that all terms involving the state-state responses *among these* states drop out. Therefore state-state responses among equally weighted energetically degenerate states can *not* be resolved from these geometrical first-order response equations. If energetically degenerate states are assigned unequal weights, the terms involving these same state-state responses remain present in Eq. (24), and it is therefore possible to resolve these state-state responses from the geometrical first order response equations *if* unequal weighting are (probably inappropriately) assigned to the corresponding degenerate states.

3.2.3. Unitary transformations of degenerate states in preparation for the distortion. In all cases where the states A and B belong to a degenerate set, Eq. (20)

expresses an important constraint, which is dependent on the distortion coordinate and which must be obeyed by the CI coefficients of these states:

$$0 = \sum_{IJ} C_I^B C_J^A \frac{\partial H_{IJ}}{\partial a}. \tag{28}$$

In general, this condition will not be fulfilled for the degenerate states originally obtained in the SA-MCSCF procedure (in the two dimensional example in Sect. 2 these states were denoted Ψ_T and Ψ_U). However, due to the energetic degeneracy among these states, arbitrary linear combinations that fufill Eq. (28) can be formed of these states. Defining the symmetric matrix K^a with elements:

$$K^a_{BA} \equiv \sum_{IJ} C_I^B C_J^A \frac{\partial H_{IJ}}{\partial a}, \tag{29}$$

the unitary transformed eigenstates (Ψ_R and Ψ_S in the example of Sect. 2) are defined in terms of the normalized eigenvectors v^a of the secular problem:

$$(K^a - E^a 1)v^a = 0. \tag{30}$$

That is, the normalized eigenvectors v^a define the unitary transformation matrix, briefly discussed in Sect. 2.2, that is used to transform the "original" degenerate eigenstates to the "transformed" degenerate eigenstates that fulfill Eq. (28). The eigenvalues E^a's of Eq. (30) are the directional energy derivatives in the direction of coordinate a for the "transformed" degenerate states.

The first order responses involving degenerate *internal* states obtained from the geometrical response equations of Ref. [12] apply to the "original" states. By using the unitary matrix defined from the v^a's, these responses must be transformed from the "original" state basis to the "transformed" state basis.

If, although likely inappropriate, unequal weights are assigned to degenerate states, it might be difficult to impose the condition expressed in Eq. (28). For example, unequal weighting of states that are supposed to be energetically degenerate (case (b) in Sect. 2) might artificially lift this degeneracy. Unitary transformations among such states will therefore not give new eigenstates, and hence the condition in Eq. (28) can not be imposed. In such cases, credible CSF-responses can only be found if equal weighting of the degenerate states is used.

3.2.4. Directional derivatives of surfaces and wave functions exist although analytical derivatives do not. The extra condition expressed in Eq. (28) was not treated in Ref. [12], nor has it, to our knowledge, been addressed in any other published work. However, this is a crucial condition, which applies to energetically degenerate CI-functions in general. For eigenstates that are energetically degenerate at a given reference geometry, but not energetically degenerate at a geometry infinitesimally distorted along the a coordinate, this condition guarantees that the eigenstates will evolve continuously with the distortion. If the condition is not fulfilled, the eigenstates will be discontinuous, as a consequence of which, the state-state responses and the related non-adiabatic coupling elements will be ill defined. This reflects the fact that intersecting potential surfaces are not analytically differentiable. Therefore an energy gradient is non-existing although the energy slope and higher derivatives for a *specific* direction are well defined.

It is appropriate at this time to clarify the above results in light of the conventional point of view on adiabatic potential energy surfaces as described by

Davidson [5]. It is convention to define the kth potential surface of global symmetry Γ as formed from that energy which, at each value of the internal nuclear coordinates, is obtained as the kth energy (in order of increasing energy) of the SA-MCSCF process. Generally, potential surfaces defined in this manner are not differentiable at crossing points; that is, for these crossing points molecular gradients or hessians can not be found, and also for the conventional adiabatic surfaces directional energy derivatives as found from Eq. (30) do not apply.

However, directional energy derivatives do apply to the surfaces which are simply defined by the energies of the continuous states detailed in Sect. 3.2.3. Herzberg and Longuet-Higgins [19] denote such surfaces as conically self-intersecting potential (CSIP) surfaces. The CSIP surfaces are closely related to the conventional adiabatic surfaces but one CSIP surface consists of two or more adiabatic surfaces. To better understand this point, let us take an example from the work of Davidson [5].

For $D_{\infty h}$ conformations of the H_3 system, the lowest $^2\Sigma_g^+$ and $^2\Sigma_u^+$ eigenstates cross. When distorted, via asymmetric stretching motion, to $C_{\infty v}$ symmetry, both of these states evolve into $^2\Sigma^+$ eigenstates. The energetically lower of the $^2\Sigma^+$ states connects to the lower of the $^2\Sigma_g^+$ and $^2\Sigma_u^+$ states (i.e., to $^2\Sigma_g^+$ at one side of the crossing and to $^2\Sigma_u^+$ at the other side of the crossing). Following a path that goes through the crossing (for instance the path along the $D_{\infty h}$ preserving coordinate) the energetically lower eigenstate adiabatically evolves into the energetically higher. A path starting and ending at the same nuclear configuration can therefore be chosen such that when adiabatically following one of the considered eigenstates, this eigenstate starts as the energetically lower and ends as the higher, or vice versa, starts as the higher and ends as the lower. The two different energies for the same nuclear conformation obviously belong to two distinct conventional adiabatic surfaces. According to the definition, however, these two energies belong to the same CSIP surface, as will all energies for the states considered in this example. See also Fig. 1.

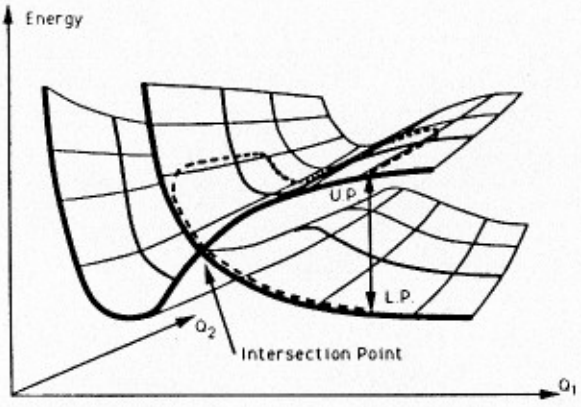

Fig. 1. Qualitative sketch of adiabatic energies as function of two nuclear coordinates Q_1 and Q_2 for two eigenstates. According to the conventional definition [5] the energies define two distinct adiabatic potential surfaces. These surfaces are connected through the intersection point, and according to our definition they are to be viewed as one CSIP surface (see text). The dashed line shows a path obtained by following the energy that corresponds to an eigenstate as this eigenstate is adiabatically distorted along a path that leads through the nuclear configuration of the intersection point. The path starts at the lower point (L.P.) and ends at the upper point (U.P.). The nuclear configuration at the L.P. is the same as at the U.P.

If one only considers potential surfaces in regions away from intersections, it is of course reasonable to treat them as separate surfaces. On the other hand, if, as in this work, one deals with potential surfaces in regions where they are connected, one needs to treat them as such and in this situation our definition of a CSIP surface is appropriate.

3.3. Second-order response equations and second-order directional energy derivatives

3.3.1. The two basic equations. To make further progress toward obtaining equations for the state-state responses among degenerate, equally weighted states, we assume that the geometrical first-order response equations have been solved for the orbital responses and for the state-state responses which they define. Further, we take as our energetically degenerate eigenstates those defined by the eigenvectors to Eq. (30) that satisfy Eq. (28).

Taking the second derivative of Eq. (8) with respect to the coordinate a gives the following equation:

$$
\begin{aligned}
0 = & \sum_{R}^{\Omega} \omega_R \sum_{P}^{\Lambda} V_{RP}^{aa} \sum_{J} C_J^P (T_{ij}^{JR} - T_{ji}^{JR}) \\
& + \sum_{S>R}^{\Omega} V_{RS}^{aa} (\omega_R - \omega_S) \sum_{J} C_J^R (T_{ij}^{JS} - T_{ji}^{JS}) \\
& + \sum_{n>k} U_{nk}^{aa} (Y_{ijnk}^{\mathrm{SA}} - Y_{jink}^{\mathrm{SA}} - Y_{ijkn}^{\mathrm{SA}} + Y_{jikn}^{\mathrm{SA}} + \delta_{ik} \varepsilon_{nj}^{\mathrm{SA}} - \delta_{jk} \varepsilon_{ni}^{\mathrm{SA}} - \delta_{in} \varepsilon_{kj}^{\mathrm{SA}} + \delta_{nj} \varepsilon_{ki}^{\mathrm{SA}}) \\
& - 2 \sum_{S>R}^{\Omega} \omega_S \sum_{I} \frac{\partial C_I^R}{\partial a} \frac{\partial C_I^S}{\partial a} \sum_{J} C_J^R (T_{ij}^{JS} - T_{ji}^{JS}) \\
& + \sum_{R}^{\Omega} \omega_R \sum_{IJ} \frac{\partial C_I^R}{\partial a} \left[2 \frac{\partial C_J^R}{\partial a} (\varepsilon_{ij}^{IJ} - \varepsilon_{ji}^{IJ}) - \frac{\partial C_I^R}{\partial a} C_J^R (T_{ij}^{JR} - T_{ji}^{JR}) \right] \\
& + 2 \sum_{R}^{\Omega} \omega_R \sum_{J} \frac{\partial C_J^R}{\partial a} \Xi_{ij}^{aJR} \\
& + \Theta_{ij}^{aa}, \qquad (31)
\end{aligned}
$$

where we have introduced the following definitions:

$$
\begin{aligned}
\theta_{ij}^{aa} \equiv & 2 \sum_{nk} U_{nk}^{a} (\delta_{ik} \varepsilon_{nj}^{\mathrm{SA}a} - \delta_{jk} \varepsilon_{ni}^{\mathrm{SA}a} + Y_{ijnk}^{\mathrm{SA}a} - Y_{jink}^{\mathrm{SA}a}) \\
& + 2 \sum_{pk} U_{pk}^{a} \sum_{n} (U_{ni}^{a} Y_{njpk}^{\mathrm{SA}} - U_{nj}^{a} Y_{nipk}^{\mathrm{SA}}) + 4 \sum_{npk} [(in \mid pk) Z_{jnpk}^{\mathrm{SA}} - (jn \mid pk) Z_{inpk}^{\mathrm{SA}}] \\
& - \sum_{n>k} \left[2 \sum_{l} (U_{nl}^{a} U_{kl}^{a} - S_{nl}^{a} S_{kl}^{a}) + S_{nk}^{aa} \right] (Y_{ijkn}^{\mathrm{SA}} - Y_{jikn}^{\mathrm{SA}} + \delta_{in} \varepsilon_{kj}^{\mathrm{SA}} - \delta_{jn} \varepsilon_{ki}^{\mathrm{SA}}) \\
& - \sum_{n} \left[\sum_{l} (U_{nl}^{a} U_{nl}^{a} - S_{nl}^{a} S_{nl}^{a}) + \tfrac{1}{2} S_{nn}^{aa} \right] (Y_{ijnn}^{\mathrm{SA}} - Y_{jinn}^{\mathrm{SA}} + \delta_{in} \varepsilon_{nj}^{\mathrm{SA}} - \delta_{jn} \varepsilon_{ni}^{\mathrm{SA}}) \\
& + \varepsilon_{ij}^{\mathrm{SA}aa} - \varepsilon_{ji}^{\mathrm{SA}aa}, \qquad (32)
\end{aligned}
$$

$$\Xi_{ij}^{aJR} \equiv T_{ij}^{aJR} - T_{ji}^{aJR} + \sum_{nk} U_{nk}^{a} \Bigg[\delta_{ik} T_{nj}^{JR} - \delta_{jk} T_{ni}^{JR} + \sum_{I} C_I^R (Y_{ijnk}^{IJ} + Y_{ijnk}^{JI} - Y_{jink}^{IJ} - Y_{jink}^{JI}) \Bigg], \quad (33)$$

$$\varepsilon_{ij}^{IJ} \equiv \sum_{k} h_{ik} \gamma_{jk}^{IJ} + 2 \sum_{klm} (ik \mid lm) \Gamma_{jklm}^{IJ}. \quad (34)$$

For shorthand notation in Eqs. (32)–(34) we have defined:

$$Y_{ijnk}^{IJ} \equiv h_{in} \gamma_{jk}^{IJ} + 2 \sum_{lm} \{(in \mid lm) \Gamma_{jklm}^{IJ} + (il \mid nm)(\Gamma_{jlkm}^{IJ} + \Gamma_{jlmk}^{IJ})\}, \quad (35)$$

$$Y_{ijnk}^{\mathrm{SA}a} \equiv h_{in}^{a} \gamma_{jk}^{\mathrm{SA}} + 2 \sum_{lm} \{(in \mid lm)^{a} \Gamma_{jklm}^{\mathrm{SA}} + (il \mid nm)^{a} (\Gamma_{ilkm}^{\mathrm{SA}} + \Gamma_{jlmk}^{\mathrm{SA}})\}, \quad (36)$$

$$T_{ij}^{aJR} \equiv \sum_{I} C_I^R \left(\sum_{k} h_{ik}^{a} (\gamma_{jk}^{IJ} + \gamma_{jk}^{JI}) + 2 \sum_{klm} (ik \mid lm)^{a} (\Gamma_{jklm}^{IJ} + \Gamma_{jklm}^{JI}) \right), \quad (37)$$

$$Z_{jnpk}^{\mathrm{SA}} \equiv \sum_{l} U_{pl}^{a} \sum_{m} [U_{km}^{a} \Gamma_{jnlm}^{\mathrm{SA}} - U_{nm}^{a} (\Gamma_{jmlk}^{\mathrm{SA}} + \Gamma_{jmkl}^{\mathrm{SA}})], \quad (38)$$

and:

$$\varepsilon_{ij}^{\mathrm{SA}aa} \equiv \sum_{k} h_{ik}^{aa} \gamma_{jk}^{\mathrm{SA}} + 2 \sum_{klm} (ik \mid lm)^{aa} \Gamma_{jklm}^{\mathrm{SA}}, \quad (39)$$

with:

$$h_{ij}^{aa} \equiv \sum_{\mu\nu} K_{\mu}^{i} K_{\nu}^{j} \frac{\partial^2 h_{\mu\nu}}{\partial a^2}, \quad (40)$$

$$(ij \mid kl)^{aa} \equiv \sum_{\mu\nu\varrho\sigma} K_{\mu}^{i} K_{\nu}^{j} K_{\varrho}^{k} K_{\sigma}^{l} \frac{\partial^2 (\mu\nu \mid \varrho\sigma)}{\partial a^2}. \quad (41)$$

Taking the second derivative of Eq. (5) with respect to the coordinate a gives:

$$0 = \delta_{BA} E_B^{aa} + (E_B^a - E_A^a) V_{BA}^a + (E_B - E_A) \left(V_{BA}^{aa} + \sum_{I} \frac{\partial C_I^B}{\partial a} \frac{\partial C_I^A}{\partial a} \right) - \sum_{IJ} \left(\frac{\partial C_I^B}{\partial a} C_J^A + C_I^B \frac{\partial C_J^A}{\partial a} \right) \frac{\partial H_{IJ}}{\partial a} - \sum_{IJ} C_I^B C_J^A \frac{\partial^2 H_{IJ}}{\partial a^2}, \quad (42)$$

with the second order directional energy derivative E_B^{aa} defined as:

$$E_B^{aa} \equiv \frac{\partial^2 E_B}{\partial a^2}. \quad (43)$$

Using Eq. (14b) it can be seen that Eq. (42) is symmetric in A and B. Equations (12), (14d), and (20) can now be exploited to rewrite Eq. (42) as:

$$0 = \delta_{Ba} E_B^{aa} + (E_B - E_A) V_{BA}^{aa} - \sum_{i>j} U_{ij}^{aa} \sum_{J} C_J^A (T_{ij}^{JB} - T_{ji}^{JB}) + \sum_{J} C_J^A \left[N_{JB}^{aa} - 2 \sum_{I} \frac{\partial C_I^B}{\partial a} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} E_B^a \right) \right], \quad (44)$$

where N^{aa}_{JB} is defined as:

$$N^{aa}_{JB} \equiv \sum_{i>j} T^{JB}_{ji}\left[S^{aa}_{ij} + 2\sum_k (U^a_{ik}U^a_{jk} - S^a_{ik}S^a_{jk})\right] + \tfrac{1}{2}\sum_i T^{JB}_{ii}\left[S^{aa}_{ii} + 2\sum_k (U^a_{ik}U^a_{ik} - S^a_{ik}S^a_{ik})\right] - \sum_I C^B_I H^{aa}_{IJ} - 2\sum_{ij} U^a_{ij}T^{aJB}_{ij} - \sum_{ij}\sum_{nk} U^a_{ij}U^a_{nk}\sum_I C^B_I(Y^{IJ}_{ijnk} + Y^{JI}_{ijnk}). \quad (45)$$

Notice that, in contrast to Eq. (42), Eq. (44) does not include products of first order CSF-responses; that is, Eq. (44) is linear in the response quantities.

3.3.2. Combining the two equations into one. In this work, we are only interested in responses that concern the *internal* states, thus we are lead to use Eq. (44) with B referring to the *internal* states (i.e. $B = R$). Since Eq. (31) and these $B = R$ cases of Eq. (44) are coupled, it is convenient to set up a single matrix equation that contains both sets. In order to simplify the notation, we assume that within the *internal* states there exist only one set of energetically degenerate states. That is, there may be a set of states that are doubly, triply, or more degenerate, but there are not two or more such degenerate sets of states. All states belonging to this degenerate set are assumed to be *internal* states and these degenerate states are all assumed to have the same weighting factor denoted ω_d. For further convenience, the indexing of the states is constructed such that these degenerate *internal* states appear first, then come the other *internal* states after which come the *externals*. The matrix equation that embodies Eq. (31) and Eq. (44) for B referring to *internal* states then reads:

$$\begin{pmatrix} \boldsymbol{A}^{11} & \tilde{\boldsymbol{A}}^{21+} & \tilde{\boldsymbol{A}}^{31+} & \boldsymbol{A}^{41+} & \boldsymbol{A}^{51+} & \boldsymbol{A}^{16} \\ \tilde{\boldsymbol{A}}^{21} & \tilde{\boldsymbol{A}}^{22} & 0 & 0 & 0 & 0 \\ \tilde{\boldsymbol{A}}^{31} & 0 & \tilde{\boldsymbol{A}}^{33} & 0 & 0 & \tilde{\boldsymbol{A}}^{36} \\ \boldsymbol{A}^{41} & 0 & 0 & \boldsymbol{A}^{44} & 0 & 0 \\ \boldsymbol{A}^{51} & 0 & 0 & 0 & \boldsymbol{A}^{55} & \boldsymbol{A}^{56} \\ \boldsymbol{A}^{61} & 0 & 0 & 0 & 0 & \boldsymbol{A}^{66} \end{pmatrix} \begin{pmatrix} \boldsymbol{V}^1 \\ \tilde{\boldsymbol{V}}^2 \\ \tilde{\boldsymbol{V}}^3 \\ \boldsymbol{V}^4 \\ \boldsymbol{V}^5 \\ \boldsymbol{V}^6 \end{pmatrix} = \begin{pmatrix} \boldsymbol{D}^1 \\ \tilde{\boldsymbol{D}}^2 \\ \tilde{\boldsymbol{D}}^3 \\ \boldsymbol{D}^4 \\ \boldsymbol{D}^5 \\ \boldsymbol{D}^6 \end{pmatrix}. \quad (46)$$

The definitions of the individual terms in the above matrix are found below.

Recall that the CSF-responses of the degenerate equally weighted states give rise to the state-state couplings that can not be obtained by solving the first-order equations. To separate out these more-difficult-to-compute state-state couplings from the couplings that must first be obtained from the first-order equations, let us express the CSF-responses of the degenerate states as follows:

$$\frac{\partial C^R_I}{\partial a} = W^{aR}_I + \sum_S^{\Omega^d} V^a_{RS}C^S_I. \quad (47)$$

The W^{aR}_I factor contains all contributions to the CSF-response of state R except those arising from the degenerate equally weighted state-state responses. Here and in the following, Ω^d is the number of energetically degenerate *internal* states. Accordingly, Ω^n is the number of *internal* states that do *not* belong to the energetically degenerate set. On the right hand side of Eq. (47) the first term, W^{aR}_I, which is defined through Eq. (12), is built from information already known

from solving the first-order geometrical response equations and from the transformation matrix found through Eq. (30). The second term is a sum that involves state-state responses among degenerate *internal* states (i.e., it contains response variables found from Eq. (46)). When Eq. (47) is inserted into Eq. (31), the terms involving products of first-order state-state responses among degenerate *internal* states combine to yield identically zero as a result of which Eq. (46) is linear in all variables.

3.3.3. Definitions of the matrix elements. The full matrix A on the left hand side of Eq. (46) is a square matrix, and the blocks of A are arranged such that rows for the block $A^{\alpha\beta}$ are labeled in the same way as columns for the block $A^{\gamma\alpha}$. In defining the matrix blocks in Eq. (46) we therefore only need to discuss the labeling of the rows. All of the matrix blocks and vectors are defined in Eqs. (48a)–(48t):

$$A^{11}_{ij,nk} \equiv Y^{SA}_{ijnk} - Y^{SA}_{jink} - Y^{SA}_{ijkn} + Y^{SA}_{jikn} + \delta_{ik}\varepsilon^{SA}_{nj} - \delta_{jk}\varepsilon^{SA}_{ni} - \delta_{in}\varepsilon^{SA}_{kj} + \delta_{jn}\varepsilon^{SA}_{ki}, \tag{48a}$$

$$A^{16}_{ij,RS} \equiv 2\omega_d \sum_J \left\{ C^S_J \Xi^{aJR}_{ij} - C^R_J \Xi^{aJS}_{ij} + W^{aR}_J (T^{JS}_{ij} - T^{JS}_{ji}) - W^{aS}_J (T^{JR}_{ij} - T^{JR}_{ji}) \right.$$
$$\left. - \sum_I \left(\sum_T^{\Omega^n} \frac{\omega_T}{\omega_d} \frac{\partial C^T_I}{\partial a} C^T_J + \sum_T^{\Omega^d} W^{aT}_I C^T_J \right) [C^S_I (T^{JR}_{ij} - T^{JR}_{ji}) - C^R_I (T^{JS}_{ij} - T^{JS}_{ji})] \right\}, \tag{48b}$$

$$D^1_{ij} \equiv 2 \sum_{S>R}^{\Omega^n} \omega_S \sum_I \frac{\partial C^R_I}{\partial a} \frac{\partial C^S_I}{\partial a} \sum_J C^R_J (T^{JS}_{ij} - T^{JS}_{ji})$$
$$+ 2\omega_d \sum_{S>R}^{\Omega^d} \sum_I W^{aR}_I W^{aS}_I \sum_J C^R_J (T^{JS}_{ij} - T^{JS}_{ji})$$
$$+ 2 \sum_R^{\Omega^n} \omega_R \sum_S^{\Omega^d} \sum_I \frac{\partial C^R_I}{\partial a} W^{aS}_I \sum_J C^R_J (T^{JS}_{ij} - T^{JS}_{ji})$$
$$+ \sum_R^{\Omega^n} \omega_R \sum_{IJ} \frac{\partial C^R_I}{\partial a} \left[\frac{\partial C^R_I}{\partial a} C^R_J (T^{JR}_{ij} - T^{JR}_{ji}) - 2 \frac{\partial C^R_J}{\partial a} (\varepsilon^{IJ}_{ij} - \varepsilon^{IJ}_{ji}) \right]$$
$$+ \omega_d \sum_R^{\Omega^d} \sum_{IJ} W^{aR}_I [W^{aR}_I C^R_J (T^{JR}_{ij} - T^{JR}_{ji}) - 2W^{aR}_J (\varepsilon^{IJ}_{ij} - \varepsilon^{IJ}_{ji})]$$
$$- 2 \sum_R^{\Omega^n} \omega_R \sum_J \frac{\partial C^R_J}{\partial a} \Xi^{aJR}_{ij} - 2\omega_d \sum_R^{\Omega^d} \sum_J W^{aR}_J \Xi^{aJR}_{ij} - \Theta^{aa}_{ij}, \tag{48c}$$

$$V^1_{ij} \equiv U^{aa}_{ij}. \tag{48d}$$

For the elements in Eqs. (48a)–(48d) the rows are labeled by the molecular orbital indices i and j, for which the orbital rotation among orbitals i and j is *allowed* and $i > j$. The orbital rotation among i and j is *allowed* if the *internal* wave functions emerging from the rotation can not alternatively be generated by a unitary transformation of the CI-coefficients.

$$\tilde{A}^{21}_{RP,nk} \equiv \tilde{A}^{31}_{RP,nk} \equiv \omega_R \sum_J C^P_J (T^{JR}_{nk} - T^{JR}_{kn}), \tag{48e}$$

$$\tilde{A}^{22}_{RP,TQ} \equiv \tilde{A}^{33}_{RP,TQ} \equiv \delta_{RT}\delta_{PQ}\omega_R (E_P - E_R), \tag{48f}$$

$$\tilde{A}^{36}_{RP,TU} \equiv 2\omega_R \sum_I (\delta_{RT} C^U_I - \delta_{RU} C^T_I) \sum_J C^P_J \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} E^a_R \right), \tag{48g}$$

$$\tilde{D}^2_{RP} \equiv \omega_R \sum_J C^P_J \left\{ N^{aa}_{JR} - 2 \sum_I \frac{\partial C^R_I}{\partial a} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} E^a_R \right) \right\}, \tag{48h}$$

$$\tilde{D}^3_{RP} \equiv \omega_R \sum_J C^P_J \left\{ N^{aa}_{JR} - 2 \sum_I W^{aR}_I \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} E^a_R \right) \right\}, \tag{48i}$$

$$\tilde{V}^2_{RP} \equiv \tilde{V}^3_{RP} \equiv V^{aa}_{RP}. \tag{48j}$$

The rows for the elements in Eqs. (48e)–(48j) are labeled by the state indices R and P. P runs over *external* states while R for $\tilde{A}^{21}_{RP,nk}$, $\tilde{A}^{22}_{RP,SQ}$, $\tilde{V}^2_{RP}$, and $\tilde{D}^2_{RP}$ belongs to Ω^n (i.e. the *internal* non-degenerate states), and for $\tilde{A}^{31}_{RP,nk}$, $\tilde{A}^{33}_{RP,SQ}$, $\tilde{A}^{36}_{RP,TU}$, $\tilde{V}^3_{RP}$, and $\tilde{D}^3_{RP}$ belongs to Ω^d (i.e. the *internal* degenerate states).

$$A^{41}_{RS,nk} \equiv A^{51}_{RS,nk} \equiv (\omega_R - \omega_S) \sum_J C^S_J (T^{JR}_{nk} - T^{JR}_{kn}), \tag{48k}$$

$$A^{44}_{RS,TU} \equiv A^{55}_{RS,TU} \equiv \delta_{RT}\delta_{SU}(\omega_R - \omega_S)(E_S - E_R), \tag{48l}$$

$$A^{56}_{RS,TU} \equiv 2(\omega_R - \omega_S) \sum_I (\delta_{RT} C^U_I - \delta_{RU} C^T_I) \sum_J C^S_J \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} E^a_R \right), \tag{48m}$$

$$D^4_{RS} \equiv (\omega_R - \omega_S) \sum_J C^S_J \left\{ N^{aa}_{JR} - 2 \sum_I \frac{\partial C^R_I}{\partial a} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} E^a_R \right) \right\}, \tag{48n}$$

$$D^5_{RS} \equiv (\omega_R - \omega_S) \sum_J C^S_J \left\{ N^{aa}_{JR} - 2 \sum_I W^{aR}_I \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} E^a_R \right) \right\}, \tag{48o}$$

$$V^4_{RS} \equiv V^5_{RS} \equiv V^{aa}_{RS}. \tag{48p}$$

For all terms in the Eqs. (48k) to (48p) the rows are labeled by the *internal* state indices R and S. S denotes states belonging to Ω^n while R denotes states that for $A^{41}_{RS,nk}$, $A^{44}_{RS,TU}$, V^4_{RS}, and D^4_{RS} belong to Ω^n but only if $\omega_R \neq \omega_S$ and $S > R$, and for $A^{51}_{RS,nk}$, $A^{55}_{RS,TU}$, $A^{56}_{RS,TU}$, V^5_{RS}, and D^5_{RS} belong to Ω^d but again only if $\omega_R \neq \omega_S$.

$$A^{61}_{RS,nk} \equiv \sum_J C^S_J (T^{JR}_{nk} - T^{JR}_{kn}), \tag{48q}$$

$$A^{66}_{RS,TU} \equiv 2 \sum_I (\delta_{RT} C^U_I - \delta_{RU} C^T_I) \sum_J C^S_J \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} E^a_R \right), \tag{48r}$$

$$D^6_{RS} \equiv \sum_J C^S_J \left\{ N^{aa}_{JR} - 2 \sum_I W^{aR}_I \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} E^a_R \right) \right\}, \tag{48s}$$

$$V^6_{RS} \equiv V^a_{RS}. \tag{48t}$$

Also, for all terms in Eqs. (48q)–(48t) the rows are labeled by the *internal* state indices R and S, where both R and S denote states belonging to Ω^d and $S > R$.

3.3.4. The diagonal equations of Eq. (44) are also useful. A careful analysis of Eqs. (44) and (46) shows that, even for B referring to *internal* states, the diagonal terms of Eq. (44) (i.e., those for which $B = A$) do not appear in Eq. (46). The coupled equations of Eq. (46) can be solved independently of these diagonal

equations, and having done so, the diagonal equations can be used to compute the directional second-order energy derivatives for all of the *internal* states including the degenerate ones. The details of this calculation are given below and in Eqs. (52).

3.3.5. Transformation to the CSF *basis.* The blocks of the matrix A and the parts of vector D marked with a tilde ($\sim$) contain CI-coefficients for the *external* states. Since these CI-coefficients are not usually known because the solution of the SA-MCSCF equations produces only the CI-coefficients of the *internal* states, it is crucial that this part of the coupled equations be transformed to a form where these *external* states' CI-coefficients are not needed.

In deriving second-order MCSCF theory for SA wave functions, Lengsfield [20] introduced a unitary tranformation that accomplishes this goal. The details of how to make this unitary transformation are described both by Lengsfield [20] and in Ref. [12], and will not be repeated here. The unitary transformation only affects the parts of Eq. (46) that are marked with tilde, and when it is applied, the final geometrical second-order response equations read:

$$\begin{pmatrix} A^{11} & A^{21+} & A^{31+} & A^{41+} & A^{51+} & A^{16} \\ A^{21} & A^{22} & 0 & 0 & 0 & 0 \\ A^{31} & 0 & A^{33} & 0 & 0 & A^{36} \\ A^{41} & 0 & 0 & A^{44} & 0 & 0 \\ A^{51} & 0 & 0 & 0 & A^{55} & A^{56} \\ A^{61} & 0 & 0 & 0 & 0 & A^{66} \end{pmatrix} \begin{pmatrix} V^1 \\ V^2 \\ V^3 \\ V^4 \\ V^5 \\ V^6 \end{pmatrix} = \begin{pmatrix} D^1 \\ D^2 \\ D^3 \\ D^4 \\ D^5 \\ D^6 \end{pmatrix}. \tag{49}$$

The parts of Eq. (49) that have not already been defined are given as:

$$A^{21}_{RK,nk} \equiv A^{31}_{RK,nk} \equiv \omega_R \sum_J M_{KJ}(T^{JR}_{nk} - T^{JR}_{kn}), \tag{50a}$$

$$A^{22}_{RK,TL} \equiv A^{33}_{RK,TL} \equiv \delta_{RT}\omega_R \left(\sum_{IJ} M_{KI} M_{JL} H_{IJ} - M_{KL} E_R + z L_{KL} \right), \tag{50b}$$

$$A^{36}_{RK,TU} \equiv 2\omega_R \sum_I (\delta_{RT} C^U_I - \delta_{RU} C^T_I) \sum_J M_{KJ} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} E^a_R \right), \tag{50c}$$

$$D^2_{RK} \equiv \omega_R \sum_J M_{KJ} \left\{ N^{aa}_{JR} - 2 \sum_I \frac{\partial C^R_I}{\partial a} \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} E^a_R \right) \right\}, \tag{50d}$$

$$D^3_{RK} \equiv \omega_R \sum_J M_{KJ} \left\{ N^{aa}_{JR} - 2 \sum_I W^{aR}_I \left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ} E^a_R \right) \right\}, \tag{50e}$$

$$V^2_{RK} \equiv V^3_{RK} \equiv \frac{\partial^2 C^R_K}{\partial a^2} - \sum_S^{\Omega} V^{aa}_{RS} C^S_K, \tag{50f}$$

with:

$$L_{KL} \equiv \sum_R^{\Omega} C^R_K C^R_L, \tag{51a}$$

$$M_{KL} \equiv \delta_{KL} - L_{KL}. \tag{51b}$$

The row labels for the elements defined in Eqs. (50a)–(50f) are R and K, with K running over the full N-dimensional CSF-space. For $A^{21}_{RK,nk}$, $A^{22}_{RK,SL}$, D^2_{RK}, and

$V^2_{RK}R$ belongs to Ω^n, while for $A^{31}_{RK,nk}$, $A^{33}_{RK,SL}$, $A^{36}_{RK,TU}$, D^3_{RK}, and $V^3_{RK}R$ belongs to Ω^d. The factor z appearing in Eq. (50b) is an arbitrary constant in units of energy, introduced to enable the transformation from the state-basis to the CSF-basis.

3.3.6. The solutions of the response equations contain first- and second-order results. The solution vector V to Eq. (49) contains both first- and second-order response information. The first-order data contained in V^6 are the state-state responses among energetically degenerate, equally weighted *internal* states. Once found, this information can be inserted into Eq. (47) to determine the full geometrical first-order CSF-responses for the energetically degenerate and equally weighted *internal* states, thereby fulfilling a primary objective of this paper.

Having determined the second-order orbital responses that appear as the V^1 vector of Eq. (49), the diagonal terms of Eq. (44) for *internal* states can then be used to determine the directional second-order energy derivatives along the coordinate a:

$$E^{aa}_R \equiv \sum_J C^R_J \left[\sum_{i>j} U^{aa}_{ij}(T^{JR}_{ij} - T^{JR}_{ji}) - N^{aa}_{JR} + 2\sum_I \frac{\partial C^R_I}{\partial a}\left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ}E^a_R\right)\right]. \quad (52)$$

These data combine with the directional first-order energy derivative obtained as the eigenvalues of the K matrix of Eq. (30) to produce full first- plus second-order directional derivative information for the energetically degenerate, equally weighted states.

Additional second-order information appears in the V solution vector of Eq. (49). In particular, the second-order CSF responses that do not include state-state responses among energetically degenerate, equally weighted states are obtained. In analogy with the first-order response case treated here, the second-order state-state responses among degenerate, equally weighted states can be found by considering the *third*-order response equations. This avenue will not be further pursued here, because it is beyond the goals of the present paper.

In addition to the diagonal terms, there were other second-order equations in Eq. (44) for B referring to *internal* states only that were not used to consturct the combined matrix in Eq. (46). These can be used to determine second-order state-state responses for *internal* states R and S that do not both belong to the energtically degenerate set, but for which the weighting factors are equal (i.e. $\omega_R = \omega_S$). For such states, Eq. (44) can be rewritten as:

$$V^{aa}_{RS} = (E_S - E_R)^{-1}\sum_J C^S_J \left[N^{aa}_{JR} - 2\sum_I \frac{\partial C^R_I}{\partial a}\left(\frac{\partial H_{IJ}}{\partial a} - \delta_{IJ}E^a_R\right) - \sum_{i>j} U^{aa}_{ij}(T^{JR}_{ij} - T^{JR}_{ji})\right]. \quad (53)$$

A detailed analysis reveals that all second-order orbital and state-state responses can be obtained from Eqs. (49) and (53) *except* for the V^{aa}_{RA} elements among the energetically degenerate, equally weighted *internal* states. The second order responses V^{aa}_{RA} for these states have to be determined from the third-order equations. Notice that second-order responses, resulting from successive infinitesimal distortions along two distinct coordinates a and b, for example V^{ab}_{RA}, are not considered in this work.

4. Conclusion and discussion

In this work, the evaluation of first-order CSF-responses and first- and second-order directional energy derivatives for energetically degenerate states has been made practical. Several different circumstances under which two or more states can be degenerate were first discussed. Situations for which symmetry dictates the first-order state-state responses among the degenerate states were mentioned, and it was stressed that these state-state responses usually have to be found by considering higher-order response equations.

In Sect. 3, it was shown how second-order geometrical response equations can be formulated such that first-order state-state responses among equally weighted, degenerate SA-MCSCF wave functions can be found. In addition, expressions were obtained for first- and second-order directional energy derivatives for these states. For directions or coordinates that do not involve rotation or translation, these directional energy derivatives apply to the CSIP energy surfaces defined in this work. Our definition of how surfaces and wave functions connect as one moves through regions of degeneracy is compared to the conventional adiabatic definition in which surfaces are connected via their energy ordering. Although the CSIP surfaces have directional energy derivatives for geometries at which states are degenerate, they are not analytically differentiable at these geometries.

Our derivation reveals that a specific linear combination of the degenerate states must be formed if the states and surfaces are to connect according to our definition. The condition that specifies this linear combination results from the first-order geometrical response equations, and it is shown that it depends upon the coordinate for which the responses are to be considered. As a consequence of this condition it has been argued that in cases where the degeneracy is symmetry imposed, credible CSF-responses can generally only be expected if the degenerate state averaged states are equally weighted as in this work.

Let us end this discussion by recapitulating the important steps that according to the shown derivations are needed for obtaining the linear CSF-responses and first- and second-order directional energy derivatives. The derivations apply to a system where the set of *internal* eigenstates contain a subset of equally weighted degenerate states. For this system it is assumed that the SA-MCSCF wave functions have been optimized, and that the SA-MCSCF first order geometrical response equations [12] have been solved for a distortion coordinate. The first important step is then to solve Eq. (30), which, dependent upon the distortion coordinate, dictates the right linear combinations of the degenerate states to be used for the calculation. The directional energy derivatives for these states, also result from Eq. (30). Equations (48a)–(48d), (48k)–(48t), and (50a)–(50f) are then used to set up the matrix equation Eq. (49). Solving Eq. (49) results in both geometrical first- and second-order responses. The first-order response are state-state responses among the energetically degenerate states. Using Eq. (47) these responses are combined with CI-coefficients and other responses obtained from the first-order response equations to evaluate the CSF-responses for the equally weighted degenerate *internal* SA-MCSCF states. Hereby we have completely determined all geometrical first-order responses for the system. The second-order orbital responses that also results from Eq. (49) are used in Eq. (52) to determine the directional second-order energy derivatives for the degenerate *internal* states.

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References

1. Mead CA, Truhlar DG (1979) J Chem Phys 70:2284
2. Mead CA (1980) Chem Phys 49:23
3. Mead CA (1980) Chem Phys 49:33
4. Mead CA (1983) J Chem Phys 78:807
5. Davidson ER (1977) J Am Chem Soc 99:397
6. Davidson ER, Borden WT (1983) J Phys Chem 87:4783
7. Frey RF, Davidson ER, To be published in Advances in Molecular Electronic Structure Theory, Vol. 1, p. 211–260, (JAI Press Inc., 1990)
8. Lengsfield BH III, Saxe P, Yarkony DR (1984) J Chem Phys 81:4549
9. Saxe P, Lengsfield BH III, Yarkony DR (1985) Chem Phys Lett 113:159
10. Lengsfield BH III, Yarkony DR (1986) J Chem Phys 84:348
11. Saxe P, Yarkony DR (1987) J Chem Phys 86:321
12. Bak KL, Boatz J, Simons J (1991) Int J Quantum Chem (to be published)
13. Nichols J, Taylor H, Schmidt P, Simons J (1990) J Chem Phys 92:340
14. Jahn HA, Teller E (1937) Proc R Soc London Ser A 161:220
15. Hernandez R, Simons J (1991) J Chem Phys (submitted)
16. Xantheas S, Elbert ST, Ruedenberg K (1990) J Chem Phys 93:7519
17. Teller E (1937) J Phys Chem 41:109
18. Mead CA (1979) J Chem Phys 70:2276
19. Herzberg G, Longuet-Higgins HC (1963) Dis Faraday Soc 35:77
20. Lengsfield BH III (1982) J Chem Phys 77:4073