Evaluation of analytic molecular orbital derivatives and gradients using the effective valence shell Hamiltonian method

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Expressions for the analytic energy gradients and the nonadiabatic derivative couplings are derived for the effective valence shell Hamiltonian theory (a variant of degenerate/quasidegenerate many-body perturbation theory) using the diagonal and off-diagonal Hellmann–Feynman formulas and a generalized set of coupled perturbed Hartree–Fock equations to evaluate the derivatives of the molecular orbitals. The method is designed for efficiently treating the energy derivatives and nonadiabatic couplings for several states simultaneously. The generalized coupled perturbed Hartree–Fock equations arise because the reference space orbitals are optimized for simultaneously describing the ground and excited states, a feature lost with the traditional partitioning where the virtual orbitals provide a poor choice for representing the low lying states. A simple correspondence emerges between the new generalized coupled perturbed Hartree–Fock and the traditional coupled-perturbed Hartree–Fock methods enabling the use of the former with straightforward modifications. The derivatives of the second and higher order portions of the effective Hamiltonian are readily obtained using a diagrammatic representation that will be described elsewhere. © *1998 American Institute of Physics.* [S0021-9606(98)30546-2]

I. INTRODUCTION

The computation of analytic energy derivatives is essential in optimizing molecular geometries, determining vibrational frequencies, and finding reaction paths. The evaluation of these analytic derivatives becomes a more daunting task both for highly open shell systems and near transition states where multireference configurational treatments are necessary to describe the near degeneracy nondynamical correlation. The complexity of multiconfigurational methods for highly correlated *ab initio* computations has until very recently precluded the development of analytical gradient approaches in conjunction with the multireference configurational perturbational (MRPT) methods whose several formulations[1–8] have been quite successful in treating highly correlated open shell systems.

We develop analytical energy derivative methods for the effective valence shell Hamiltonian (H^v), a complete active space MRPT approach of the ''perturb then diagonalize'' variety. This *ab initio* analytic energy derivative MRPT formulation is facilitated by two special features of the H^v method. The use of complete active space implies that the H^v computations proceed by diagonalizing an effective valence shell Hamiltonian H^v, and, therefore, the analytical derivatives may be represented through the H^v Hellmann–Feynman theorem[9] in terms of matrix elements of the analytical derivatives of H^v. The latter, in turn, may be expressed in diagrammatic form as derivatives of individual MRPT many-body Feynman diagrams for H^v. Once a suitable diagrammatic representation is introduced for the derivatives of the Feynman diagrams, the determination of the

diagrams becomes a straightforward process, but the details are fairly lengthy due to the large number of diagrams contributing to H^v even in the lowest nontrivial second order. Thus, this portion of the theory is deferred to the next paper in this series.[10]

Before proceeding to the theory for the MRPT analytic H^v energy derivatives, we note that an important by-product of this approach enables the computation of nonadiabatic derivative coupling matrix element which describe the breakdown of the Born–Oppenheimer (BO) approximation when there exists a degeneracy or near degeneracy of the electronic states along the potential energy surface. In such regions of space, interconversion of electronic and nuclear energy occurs, and nonadiabatic transitions may proceed between different adiabatic potential energy surfaces. These transitions are responsible for phenomena like photodissociation, predissociation, and the quenching of electronically excited states, etc. The interpretation of these radiationless transitions requires computation of the *nonadiabatic coupling* matrix elements between the nearly degenerate electronic states as represented either in an diabatic or adiabatic representation.

Within an adiabatic formalism, the breakdown of the BO approximation originates, in part, from nonvanishing derivative coupling integrals of the form $\langle \Psi^I | (\partial/\partial R_\alpha) \Psi^J \rangle_e$ and $\langle \Psi^I | \partial^2/\partial R_\alpha^2 \Psi^J \rangle_e$, where R_α is an appropriate nuclear degree of freedom, the expectation value $\langle | \rangle_e$ denotes an integration over electronic coordinates ($\mathbf{r}$), and $\Psi^I \equiv \Psi^I(\mathbf{r};\mathbf{R})$ is an eigenfunction of the BO Hamiltonian. The coupling $\langle \Psi^I | (\partial/\partial R_\alpha) \Psi^J \rangle_e$ is of prime importance in describing nonadiabatic phenomena. The diabatic representation formally incorporates a portion of the nonadiabatic derivative

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couplings by implementing one of several diabatization schemes[11,12] which transform the adiabatic BO potential energy surfaces to a basis where a dominant portion of the nuclear derivative coupling are removed.[13] The derivative couplings between the diabatic states are then treated by the evaluation of the configuration interaction (CI) matrix elements coupling the states. Unfortunately, diabatization cannot completely remove the derivative couplings, and there is poor understanding concerning the influence of the residual derivative couplings within various diabatization schemes.[11–13]

The direct computation (through numerical or finite difference techniques[14,15]) of the derivative couplings (or energy gradients) requires differentiation of the electronic wave functions with respect to the nuclear coordinates, a very expensive and cumbersome procedure for molecules with more than two atoms where separate numerical derivatives are needed for each degree of freedom. Alternatively, these nonadiabatic coupling terms can be evaluated directly through the use of the Hellmann–Feynman theorem or the Sidis formula,[16] provided the wave functions are exact. Recent advances in analytic gradient methods for differentiating energy functionals have enabled the direct evaluation of the nonadiabatic derivative coupling matrix elements for polyatomic molecules.[17–22] The analytic evaluation of energy gradients and nonadiabatic derivative couplings involves the direct computation of derivatives of the molecular orbitals and of the CI wave functions with respect to the nuclear degrees of freedom. Considerable effort has enabled evaluating these derivatives for various self-consistent field (SCF), CI, and single reference perturbative (SRPT) methods.[17,23–26] Typically energy gradient calculations are performed for the ground electronic state, but these calculations can, in principle, be performed for the excited states as well. The evaluation of nonadiabatic derivative couplings emerges as an extension of the energy gradient methods. However, MRPT treatments have not been available for the evaluation of analytic energy gradient and nonadiabatic derivative couplings, in part, because of the complexity of all MRPT methods and of the prior widespread mistaken belief that the ''diagonalize, then perturb'' methods are unsuitable for computing global potential energy surfaces.

The present work provides the first formal treatment of analytic energy gradients and nonadiabatic derivative couplings using a ''perturb, then diagonalize'' multireference *ab initio* approach, the effective valence shell Hamiltonian (H^v) method. The H^v method formulation of multireference perturbation theory has been demonstrated to be accurate for calculating atomic spectra,[27–29] diatomic potential energy curves,[30,31] and the electronic spectra of conjugated π-electronic spectra at their equilibrium geometries.[32–34] Recent calculations for global potential energy surfaces of CH_3SH,[35] H_2S,[36] $CaOH$,[37] and C_2H^+ (Ref. 38) demonstrate the ability of the method to generate the ground and excited potential energy surfaces simultaneously from a single computation for quite nontrivial molecular systems. The calculations for CH_3SH and H_2S yield insight into experiments probing the nonadiabatic photodissociation dynamics,[39] but fully *ab initio* quantum scattering calculations upon *ab initio*

potential energy surfaces require the evaluation of the nonadiabatic derivative couplings between the excited states.

Essential to the calculation of the nonadiabatic couplings and energy gradient is the computation of the orbital derivatives with respect to the nuclear displacements. While the orbital derivatives are generally obtained from the solutions of coupled-perturbed Hartree–Fock (CPHF) equations[40,41] or couple-perturbed multiconfiguration self-consistent field (CP-MCSCF) equations,[42–44] acquiring orbital derivatives for the H^v method presents a more complicated task because this approach introduces a set of orbitals designed to minimize the perturbative corrections for the low lying electronic excited states. The first order H^v computation corresponds to a complete active space CI treatment, which, in principle, provides upper bounds to all state energies, but which, in practice, can be expected to be reasonable accurate only for the lower lying states. The traditional choice of some active orbitals as virtual orbitals from a ground state SCF computation introduces low lying virtual orbitals that are, at best, suited for describing the negative ion and not the low lying excited states of interest. Thus, those active orbitals not occupied in the ground state SCF approximation should be chosen as more representative of orbitals suitable for these excited states. One possible choice emerges from restricted single excitation CI computations where excitations are only permitted from the highest occupied ground state orbital[45] (HOMO), but a simpler and often equivalent approach involves using improved virtual orbitals (IVOs) in the H^v valence space. These IVOs are generated by single orbital SCF optimizations in which the Fock operator is defined by promoting an electron from the HOMO into the orbital being optimized, while all previously determined orbitals are kept frozen. Hence, the resulting IVOs are eigenfunctions of a set of Fock operators which all differ from the ground state Fock operator. Since the IVOs and the ground state occupied Hartree–Fock orbitals appearing in the H^v calculations emerge as eigenfunctions of different Fock operators, the analytical derivatives of these orbitals can, in principle, be obtained by an extension of the single Fock operator based traditional CPHF approaches. This extension actually requires far more theoretical analysis than the evaluation of analytical derivatives of the H^v energy diagrams, so the present paper focuses on this portion of the theory.

Section II briefly outlines required elements of the H^v theory. Section III describes the treatment of the energy gradients and the nonadiabatic derivative coupling matrix elements within the H^v formulation. Because the exact H^v yields exact eigenvalues of the full Hamiltonian, the derivative formulation should, in principle, approach the exact derivatives as the perturbative order increases (so long as the series converges[46,47]). More practically, however, the H^v is designed to produce accurate energies at low orders of truncation[46,47] where accurate derivatives and nonadiabatic couplings should likewise emerge. Section IV describes the multiple Fock operator based coupled-perturbed Hartree–Fock method that is necessary for evaluating the energy gradients and nonadiabatic couplings within the H^v method. Similar methods may be used to deal with the orbital derivatives for methods which introduce more complicated defini-

tions of orbitals and zeroth order Hamiltonians, and the solution of the generalized coupled-perturbed Hartree–Fock equations may be represented as a sum to all orders of particular classes of diagrams in ordinary MBPT similar to the description for the traditional case.[48] Although computations solely involving geometry optimizations might be treated more efficiently using Z-matrix techniques,[20] the coupled-perturbed Hartree–Fock approach used here is simpler for a first implementation and checking of the theory, and this method is also used because our main interest lies in excited state systems whose full *ab initio* dynamics requires computation of the nonadiabatic couplings. While this manuscript was in preparation, a paper appeared[49] providing analytical gradients in the ''diagonalize, then perturb'' formulation of Hirao. Their approach is quite different from the present one and does not use CPHF methods to obtain the orbital derivatives.

II. THEORY

Perturbation theory begins with the decomposition of the molecular electronic Hamiltonian H into a zeroth order part H_0 and a perturbation V,

$$H = H_0 + V, \tag{2.1}$$

where H_0 is constructed as a sum of one-electron Fock operators. The full many-electron Hilbert space is then partitioned into a primary space (also called model or reference space) with projector P and its orthogonal complement with projector $Q = 1 - P$. The P space spans the valence space of all distinct configuration state functions involving a filled core and the remaining electrons distributed among the valence orbitals in all possible way to ensure completeness of the P-space. Hence, the Q-space contains all basis functions with at least one core-hole and/or one occupied-excited orbitals. The H^v method transforms the full Schrodinger equation,

$$H\Psi_i = E\Psi_i, \tag{2.2}$$

into the P-space effective valence shell Schrodinger equation,

$$H^v\Psi_i^v = E\Psi_i^v, \tag{2.3}$$

where the valence space projections $\Psi_i^v = P\Psi_i$ are the projections of the exact eigenfunctions and the energies E are the corresponding exact eigenvalues of the full Schrodinger equation. The H^v method provides the unique second order approximation,

$$H^v = PHP + \frac{1}{2}\sum_{\Lambda,\Lambda'}[P(\Lambda)VQ(E_\Lambda - H_0)^{-1}QVP(\Lambda')$$

$$+ \text{h.c.}], \tag{2.4}$$

where h.c. designates the Hermitian conjugate of the preceding term and $P(\Lambda)$ designates the projector onto the valence space basis function $|\Lambda\rangle$.

III. H^v APPROACH FOR THE DIRECT COMPUTATION OF $\langle\Psi^I|(\partial/\partial R_\alpha\Psi^J)\rangle$

A. Basic formalism

Let $\Psi^I(\mathbf{R})$ be the eigenfunctions of the nonrelativistic effective valence shell Born–Oppenheimer Hamiltonian (H^v) in the space of zeroth order reference functions $\Phi_k(\mathbf{r}:\mathbf{R})$, $k = 1, M$, i.e.,

$$H^v(\mathbf{R})|\Psi^I(\mathbf{r};\mathbf{R})\rangle = E^I(\mathbf{R})|\Psi^I(\mathbf{r};\mathbf{R})\rangle. \tag{3.1}$$

Here $\Psi^I(\mathbf{r};\mathbf{R})$ is given by

$$\Psi^I(\mathbf{r};\mathbf{R}) = \sum_{k=1}^M C_k^I(\mathbf{R})\Phi_k(\mathbf{r};\mathbf{R}), \tag{3.2}$$

where $\Phi_k(\mathbf{r};\mathbf{R})$ are the symmetry adapted configuration state functions (CSFs) and $C_k^I(\mathbf{R})$ are their corresponding coefficients (CI coefficient). Therefore, the CSF $\Phi_k(\mathbf{r};\mathbf{R})$ can be expressed in terms of Slater determinants containing orthonormal molecular orbitals $\phi_a(\mathbf{r};\mathbf{R})$,

$$\Phi_k(\mathbf{r};\mathbf{R}) = \sum_\lambda m_\lambda^k \frac{1}{\sqrt{N!}}$$

$$\times \sum_P^{N!} (-1)^P P\{\phi_1(1)\phi_2(2)\cdots\phi_k(N)\}, \tag{3.3}$$

where P is a permutation operator and m_λ^k are $\mathbf{R}$-independent Clebsch–Gordan-type coupling constants. Further, the molecular orbitals can be written as a linear combination of atom centered basis functions $\chi_l(\mathbf{r};\mathbf{R})$,

$$\phi_a(\mathbf{r};\mathbf{R}) = \sum_I t_l^a(\mathbf{R})\chi_l(\mathbf{r};\mathbf{R}), \tag{3.4}$$

where t_j^a are the molecular orbital expansion coefficients.

Because the eigenfunctions $\Psi^J(\mathbf{r};\mathbf{R})$ are obtained by diagonalizing the effective Hamiltonian H^v, the diagonal and off-diagonal Hellmann–Feynman theorems may be used to represent energy gradients and the derivative coupling matrix elements, respectively. Hence, differentiating Eq. (3.1) with respect to the nuclear coordinate $\mathbf{R}$ and then projecting the derivative onto $\Psi^J(\mathbf{r};\mathbf{R})$ yields the desired expressions for the nonadiabatic coupling matrix elements,

$$\left\langle \Psi^J(\mathbf{r};\mathbf{R})\left| \frac{\partial}{\partial\mathbf{R}} \Psi^I(\mathbf{r};\mathbf{R})\right\rangle\right.$$

$$= [E^J(\mathbf{R}) - E^I(\mathbf{R})]^{-1}$$

$$\times \langle\Psi^J(\mathbf{r};\mathbf{R})| \frac{\partial H^v(\mathbf{R})}{\partial\mathbf{R}} |\Psi^I(\mathbf{r};\mathbf{R})\rangle, \quad I \neq J, \tag{3.5}$$

and the energy gradients,

$$\frac{\partial E^I(\mathbf{R})}{\partial\mathbf{R}} = \langle\Psi^I(\mathbf{r};\mathbf{R})| \frac{\partial H^v(\mathbf{R})}{\partial\mathbf{R}} |\Psi^I(\mathbf{r};\mathbf{R})\rangle. \tag{3.6}$$

Since the exact H^v in Eq. (3.1) yields the exact energies E^I, it appears that the exact H^v and its eigenvectors produce the exact derivative couplings and gradients in Eqs. (3.5) and (3.6), respectively. However, the high quality of low order

H^v computations of energies, dipole moments, and transition dipole moments lends confidence that low order derivatives should display similar high order accuracy. Indeed, the first order treatment corresponds to a CASCI computation, and the second order H^v provides both dynamical and nondynamical correlation corrections. The general formulas presented in Eqs. (3.5)–(3.6) and below involve derivatives with respect to nuclear positions, but, more generally, these derivatives may be taken with respect to any parameter in the original Hamiltonian, including derivatives with respect to an external field.

B. Formal structure of the nonadiabatic coupling and energy gradient matrix elements

Given the definitions of the H^v eigenfunctions $\Psi^I(\mathbf{r};\mathbf{R})$ from Eq. (3.1), the evaluation of the nonadiabatic coupling matrix and energy gradient elements requires the computation of the derivatives of these eigenfunctions,

$$\left| \frac{\partial}{\partial R_\alpha} \Psi^I(\mathbf{r};\mathbf{R}) \right\rangle = \sum_l \left(\frac{\partial}{\partial R_\alpha} C_l^I \right) |\Phi_l\rangle$$
$$+ \sum_l C_l^I \left(\left| \frac{\partial}{\partial R_\alpha} \Phi_l \right\rangle \right). \quad (3.7)$$

The corresponding matrix elements decompose as

$$\left\langle \Psi^J(\mathbf{r};\mathbf{R}) \left| \frac{\partial}{\partial R_\alpha} \Psi^I(\mathbf{r};\mathbf{R}) \right\rangle \right.$$
$$= \left\langle C^J \left| \frac{\partial}{\partial R_\alpha} C^I \right\rangle_{\text{CSF}} + \sum_{k,l} C_k^J C_l^I \left\langle \Phi_k \left| \frac{\partial}{\partial R_\alpha} \Phi_l \right\rangle_e \quad (3.8)$$

which is written in more compact notation as

$$\left\langle \Psi^J(\mathbf{r};\mathbf{R}) \left| \frac{\partial}{\partial R_\alpha} \Psi^I(\mathbf{r};\mathbf{R}) \right\rangle \right.$$
$$= D^{\text{CI}}(J,I,\alpha) + D^{\text{CSF}}(J,I,\alpha), \quad (3.9)$$

where $D^{\text{CI}}(J,I,\alpha)$ and $D^{\text{CSF}}(J,I,\alpha)$ represent the CI and orbital derivative contributions to the nonadiabatic coupling matrix elements, respectively, and where the energy gradient follows simply by setting $I=J$.

Use of Eq. (3.3) simplifies the evaluation of $D^{\text{CSF}}(J,I,\alpha)$ which can be expressed as

$$D^{\text{CSF}}(J,I,\alpha) = \sum_{k,l} \gamma_{kl}^{J,I} \langle \phi_k | d_\alpha | \phi_l \rangle, \quad (3.10)$$

where $\gamma_{kl}^{J,I}$ is the one-particle transition density matrix and the operator d_α is defined as

$$d_\alpha(i)|\phi_k(r_i)\rangle = \frac{\partial}{\partial \mathbf{R}_\alpha} |\phi_k(r_i)\rangle. \quad (3.11)$$

The CI contribution $D^{\text{CI}}(J,I,\alpha)$ may be determined directly by differentiating the perturbative expansion of the H^v Hamiltonian with respect to the nuclear coordinates $\mathbf{R}_\alpha$ and then by evaluating the scalar product in the CSF space, i.e.,

$$\left\langle C^J(\mathbf{R}) \left| \frac{\partial}{\partial \mathbf{R}_\alpha} C^I(\mathbf{R}) \right\rangle \right.$$
$$= [E^I(\mathbf{R}) - E^J(\mathbf{R})]^{-1} \left\langle C^J(\mathbf{R}) \left| \left(\frac{\partial H^v}{\partial \mathbf{R}_\alpha} \right) \right| C^I(\mathbf{R}) \right\rangle_{\text{CSF}}. \quad (3.12)$$

The second term on the right-hand side of Eq. (3.12) can be decomposed further into two parts,

$$\left\langle C^J(\mathbf{R}) \left| \frac{\partial H^v(\mathbf{R})}{\partial \mathbf{R}_\alpha} \right| C^I(\mathbf{R}) \right\rangle_{\text{CSF}}$$
$$= \langle C^J(\mathbf{R}) | H^{v\alpha} + H^v U(\alpha) | C^I(\mathbf{R}) \rangle_{\text{CSF}}, \quad (3.13)$$

where $H^{v\alpha}$ is the derivative with respect to $\mathbf{R}_\alpha$ of the H^v Hamiltonian matrix in the CSF basis and the second term represents the contribution from the orbital derivatives part which enters through the matrix $U(\alpha)$ defined below in Eq. (3.15).

Since the H^v matrix is represented as a perturbation expansion,

$$H^v = H^{v(0)} + \eta H^{v(1)} + \tfrac{1}{2}\eta^2 H^{v(2)} + \cdots,$$

derivatives must be taken of each individual H^v matrix element in order to apply Eq. (3.13). Because the matrix elements contained in $H^{v(0)} + H^{v(1)}$ are just matrix elements of the original Hamiltonian H in the valence space, each matrix element of $H^{v(0)} + H^{v(1)}$ can be represented in terms of one-electron (h_{ij}) and two-electron (g_{ijkl}) integrals in the molecular orbital (MO) basis and of the CSF expansion coefficients m_α^k. These one- and two-electron molecular orbital integrals are essentially constructed by transforming the one- and two-electron atomic orbital derivative integrals into the molecular orbital basis. Because the matrix $H^{v(0)} + H^{v(1)}$ is simply a complete CI for the valence space, the representation of the derivatives $(\partial/\partial \mathbf{R}_\alpha)(H^{v(0)} + H^{v(1)})_{IJ}$ in terms of the atomic orbital integral derivatives is already well known[50,51] and need not be repeated here. The representation of the derivatives of the perturbation corrections, such as $(\partial/\partial \mathbf{R}_\alpha)(H^{v(2)})_{IJ}$, is considerably more complicated and will be the subject of a subsequent paper. Suffice it to say that the diagrammatic representation for $H^{v(2)}$ enables us to devise a diagrammatic method for determining the $(\partial/\partial \mathbf{R}_\alpha) \times (H^{v(2)})_{IJ}$, etc.

The first term on the right-hand side of Eq. (3.13) $[\langle C^J(\mathbf{R}) | H^{v\alpha} | C^I(\mathbf{R}) \rangle_{\text{CSF}}]$ may be expressed in terms of the derivatives (h_{ij}^α and g_{ijkl}^α, respectively) of the one-electron (h_{ij}) and two-electron integrals (g_{ijkl}) in the molecular orbital basis, i.e.,

$$\langle C^J(\mathbf{R}) | H^{v\alpha} | C^I(\mathbf{R}) \rangle_{\text{CSF}}$$
$$= \sum_{i,j} \left[\gamma_{ij}^{J,I} h_{ij}^\alpha + 2 \sum_{i,j,k,l} \Gamma_{ijkl}^{J,I} g_{ijkl}^\alpha \right], \quad (3.14)$$

where the contributions from $H^{v(0)}$ and $H^{v(1)}$ yield $\gamma_{ij}^{J,I}$ and $\Gamma_{ijkl}^{J,I}$ as the one- and two-particle transition density matrix elements while the additional terms arising from derivatives of $H^{v(2)}$ will be provided elsewhere. The derivatives h_{ij}^α and g_{ijkl}^α of the molecular orbital one- and two-electron integrals are obtained as in prior derivative treatments by transforming the derivatives from an atomic orbital basis as described in

the next subsection. The second term on the right-hand side of Eq. (3.13) involves the orbital derivative matrix $U_{ij}(\alpha)$ which is given by

$$\langle C^J(\mathbf{R})|H^v U_{ij}(\alpha)|C^I(\mathbf{R})\rangle_{\text{CSF}} = 2\sum_{ij} L_{ij}^{J,I} U_{ij}(\alpha), \quad (3.15)$$

where

$$L_{r,i}^{J,I} = \sum_j \gamma_{ij}^{J,I} h_{rj} + 2\sum_{jkl} \Gamma_{ijkl}^{J,I} g_{rjkl}, \quad (3.16)$$

and where the transition density matrix elements $\gamma_{ij}^{J,I}$ and $\Gamma_{ijkl}^{J,I}$ again appear. The orbital derivative matrix $U_{ij}(\alpha)$ satisfies the equation

$$\frac{\partial}{\partial \mathbf{R}_\alpha}|\phi_i(\alpha)\rangle = \sum_k [U_{ki}(\alpha)|\phi_k(0)\rangle + t_k^i\left(\frac{\partial}{\partial \mathbf{R}_\alpha}\right)|\chi_k(\alpha)\rangle], \quad (3.17)$$

where Eq. (3.4) has been used to express the orbital derivative on the right-hand side in terms of atomic orbital derivatives. The matrix $U_{ij}(\alpha)$ is, therefore, determined from a generalized set of coupled perturbed Hartree–Fock (GCPHF) equations. This generalization involves the use of multiple Fock operators because the H^v unoccupied valence orbitals are chosen to represent low lying excited states and, consequently, are not eigenfunction of a Fock operator with a single potential. This appearance of multiple Fock operators represents one unique aspect of the theory that differs from the standard CPHF formalism for analytical derivatives. Thus, the next subsection briefly outlines the multiple Fock operator GCPHF scheme that has been implemented in the computation of the molecular orbital derivatives contributing to the energy gradients and the nonadiabatic coupling matrix elements.

C. CPHF equations for multiple Fock operators

One approach in obtaining the molecular orbital derivative integrals, necessary for the analytical evaluation of energy gradients and the nonadiabatic coupling matrix elements, using the H^v method (as discussed in the previous section) requires the computation of the various derivative matrices as in the methods developed by Gerrat and Mills[23] and by Pople et al.[17] in their studies of energy derivatives in Hartree–Fock and Møller–Plesset theories. We begin this subsection following the general approach of Gerrat and Mills for deriving the appropriate set of CPHF equations for single configurational problems in order to derive some necessary relations, particularly relating derivatives of the molecular orbital integrals to atomic orbital derivatives.

The normal-ordered Hamiltonian for a system in presence of a perturbation is represented as the expansion

$$H_N(\lambda) \equiv H - \langle 0|H|0\rangle = H_N^{(0)} + \lambda H_N^{(1)} + \tfrac{1}{2}\lambda^2 H_N^{(2)} + \cdots, \quad (3.18)$$

where λ is the perturbation parameter and $|0\rangle$ is the single configurational reference space function. When the perturbation λ is taken to correspond to a shift in molecular geometry, the derivative $H_N^{(1)}$ is related to the quantity of interest. The unperturbed Hamiltonian $H_N^{(0)}$ is given by

$$H_N^{(0)} = F_N^{(0)} + V_N^{(0)} = \sum_{a,b} \langle a|F^{(0)}|b\rangle\{a_a^\dagger a_b\}$$
$$+ \sum_{a,b,c,d} \frac{1}{4} \langle ab||cd\rangle^{(0)}\{a_a^\dagger a_b^\dagger a_d a_c\}, \quad (3.19)$$

where $F_N^{(0)}$ and $V_N^{(0)}$ are the unperturbed Fock operator and the antisymmetrized two-electron repulsion operator in the unperturbed molecular orbital basis $\phi^{(0)} \equiv |a\rangle$. The operators $\{a_a^\dagger a_b\}$ and $\{a_a^\dagger a_b^\dagger a_d a_c\}$ are normal-ordered second quantized operators written in terms of creation $(a_a^\dagger)$ and annihilation (a_a) operators. The notation for the molecular orbitals is as follows:

(a) The indices a,b,c,d,r,s,t,u signify any molecular orbitals.
(b) The indices i,j,k,l indicate occupied orbitals in the ground state reference configuration.
(c) The indices α, β, γ denote improved virtual orbitals (IVOs).
(d) The indices m,n denote orbitals which are not IVOs.
(e) p and q specify virtual or excited orbital, respectively.

The atomic orbital basis functions are designated by the indices μ, ν, δ, η.

The first order Hamiltonian $H_N^{(1)}$,

$$H_N^{(1)} = \left.\frac{\partial H_N(\lambda)}{\partial \lambda}\right|_{\lambda=0}$$
$$= \sum_{a,b} \langle \phi_a|F|\phi_b\rangle^{(1)}\{a_a^\dagger a_b\}$$
$$+ \sum_{a,b,c,d} \frac{1}{4} \langle \phi_a\phi_b||\phi_c\phi_d\rangle^{(1)}\{a_a^\dagger a_b^\dagger a_d a_c\} \quad (3.20)$$

contains the derivatives $F_{ab}^{(1)} = \langle \phi_a|F|\phi_b\rangle^{(1)}$ and $\langle \phi_a\phi_b||\phi_c\phi_d\rangle^{(1)}$ of integrals in the molecular orbital basis. Expansion of the molecular orbital $\phi_a(\lambda)$ in the atomic orbital basis $(\chi_\mu(\lambda))$

$$\phi_a(\lambda) = \sum_\mu C_{\mu a}(\lambda)\chi_\mu(\lambda) \quad (3.21)$$

converts the first derivative $F_{ab}^{(1)}$ of the Fock matrix element F_{ab} with respect to the perturbation parameter λ into

$$F_{ab}^{(1)} = \left[\sum_{\mu,\nu} C_{\mu a}^* C_{\nu b}\left\{\langle \mu|\frac{\partial \mathbf{f}}{\partial \lambda}|\nu\rangle + \left\langle\frac{\partial \mu}{\partial \lambda}\left|\mathbf{f}\right|\nu\right\rangle\right.\right.$$
$$\left.+ \left\langle \mu\left|\mathbf{f}\left|\frac{\partial \nu}{\partial \lambda}\right\rangle\right\} + \left\{\frac{\partial C_{\mu a}^*}{\partial \lambda}C_{\nu b} + C_{\mu a}^*\frac{\partial C_{\nu b}}{\partial \lambda}\right\}\right.$$
$$\left.\times\langle\mu|\mathbf{f}|\nu\rangle\right]\Bigg|_{\lambda=0}, \quad (3.22)$$

while the first derivative of the antisymmetrized two-electron repulsion integral becomes

$$\langle ab||cd\rangle^{(1)} = \left[\sum_{\mu,\nu,\delta,\eta} C_{\mu a}^* C_{\nu b}^* C_{\eta d} C_{\delta c} \frac{\partial \langle \mu\nu||\delta\eta\rangle}{\partial\lambda} \right.$$
$$\left. + \frac{\partial (C_{\mu a}^* C_{\nu b}^* C_{\eta d} C_{\delta c})}{\partial\lambda} \langle \mu\nu||\delta\eta\rangle \right]_{\lambda=0},$$

$$(3.23)$$

where μ, ν, etc., are atomic orbital basis functions and the $\{C\}$ are the molecular orbital (MO) expansion coefficients. The first term on the right-hand side of Eq. (3.22) contains the derivative of the Fock operator $\mathbf{f}$; the second and third arise from the derivatives of the atomic orbital basis functions; and remaining two terms contain the derivative of the MO coefficients. Similarly, the first term on the right-hand side of Eq. (3.23) involves the derivative of the two-electron matrix element in the atomic orbital basis, while the second term emerges from the derivatives of the MO coefficients. As noted above the derivatives of the one and two-electron atomic orbital integrals are readily available from previous works.[52–54]

The molecular orbital derivative required for evaluating Eqs. (3.14) and (3.15) is of the general form,

$$\left\langle \phi_a(\lambda) \left| \frac{\partial\phi_b(\lambda)}{\partial\lambda} \right\rangle \right., \tag{3.24}$$

where ϕ_a and ϕ_b are any two λ-dependent molecular orbitals. The expansion Eq. (3.21) enables Eq. (3.24) to be represented likewise in terms of atomic orbital derivatives and the MO coefficient derivatives as

$$\left\langle \phi_a(\lambda) \left| \frac{\partial\phi_b(\lambda)}{\partial\lambda} \right\rangle = \sum_{\mu,\nu} C_{\mu a}^* C_{\nu b} \left\langle \mu \left| \frac{\partial\nu}{\partial\lambda} \right\rangle \right.\right.$$
$$+ \sum_{\mu,\nu} C_{\mu a}^* \frac{\partial C_{\nu b}}{\partial\lambda} \delta_{\mu,\nu}. \tag{3.25}$$

While the evaluation of the derivatives of the primitive atomic orbital basis functions [the first term on the right-hand side of Eq. (3.25)] is trivial,[15] the direct evaluation of the derivative of the MO coefficients $C_{\mu a}(\lambda)$ [the second term in Eq. (3.25)] is rather cumbersome. Hence, it is convenient for evaluating the latter derivative to expand the perturbed molecular orbitals ϕ_a in the basis of unperturbed molecular orbitals $\phi_a^{(0)}$,

$$\phi_a(\lambda) = \sum_\mu U_{\mu a}(\lambda) \phi_a^{(0)} \equiv \sum_\mu U_{\mu a}(\lambda) |a\rangle, \tag{3.26}$$

thereby returning to the computation of the matrix $U_{\mu a}(\lambda)$ introduced in Eq. (3.13). Expanding the unperturbed molecular orbitals $\phi_a^{(0)}$ in a basis of the perturbed λ-dependent atomic orbital basis

$$\phi_a^{(0)} = \sum_\mu C_{\mu i}(0) \chi_\mu(\lambda), \tag{3.27}$$

the perturbed molecular orbital $\phi_a(\lambda)$ can be expressed in the perturbed atomic orbital basis as

$$\phi_a(\lambda) = \sum_\mu C_{\mu a}(\lambda) \chi_\mu(\lambda), \tag{3.28}$$

where the $C_{\mu i}(0)$ are the MO expansion coefficients at the undisplaced geometry, i.e., at $\lambda = 0$. Substituting Eq. (3.27) into Eq. (3.26) and comparing with Eq. (3.28) shows that the determination of the derivatives of the $U_{\nu a}(\lambda)$ matrix permits the computation of the derivatives of the λ-dependent basis function expansion coefficients $C_{\mu a}(\lambda)$ through the relation

$$C_{\mu a}(\lambda) = \sum_\nu C_{\mu\nu}(0) U_{\nu a}(\lambda). \tag{3.29}$$

We, therefore, evaluate the derivatives of the $U_{\nu a}(\lambda)$ matrix employing a method similar to solving the CPHF equations. This method also avoids the direct evaluation of the MO coefficient derivatives. The evaluation of $U_{\nu a}(\lambda)$ is accomplished by deriving a set of CPHF equations that is particular to the orbitals used in the H^v formalism.

Although the IVOs are determined from different Fock operators, the set of Fock operators used to generate all orbitals may be combined formally into a single Fock operator by using projection operators. This single λ-dependent Fock operator describes all the improved virtual orbitals *as moving under the influence* of an excited state potential identical to that used in their generation, while the remaining orbitals *experience* the typical ground state Fock operator. Our derivation of the GCPHF (generalized CPHF) equations closely follows the notation of Pople *et al.*[17] For this purpose, λ represents the nuclear coordinate, and $\lambda = 0$ is the molecular geometry at which the orbital derivatives are to be evaluated.

We reiterate for emphasis that the core, excited, and occupied valence orbitals are defined as the eigenfunctions of a ground state Fock operator $h + G^N$, where h is the one-electron part of the Hamiltonian and G^N contains all the Coulomb and exchange interactions. The IVOs (valence orbitals not occupied in the ground state configuration) are eigenfunctions of other Fock operators $h + G^{N-1}$ as discussed in the Introduction. The use of projection operators enables the construction of a single λ-dependent Fock operator whose eigenvectors provide all the molecular orbitals from

$$\mathbf{f}(\lambda) = h(\lambda) + P_1 G^N(\lambda) P_1 + Q_1 G^{N-1}(\lambda) Q_1, \tag{3.30}$$

where the projector onto the IVOs is Q_1 while that onto all other molecular orbitals is $P_1 = 1 - Q_1$, i.e.,

$$P_1 = \sum_m |\phi_m(\lambda)\rangle\langle\phi_m(\lambda)|; \quad Q_1 = \sum_\gamma |\phi_\gamma(\lambda)\rangle\langle\phi_\gamma(\lambda)|, \tag{3.31}$$

and the potentials are written as

$$G^N = \sum_i^N \langle\phi_i(\lambda)|v|\phi_i(\lambda)\rangle;$$

$$G^{N-1} = \sum_i^{N-1} \langle\phi_i(\lambda)|v|\phi_i(\lambda)\rangle, \tag{3.32}$$

where the second sum omits one electron from the highest occupied molecular orbital in the ground state reference configuration. Equation (3.30) contains h as the one-electron operator, the operator $v \equiv r_{12}^{-1}(1 - P_{12})$ represents the differ-

ence between the direct and exchange potentials with $\mathbf{P}_{12}$ the permutation operator for electron coordinates 1 and 2.

Using the resolution of identity $(P_1+Q_1=1)$, Eq. (3.30) can be converted to the more convenient form,

$$\mathbf{f}(\lambda)=h(\lambda)+G^N(\lambda)-Q_1 G^N(\lambda)-G^N(\lambda)Q_1$$
$$+Q_1 G^N(\lambda)Q_1+Q_1 G^{N-1}(\lambda)Q_1. \qquad (3.33)$$

Expansion of the projection operator Q_1 in terms of unperturbed MOs using Eq. (3.31) transforms Eq. (3.33) into the explicit representation,

$$\mathbf{f}(\lambda)=h(\lambda)+G^N(\lambda)-\sum_{c,\alpha} U_{c\alpha}(\lambda)U^*_{c\alpha}(\lambda)|c\rangle\langle c|G^N(\lambda)$$

$$-\sum_{c,\alpha} U_{c\alpha}(\lambda)U^*_{c\alpha}(\lambda)G^N(\lambda)|c\rangle\langle c|$$

$$+\sum_{c,d,\alpha,\beta} U_{c\alpha}(\lambda)U^*_{c\alpha}(\lambda)U_{d\beta}(\lambda)U^*_{d\beta}(\lambda)|c\rangle$$

$$\times\langle c|G^N(\lambda)|d\rangle\langle d|+\sum_{c,d,\alpha,\beta} U_{c\alpha}(\lambda)U^*_{c\alpha}(\lambda)$$

$$\times U_{d\beta}(\lambda)U^*_{d\beta}(\lambda)|c\rangle\langle c|G^{N-1}(\lambda)|d\rangle\langle d|. \qquad (3.33a)$$

The projected Fock operator $\mathbf{f}(\lambda)$ acts upon core, excited, and ground state occupied valence orbitals with what is formally an N-electron potential. However, a direct and exchange integral cancel when acting on any of the ground state occupied orbitals, leaving, in effect, an $(N-1)$-electron potential. The operator $\mathbf{f}(\lambda)$ is constructed to act on the IVOs with an $(N-1)$-electron potential in which an electron has been removed from the highest occupied molecular orbital (HOMO) of the ground state. (The latter is equivalent to using an N-electron potential that is formed by placing the removed electron into the IVO to be optimized.) Thus, our task is to derive analytical orbital derivative formulas for the eigenfunctions of $\mathbf{f}(\lambda)$. Note that the general practice of averaging valence orbital energies in the H^v calculations is relevant to obtain these orbital derivative formulas.

Several key equations from Pople $et\ al.$[17] also apply for the projected Fock operator of Eq. (3.30). Assuming, for convenience, that the $U(\lambda)$ are real, Eq. (37) of Pople $et\ al.$ allows us to write

$$U^{(1)}_{ab}+U^{(1)}_{ba}+S^{(1)}_{ab}=0, \qquad (3.34)$$

where $U^{(1)}_{ab}$ is the derivative $[(\partial/\partial\lambda)U_{ab}(\lambda)]_{\lambda=0}$ we seek, while $S^{(1)}_{ab}$ is the derivative $[(\partial/\partial\lambda)\langle\phi_a(\lambda)|\phi_b(\lambda)\rangle]_{\lambda=0}$ of the molecular orbital overlap matrix. Another useful relation[17] used here is

$$U^{(1)}_{ab}=\frac{F^{(1)}_{ab}-S^{(1)}_{ab}\epsilon^{(0)}_b}{\epsilon^{(0)}_a-\epsilon^{(0)}_b}. \qquad (3.35)$$

Consider now the general matrix element

$$\mathbf{f}_{ab}(\lambda)=\langle\phi^{(0)}_a|\mathbf{f}(\lambda)|\phi^{(0)}_b\rangle \qquad (3.36)$$

of the projected Fock operator between any two unperturbed molecular orbitals. The matrix element then can be written explicitly with the aid of Eq. (3.33) as

$$\mathbf{f}_{ab}(\lambda)=h_{ab}(\lambda)+G^N_{ab}(\lambda)-\sum_{\alpha,c}[U_{a\alpha}(\lambda)U^*_{c\alpha}(\lambda)G^N_{cb}(\lambda)$$

$$+G^N_{ac}(\lambda)U_{c\alpha}(\lambda)U^*_{b\alpha}(\lambda)]$$

$$+\sum_{\alpha,\beta,c,d} U_{a\alpha}(\lambda)U^*_{c\alpha}(\lambda)[G^N_{cd}(\lambda)$$

$$+G^{N-1}_{cd}(\lambda)]U_{d\beta}(\lambda)U^*_{b\beta}(\lambda), \qquad (3.36a)$$

where the ground state potential is

$$G^N_{ab}(\lambda)=\sum_{i=1}^{N}\sum_{c=1}^{all}[\langle ac||bi\rangle U^*_{ci}(\lambda)+\langle ai||bc\rangle U_{ci}(\lambda)]$$

$$=\sum_{i=1}^{N}\sum_{c=1}^{all}[\langle ac||bi\rangle+\langle ai||bc\rangle]U_{ci}(\lambda), \qquad (3.37)$$

while the V^{N-1} potential for the IVOs is

$$G^{N-1}_{ab}(\lambda)=\sum_{i=1}^{N-1}\sum_{c=1}^{all}\langle ac||bi\rangle U^*_{ci}(\lambda)+\langle ai||bc\rangle U_{ci}(\lambda)]$$

$$=\sum_{i=1}^{N-1}\sum_{c=1}^{all}[\langle ac||bi\rangle+\langle ai||bc\rangle]U_{ci}(\lambda). \qquad (3.38)$$

The notation $\langle cd||rs\rangle=\langle cr|ds\rangle-\langle cr|sd\rangle$ represents the antisymmetrized two-electron integral in the unperturbed MO basis with the two-electron integral $\langle cd|rs\rangle$ given as usual by

$$\langle cd|rs\rangle=\int\int \phi^{(0)}_c(1)\phi^{(0)}_r(2)\frac{1}{r_{12}}\phi^{(0)}_d(1)$$

$$\times\phi^{(0)}_s(1)dr(1)dr(2). \qquad (3.39)$$

Now differentiating the Fock operator [Eq. (3.36) or its expanded from given in Eq. (3.36a)] with respect to the nuclear coordinate λ and substituting it in Eq. (3.35) yields three sets of CPHF equations among which there is only one independent set of GCPHF equations that couple the IVO (ϕ_α)–non-IVO (ϕ_m) blocks of orbitals (the latter includes occupied and excited orbitals) and two linearly dependent sets of equations that couple the IVO (ϕ_0)–IVO (ϕ_β) and non-IVO (ϕ_m)–non-IVO (ϕ_n) blocks of orbitals, respectively. The GCPHF equations coupling the non-IVO (ϕ_m)–non-IVO (ϕ_n) orbital blocks implicitly contain two additional sets of linearly dependent GCPHF equations which connect the occupied–occupied and excited–excited block of non-IVO orbitals.

$Case\ (1)$: The orbital $\phi^{(0)}_a$ is not an IVO (i.e., $\phi^{(0)}_m$) but $\phi^{(0)}_b$ is an IVO (i.e., $\phi^{(0)}_\gamma$). In this case, differentiation of $\mathbf{f}_{ab}(\lambda)$ [Eq. (3.36)] with respect to the nuclear coordinate λ yields

$$\mathbf{f}^{(1)}_{m\gamma}=\frac{\partial}{\partial\lambda}\mathbf{f}_{m\gamma}(\lambda)=h^{(1)}_{m\gamma}+\sum_\alpha[U^{(1)}_{m\alpha}G^{N-1}_{\alpha\gamma}+G^N_{m\alpha}S^{(1)}_{\alpha\gamma}]$$

$$-\sum_n G^N_{mn}U^{(1)}_{n\gamma}. \qquad (3.40)$$

Substituting Eq. (3.40) in Eq. (3.35) produces the desired equation for the block of $U_{m\gamma}^{(1)}$ coupling the IVO–non-IVO orbitals as

$$(\epsilon_\gamma^{(0)} - \epsilon_m^{(0)}) U_{m\gamma}^{(1)} = \mathbf{f}_{m\gamma}^{(1)} - S_{m\gamma}^{(1)} \epsilon_\gamma^{(0)}. \tag{3.41}$$

Equation (3.41) represents a set of linear equations which may be solved for the $U_{m\gamma}^{(1)}$ block. This $U_{m\gamma}^{(1)}$ block then may be used to find the $U_{\gamma m}^{(1)}$ block from Eq. (3.34). Since the solutions for the $U_{m\gamma}^{(1)}$ block does not require knowledge of U from any other block (IVO–IVO or non-IVO–non-IVO), the equations for $U_{m\gamma}^{(1)}$ are linearly independent.

Case (2): Orbitals $\phi_a^{(0)}$ and $\phi_b^{(0)}$ are not IVOs. Three subcases must be considered here; (a) $\phi_a^{(0)}$ is an occupied orbital and $\phi_b^{(0)}$ is an unoccupied orbital; (b) $\phi_a^{(0)}$ and $\phi_b^{(0)}$ are occupied orbitals; and (c) $\phi_a^{(0)}$ and $\phi_b^{(0)}$ are excited orbitals.

Let us first consider $\phi_a^{(0)}$ and $\phi_b^{(0)}$ to be a general non-IVO, i.e., $\phi_a^{(0)}$, $\phi_b^{(0)}$ can be both occupied or excited orbitals or only either of them may be occupied orbitals. For this case, differentiating $\mathbf{f}_{ab}(\lambda)$ with respect to the nuclear coordinate λ yields

$$\mathbf{f}_{ab}^{(1)} = h_{ab}^{(1)} + \sum_{i=1}^{N} \sum_{c=1}^{\text{all}} [\langle ai||bc\rangle + \langle ac||bi\rangle] U_{ci}^{(1)}$$
$$+ \sum_{i=1}^{N} (ai||bi)^{(1)} - \sum_{\alpha} [U_{a\alpha}^{(1)} G_{\alpha b}^{N} + G_{a\alpha}^{N} U_{b\alpha}^{(1)}], \tag{3.42}$$

where the quantity $(ab||cd)^{(1)}$ again denotes the derivative of the two-electron integral in an MO basis. When $a=p$ and $b=i$, i.e., $\phi_a^{(0)}$ is an excited orbital and $\phi_b^{(0)}$ is an occupied orbital, then Eqs. (3.42) and (3.35) produce

$$(\epsilon_i^{(0)} - \epsilon_p^{(0)}) U_{pi}^{(1)}$$
$$= h_{pi}^{(1)} - \sum_{k,l=1}^{N} S_{kl}^{(1)} \langle pk||il\rangle + \sum_{k=1}^{N} \sum_{\alpha} [4\langle p\alpha|ik\rangle$$
$$- \langle p\alpha|ki\rangle - \langle pi|\alpha k\rangle] U_{\alpha k}^{(1)} + \sum_{k=1}^{N} \sum_{q} [4\langle pq|ik\rangle$$
$$- \langle pq|ki\rangle - \langle pi|qk\rangle] U_{qk}^{(1)} + \sum_{k=1}^{N} (pk||ik)^{(1)}$$
$$- \sum_{\alpha} [U_{p\alpha}^{(1)} G_{\alpha i}^{N} + G_{p\alpha}^{N} U_{i\alpha}^{(1)}] - S_{pi}^{(1)} \epsilon_i^{(0)}, \tag{3.43}$$

where we have exploited the exchange symmetry of the two-electron integrals $[\langle ab|cd\rangle = \langle ad|bc\rangle]$ to arrive at Eq. (3.43).

Equation (3.43) is a set of linear equations which may be solved for the unknowns $U_{pi}^{(1)}$ provided the $U_{\alpha k}^{(1)}$ are known. Thus, in order to solve the GCPHF equations for the occupied-excited block, the GCPHF equations for IVO–non-IVO must be resolved first. Also, note that in the absence of unoccupied valence orbital, the GCPHF equations for the occupied-excited orbital block reduces to the standard CPHF equations since that situation implies $U_{a\alpha}^{(1)} = 0$ and the sum over IVO orbital vanishes. Once the block $U_{pi}^{(1)}$ has been

determined, the evaluation of the $U_{ip}^{(1)}$, $U_{ij}^{(1)}$ (occupied–occupied) and $U_{pq}^{(1)}$ (excited–excited) blocks from Eq. (3.43) is trivial.

Case (3): The orbital $\phi_a^{(0)}$ and $\phi_b^{(0)}$ are both IVOs. Differentiating the Fock matrix elements with respect to the nuclear coordinate λ [i.e., $(\partial/\partial\lambda)\mathbf{f}_{ab}(\lambda)$] produces

$$\mathbf{f}_{\alpha\beta}^{(1)} = h_{\alpha\beta}^{(1)} \sum_{\gamma} [U_{\alpha\gamma}^{(1)} G_{\gamma\beta}^{N-1} + G_{\alpha\gamma}^{N-1} U_{\beta\gamma}^{(1)}]$$
$$+ \sum_{a} [U_{a\alpha}^{(1)} G_{a\beta}^{N-1} + G_{\alpha a}^{N-1} U_{a\beta}^{(1)}] + \sum_{i}^{N-1} (\alpha i||\beta i)^{(1)}$$
$$+ \sum_{i}^{N-1} \sum_{a}^{\text{all}} [\langle \alpha a||\beta i\rangle + \langle \alpha i||\beta a\rangle] U_{ai}^{(1)}. \tag{3.44}$$

Note that in Eq. (3.44) for the derivatives $\mathbf{f}_{\alpha\beta}^{(1)}$, all the other $U^{(1)}$ amplitudes except the $U_{\alpha\beta}^{(1)}$ block are available from the prior two cases. Hence, substitution of $f_{\alpha\beta}$ from Eq. (3.35) into Eq. (3.44) provides the necessary equation for obtaining the $U_{\alpha\beta}^{(1)}$ amplitudes. Thus, to determine the $U_{\alpha\beta}^{(1)}$ block, it is necessary to solve sequentially for the IVO–IVO, occupied–excited, occupied–occupied, and excited–excited blocks.

IV. SUMMARY

The present work describes an efficient scheme for computing nonadiabatic coupling and energy gradients matrix elements within the ''perturb, then diagonalize'' multireference *ab initio* H^v method. Unlike the SRPT approach, the H^v treatment is more stable near transition states or at distorted geometries and, hence, can treat the ground as well as excited states more accurately near these regions of space and over the entire potential energy surface. Since the new derivative procedure is based on analytic gradient methods, it is numerically more efficient and superior to finite difference approaches. The present method also describes an alternative route to compute the cumbersome CI-coefficient derivative contribution to the energy gradient and nonadiabatic coupling matrix elements. Here, the derivatives of the CI-coefficients are represented through the H^v Hellmann–Feynman theorem in terms of matrix elements containing analytic derivatives of the H^v matrix. These H^v derivative matrix elements, in turn, can be represented through Feynman diagrams. Once a diagramatic scheme is introduced for the derivatives of the H^v matrix, the evaluation of diagrams, i.e., the matrix elements, is straightforward. The molecular orbital derivatives which directly contribute both to the energy gradients and to the nonadiabatic coupling matrix elements (and which contribute indirectly through CI-coefficient derivatives) are evaluated from the solution of general coupled-perturbed Hartree–Fock equations, a generalization necessary because the valence orbitals used in H^v method are not eigenfunctions of a single Fock operator. However, the evaluation of the molecular orbital derivatives through the GCPHF equations is quite cost effective since the number of unknown amplitudes ($U_{ab}^{(1)}$) in the GCPHF and CPHF formalisms are the same.

Previous H^v computations yield highly accurate energies from the third order H^v and, in many instances even at sec-

ond order.[10] Thus, an optimal use of the present derivative scheme should employ H^v valence spaces that already provide highly accurate second order energies for the states of interest in order to ensure that the derivative couplings and gradients are of comparable quality. While the present methods could be applied with the third order H^v, a large number of additional diagrams are required, and the complication is to be avoided by making it unnecessary through the appropriate choice of valence space and valence orbitals.

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