

Analytic energy gradients for multiconfigurational self-consistent field second-order quasidegenerate perturbation theory (MC-QDPT)

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An analytic energy gradient method for second-order quasidegenerate perturbation theory with multiconfigurational self-consistent field reference functions (MC-QDPT) is derived along the lines of the response function formalism (RFF). According to the RFF, the gradients are calculated without solving coupled perturbed equations. Instead, it is necessary to solve seven sets of linear equations in order to determine Lagrangian multipliers, corresponding to four sets of parameter constraining conditions and three sets of additional parameter defining conditions in the Lagrangian. Just one of these linear equations is a large scale linear equation; the others are reducible to just partial differentiations or simple equations solvable by straightforward subroutines. © 1998 American Institute of Physics. [S0021-9606(98)00514-5]

I. INTRODUCTION

Energy derivative methods for wave functions of highly correlated methods are increasing in importance as computational resources improve to the point that using such derivatives becomes feasible.¹⁻³ In fields of current importance, such as classical or quantum dynamics and accurate potential energy surfaces (PES's), upon which the dynamics is based, gradients for highly accurate wave functions are crucial if one is to obtain quantitatively reliable results. In determining accurate potential energy surfaces, it is essential to locate key stationary points, such as equilibrium geometries and transition states for chemical reactions.

Analytic gradient methods have been developed for several levels of theory beyond Hartree-Fock. The most efficient wave function that includes electron correlation is second-order many-body or Møller-Plesset (MBPT2 or MP2) perturbation theory.^{4,5} However, as is often noted, the MP2 wave function is frequently unstable at distorted geometries, since at such points on the PES, the single configuration wave function is not an appropriate zeroth-order approximation. The complete active space self-consistent field (CASSCF)⁶ or the full optimized reaction space (FORS)⁷ method is also often used to locate stationary points,⁸ since the CASSCF wave function is well-defined and thus stable even at distorted molecular structures if we choose an appropriate active space. However, if one realizes that CASSCF is a multiconfigurational analog of the Hartree-Fock approximation that is introduced to correct for near degeneracies in the wave function, it comes as no surprise that this level of theory can yield incorrect potential energy curves, sometimes predicting (for example) a fictitious transition state which disappears upon the addition of dynamic correlation. Moreover, it is difficult to use fully optimized CASSCF wave functions for a pure excited electronic state; that is a state that is not the lowest of its spin and symmetry, since the

CASSCF iterative procedure for such cases frequently diverges. A desirable and accurate alternative is clearly to turn to multireference configuration interaction (MRCI) gradients⁹ built upon the CASSCF wave function as a reference. However, the dimension of the MRCI Hamiltonian grows rapidly with the size of the basis set and the active space, so that MRCI gradients are not yet a general practical alternative. There is therefore clearly a need for an analytic gradient for a wave function that goes beyond CASSCF and that is efficient enough to be broadly applicable.

We have recently proposed perturbation theory methods based on multiconfigurational reference functions, MRMP PT (multireference Møller-Plesset perturbation theory)¹⁰ and MC-QDPT (quasidegenerate perturbation theory with MCSCF reference functions)¹¹ as methods which may efficiently provide accurate potential energy surfaces. Several approaches to multireference perturbation theory have been proposed and implemented.¹² MRMP perturbation theory is a multiconfigurational but single reference state method based on Rayleigh-Schrödinger perturbation theory. MC-QDPT is a multiconfigurational and multi-state perturbation method based on Van Vleck perturbation theory and includes MRMP PT as a subset. Using these perturbation methods we have clarified the electronic structures of various systems and demonstrated that they are powerful tools for investigating excited states¹³ as well as ground states.¹⁴

In this paper, we present a derivation for the analytic gradient for second-order MC-QDPT (for which MRMP is a special single-reference-state case), based on the response function formalism (RFF).^{3,15} Several methods have been developed for the derivation of efficient formulas for the gradient and higher-order energy derivatives for molecular wave functions. In the mid 1980s, Handy and Schaefer proposed a method,¹⁶ now called the Z-vector method, designed to avoid solving time-consuming coupled-perturbed (CP) equations,

such as the CP Hartree–Fock (CPHF) equation, in computing gradients of configuration interaction (CI) energies. The response function formalism,¹⁷ developed by Jørgensen, Helgaker, and their co-workers, extends the applicability of the Z-vector method to any order of energy derivatives. This method minimizes the number of coupled perturbed equations in a systematic way, and derives the formulas that satisfy the $(2n+1)$ rule for the perturbation (nuclear displacements) automatically. Moreover, with this method one can also systematically treat many constraining conditions.

In the original RFF derivation, the second-quantization formalism proved to be a useful way to express the energy and the constraining equations for the MO and CI coefficients, as well as the unitary exponential forms for parameter relaxation in the OMO (orthonormal molecular orbital¹⁵) basis. This formalism avoids using redundant parameters, and results in simple formulas for variational (and some nonvariational) wave function methods for which the energy expressions are relatively simple. However, for the nonvariational MC-QDPT method, the energy expression is more complex, so second-quantization formalism complicates, rather than simplifies, the derivation. Hence, in the present derivation the conventional approach is used.

The contents of this article are as follows. In Sec. II, the Lagrangian multiplier method in the response function formalism is very briefly reviewed. In Sec. III, the MC-QDPT Lagrangian is defined. In Sec. IV, the linear equations for determining the Lagrangian multipliers, which are necessary for the gradient calculation used in later sections, are derived, and in Sec. V the method used to obtain the gradients is discussed. In the final section, VI, the method described in Secs. III–V is discussed and concluding remarks are drawn.

II. RESPONSE FUNCTION FORMALISM: LAGRANGIAN MULTIPLIER METHOD

We review very briefly the Lagrangian multiplier method in the response function formalism (RFF). The details of the method have been described elsewhere;¹⁵ this discussion focuses on those aspects that are related to the first derivative calculation.

The Lagrangian is defined by

$$L(X, \zeta, C) = W(X, C) + \zeta e(X, C), \quad (1)$$

where X is a nuclear coordinate, C represents the molecular orbital (MO) and configuration interaction (CI) coefficients, W is the energy, e represents constraints on the parameters C , and ζ are the Lagrangian multipliers. The C in Eq. (1) is determined by

$$e(X, C) = 0. \quad (2)$$

On the other hand, ζ is arbitrary since $e(X, C)$ is identically zero in Eq. (1). Thus, we may place any constraining condition on ζ . In the response function formalism, ζ is determined such that the first derivative of the Lagrangian with respect to the C s is zero,

$$\frac{\partial L}{\partial C} = \frac{\partial W}{\partial C} + \zeta \frac{\partial e}{\partial C} = 0, \quad (3)$$

which will make the gradient calculation simpler. Using Eqs. (2) and (3), the first derivative of the Lagrangian with respect to nuclear coordinates,

$$\begin{aligned} \frac{dL}{dX} &= \left(\frac{\partial W}{\partial C} \frac{dC}{dX} + \frac{\partial W}{\partial X} \right) + \frac{d\zeta}{dX} e + \zeta \left(\frac{\partial e}{\partial C} \frac{dC}{dX} + \frac{\partial e}{\partial X} \right) \\ &= \frac{\partial W}{\partial X} + \zeta \frac{\partial e}{\partial X} + \left(\frac{\partial W}{\partial C} + \zeta \frac{\partial e}{\partial C} \right) \frac{dC}{dX} + \frac{d\zeta}{dX} e, \end{aligned} \quad (4)$$

is reduced to a more compact form,

$$\frac{dL}{dX} = \frac{\partial W}{\partial X} + \zeta \frac{\partial e}{\partial X}, \quad (5)$$

that requires neither the first derivatives of the parameters, dC/dX , nor those of Lagrange multipliers, $d\zeta/dX$. The energy W and the constraining conditions e depend on X explicitly through the molecular integrals. Hence, we may write the gradient of integrals over molecular orbitals (indices p, q, r, s) in terms of only derivatives over atomic basis functions (indices μ, ν, ρ, σ),

$$(p|q)^X = \sum_{\mu\nu} c_{\mu p} c_{\nu q} \frac{d}{dX} (\mu|\nu), \quad (6)$$

$$(p|h|q)^X = \sum_{\mu\nu} c_{\mu p} c_{\nu q} \frac{d}{dX} (\mu|h|\nu), \quad (7)$$

$$(pq|rs)^X = \sum_{\mu\nu\rho\sigma} c_{\mu p} c_{\nu q} c_{\rho r} c_{\sigma s} \frac{d}{dX} (\mu\nu|\rho\sigma), \quad (8)$$

with ζ determined by Eq. (5).

III. MC-QDPT LAGRANGIAN

A. The MC-QDPT energy expression to second order

The effective Hamiltonian to the second order in MC-QDPT is given by

$$\begin{aligned} (K_{\text{eff}})_{\alpha\beta} &= \langle \alpha | H | \beta \rangle + \frac{1}{2} \left\{ \sum_I \frac{\langle \alpha | V | I \rangle \langle I | V | \beta \rangle}{E_{\alpha}^{(0)} - E_I^{(0)}} \right. \\ &\quad \left. + (\alpha \leftrightarrow \beta) \right\}, \end{aligned} \quad (9)$$

where $\{|I\rangle\}$ is the set of all singly and doubly excited configurations from the reference configurations in the CAS. The wave functions $|\alpha\rangle$ and $|\beta\rangle$ are CASSCF eigenfunctions, and the notation $\alpha \leftrightarrow \beta$ means interchange α with β from the first term in curly brackets. The first term on the right-hand side (rhs) of Eq. (9) is a diagonal matrix whose diagonal elements are the CASSCF energies. If we substitute the second-quantized operator defined by Eq. (A1) in the Appendix for V , Eq. (9) becomes

$$\begin{aligned}
(K_{\text{eff}})_{\alpha\beta} = & \frac{1}{2} \left\{ \langle \alpha | H | \beta \rangle - \sum_{pq,B} \langle \alpha | E_{pq} | B \rangle C_B(\beta) \sum_e \frac{(p|v|e)(e|v|q)}{\epsilon_e - \epsilon_q + \Delta E_{B\alpha}} - \sum_{pqrs,B} \langle \alpha | E_{pq,rs} | B \rangle C_B(\beta) \right. \\
& \times \left[\sum_e \frac{(p|v|e)(eq|rs)}{\epsilon_e - \epsilon_q + \epsilon_r - \epsilon_s + \Delta E_{B\alpha}} + \sum_e \frac{(pe|rs)(e|v|q)}{\epsilon_e - \epsilon_q + \Delta E_{B\alpha}} + \frac{1}{2} \sum_{(a,b)} \frac{(pa|rb)(aq|bs)}{\epsilon_a - \epsilon_q + \epsilon_b - \epsilon_s + \Delta E_{B\alpha}} \right] \\
& \left. - \sum_{pqrstu,B} \langle \alpha | E_{pq,rs,tu} | B \rangle C_B(\beta) \sum_e \frac{(pe|rs)(eq|tu)}{\epsilon_e - \epsilon_q + \epsilon_t - \epsilon_u + \Delta E_{B\alpha}} + (\alpha \leftrightarrow \beta) \right\}. \quad (10)
\end{aligned}$$

In Eq. (10), B refers to a configuration state function (CSF) in the CASSCF wave function, $C_B(\beta)$ are CASSCF CI coefficients for the CSF's B in state β , E_{pq} is a unitary group generator,

$$E_{pq} = a_{p\alpha}^+ a_{q\alpha} + a_{p\beta}^+ a_{q\beta}, \quad (11)$$

and

$$E_{pq,rs} = E_{pq} E_{rs} - \delta_{qr} E_{ps}, \quad (12)$$

$$E_{pq,rs,tu} = E_{pq,rs} E_{tu} - \delta_{qt} E_{pu,rs} - \delta_{st} E_{pq,ru}. \quad (13)$$

The operator v is one-particle perturbation operator whose elements are given by

$$(p|v|q) = (p|h|q) - \epsilon_p \delta_{pq}, \quad (14)$$

and ϵ_p are orbital energies. Active orbitals are indicated by the indices p, q, r, s, t, u , while the external (virtual) orbitals are indicated by indices e, f . The symbol (a, b) in the summation in the third term of Eq. (10) means that a and b run over both active and external orbitals, but that a and b cannot both be external orbitals simultaneously. $\Delta E_{B\alpha}$ is the difference (shift) between the energies of the zeroth-order state α and configuration (CSF) B ,

$$\Delta E_{B\alpha} = E_B^{(0)} - E_\alpha^{(0)}. \quad (15)$$

In this article we employ an energy formula omitting the doubly occupied orbitals for simplicity. While it is straightforward to include these in practice, they unnecessarily complicate the derivation. The full formula, including doubly occupied orbitals, will be discussed in Sec. VI.

The MC-QDPT total energy to second order is expressed using the above effective Hamiltonian by

$$W = \sum_{\alpha\beta} D_\alpha D_\beta (K_{\text{eff}})_{\alpha\beta} / \sum_{\alpha} D_\alpha^2, \quad (16)$$

where D_α are elements of the eigenvectors which diagonalize the effective Hamiltonian.

B. The constraining conditions for determining the parameters

The parameters in the energy expression, that is, the molecular orbital coefficients, orbital energies, and CI coefficients, are determined from the orbital canonicalization conditions of the CASSCF equations. These equations are used as constraining conditions in the response function formalism.

1. The state-averaged CASSCF equations

The state-averaged CASSCF equations determine the CI and MO coefficients, except for the freedom due to the rotational invariance within the doubly occupied (doc-doc), active (act-act), and external (ext-ext) orbital subspaces. The variational conditions for the CI coefficients are

$$\sum_B (H_{AB} - \delta_{AB} E^{\text{CAS}}(\alpha)) C_B(\alpha) = 0, \quad (17)$$

where the normalization conditions,

$$\sum_A C_A(\alpha)^2 = 1, \quad (18)$$

are assumed implicitly, since the energy expression (16) is written with normalized CI coefficients. The variational conditions for the MO coefficients are expressed as a symmetry condition on the matrix x_{pq} defined in Eqs. (A2)–(A4) in the Appendix,

$$x_{pq} = x_{qp}. \quad (19)$$

2. The orbital canonicalization and the definition of the orbital energies

Following the CASSCF optimization, canonicalization removes the rotational freedom of the CASSCF orbitals, since the MC-QDPT energy (unlike the CASSCF energy) is not invariant to rotations within the doubly occupied, active, and external subspaces. For the doubly occupied, active, and external diagonal block (D),

$$F_{pq} = (p|h|q) + \sum_{rs} D_{rs}^{\text{Ave}} [(pq|rs) - \frac{1}{2}(pr|sq)] \quad (p > q \in D), \quad (20)$$

where D_{rs}^{Ave} is the state-averaged one-particle density matrix [see Eq. (A5) in the Appendix]. The orbital energies are defined simultaneously as the eigenvalues of the Fock matrix. These conditions may all be expressed in one set of equations:

$$\begin{aligned}
F_{pq} - \epsilon_p \delta_{pq} = & (p|h|q) + \sum_{rs} D_{rs}^{\text{Ave}} [(pq|rs) - \frac{1}{2}(pr|sq)] \\
& - \epsilon_p \delta_{pq} = 0 \quad (p \geq q \in D). \quad (21)
\end{aligned}$$

3. The orthonormalization condition for the molecular orbitals

Equations (17)–(20) do not determine the molecular orbitals completely, since there are only $n_{\text{MO}}(n_{\text{MO}} - 1)/2$ constraints for n_{MO}^2 orbital coefficients. The orthonormality condition,

$$(p|q) = \delta_{pq} \quad (p \geq q), \quad (22)$$

is assumed implicitly for the orbitals. It must be included in the Lagrangian explicitly.

4. The diagonalization condition of the effective Hamiltonian

In the last step of the MC-QDPT calculation, we diagonalize the effective Hamiltonian to obtain the energy of the target state. This may be expressed as

$$\sum_{\beta} \{(K_{\text{eff}})_{\alpha\beta} - \delta_{\alpha\beta} E\} D_{\beta} = 0 \quad \text{and} \quad \sum_{\alpha} D_{\alpha}^2 = 1, \quad (23)$$

where the latter expression is the normality condition. The total energy E is a parameter constrained by the above equations. Note that while E is a parameter that arises from the diagonalization condition, W [see Eq. (16)] is a function of the parameters and nuclear coordinates.

$$\begin{aligned} L = & \sum_{\alpha\beta} D_{\alpha} D_{\beta} (K_{\text{eff}})_{\alpha\beta} / \left[\sum_{\alpha} D_{\alpha}^2 + \sum_{\alpha} \sum_A \zeta_{\text{CAS,CI}}^{A\alpha} \left\{ \sum_B (H_{AB} - \delta_{AB} E^{\text{CAS}}(\alpha)) C_B(\alpha) \right\} + \sum_{\alpha} \zeta_{\text{CAS,E}}^{\alpha} \left(1 - \sum_A C_A(\alpha)^2 \right) \right] \\ & + \sum_{p>q \in O} \zeta_{\text{CAS,MO}}^{pq} (x_{pq} - x_{qp}) + \sum_{p \geq q \in D} \zeta_{\text{CAS,MO}}^{pq} (F_{pq} - \epsilon_p \delta_{pq}) + \sum_{p \geq q} \zeta_S^{pq} \{(p|q) - \delta_{pq}\} + \sum_{\alpha} \zeta_K^{\alpha} \left\{ \sum_{\beta} (K_{\text{eff}})_{\alpha\beta} D_{\beta} - E D_{\alpha} \right\} \\ & + \zeta_K \left(1 - \sum_{\alpha} D_{\alpha}^2 \right) + \sum_{B\alpha} \zeta_{\Delta E}^{B\alpha} \left\{ \sum_p [\langle B|E_{pp}|B\rangle - \langle \alpha|E_{pp}|\alpha\rangle] \epsilon_p - \Delta E_{B\alpha} \right\} + \sum_{pq} \zeta_u^{pq} \{(p|h|q) - u_{pq}\} \\ & + \sum_{pqrs} \zeta_g^{pqrs} \{(pq|rs) - g_{pqrs}\}. \end{aligned} \quad (27)$$

Note that the energy is now expressed only in terms of the molecular orbital coefficients, (CAS-)CI coefficients, u_{pq} , g_{pqrs} , etc., but not explicitly in terms of the molecular integrals. That is, it does not depend on the nuclear coordinates explicitly.

IV. LAGRANGE MULTIPLIERS

Initially, Lagrangian multipliers ζ s must be computed for the energy gradient. The linear equation determining the ζ s,

$$\frac{\partial}{\partial C} L \Big|_{X=X_0} = 0 \leftrightarrow \zeta \frac{\partial e}{\partial C} \Big|_{X=X_0} = - \frac{\partial W}{\partial C} \Big|_{X=X_0}, \quad (28)$$

may be decoupled into several sets of equations corresponding to the step-wise wave function determination described in Sec. III B.

C. The MC-QDPT Lagrangian

Now we may write down the Lagrangian using the energy expression Eq. (16) and the constraining conditions Eqs. (17)–(23) according to the definition of the Lagrangian in Eq. (1). To reduce the complexity of the energy expression Eq. (16), we introduce the following compact notation:

$$\begin{aligned} u_{pq} &= (p|h|q) = \sum_{\mu\nu} c_{\mu p} c_{\nu q} (\mu|h|\nu) \\ &= (p|v|q) \quad (p \neq q), \end{aligned} \quad (24)$$

$$g_{pqrs} = (pq|rs) = \sum_{\mu\nu\rho\sigma} c_{\mu p} c_{\nu q} c_{\rho r} c_{\sigma s} (\mu\nu|\rho\sigma). \quad (25)$$

These equations may then be used as constraining conditions that determine the parameters u_{pq} and g_{pqrs} . The energy differences between the zeroth-order state and configuration energies in the energy expression may be treated as parameters,

$$\Delta E_{B\alpha} = E_B^{(0)} - E_{\alpha}^{(0)} = \sum_p \{ \langle B|E_{pp}|B\rangle - \langle \alpha|E_{pp}|\alpha\rangle \} \epsilon_p. \quad (26)$$

Using the energy expression Eq. (16) and the constraining conditions, we may write the Lagrangian,

A. The multipliers for diagonalization of the effective Hamiltonian

Since the effective Hamiltonian is diagonalized without any approximation, the energy is stationary with respect to changes in all D_{α} ,

$$\frac{\partial}{\partial D_{\alpha}} W \Big|_{X=X_0} = 0 \quad \text{and} \quad \frac{\partial}{\partial E} W \Big|_{X=X_0} = 0. \quad (29)$$

The solutions for these linear equations are clearly

$$\zeta_K^{\alpha} = 0 \quad \text{and} \quad \zeta_K = 0. \quad (30)$$

B. The multipliers for the one- and two-electron integrals

The multipliers for the one- and two-electron integrals are obtained by simple partial differentiation as

$$\zeta_u^{ab} = \frac{\partial}{\partial u_{ab}} W \Big|_{X=X_0} = \sum_{\alpha} D_{\alpha}^2 \langle \alpha | E_{ab} | \alpha \rangle + 2d_{ab}^{E(2)}, \quad (31)$$

$$\begin{aligned} \zeta_g^{abcd} &= \frac{\partial}{\partial g_{abcd}} W \Big|_{X=X_0} \\ &= \frac{1}{2} \sum_{\alpha} D_{\alpha}^2 \langle \alpha | E_{ab,cd} | \alpha \rangle + 2D_{abcd}^{E(2)}, \end{aligned} \quad (32)$$

where $d_{ab}^{E(2)}$ and $D_{abcd}^{E(2)}$ denote the one- and two-electron densities in the MO basis for the second-order energy [see Eqs. (A6)–(A9) in the Appendix] and the first term on the rhs of Eq. (32) is the two-electron density for the zeroth plus first-order energy.

C. The multipliers for the definition of energy shift

The equation for obtaining the multipliers for the energy shifts,

$$\frac{\partial}{\partial \Delta E_{B\alpha}} L \Big|_{X=X_0} = 0 \quad (33)$$

easily reduces to a formula which gives the multipliers directly,

$$\begin{aligned} \zeta_{\Delta E}^{B\alpha} &= \frac{\partial}{\partial \Delta E_{B\alpha}} E \Big|_{X=X_0} \\ &\equiv \frac{1}{2} \sum_{\alpha\beta} D_{\alpha} D_{\beta} \left\{ \sum_{pq,B} \langle \alpha | E_{pq} | B \rangle C_{B\beta} \right. \\ &\quad \times \sum_e \frac{u_{pe} u_{eq}}{(\epsilon_e - \epsilon_q + \Delta E_{B\alpha})^2} + (\alpha \leftrightarrow \beta) \Big\} \\ &\quad + (2\text{-} + 3\text{-body terms}). \end{aligned} \quad (34)$$

The two- and three-body terms in Eq. (34) are readily derived by analogy to the one-body term, since $\partial/\partial \Delta E_{B\alpha}$ operates only on the energy denominators in the Lagrangian. The symbol \equiv indicates that the full formula is given in the Appendix [Eq. (A10)]. The structure of the algebra is the same as that for the energy expression (16), so that the computation is performed using the same approach as for the effective Hamiltonian.

D. The multipliers for the orbital energies

The orbital energy appears in the definition of energy shift (26), that of orbital energies themselves, and the energy expression. The multipliers for $\Delta E_{B\alpha}$ are already determined; thus the multipliers for orbital energies are again given by the partial differentiation of the energy expression and the occupation numbers,

$$\begin{aligned} \frac{\partial}{\partial \epsilon_p} L \Big|_{X=X_0} &\leftrightarrow \zeta_{\text{CAS,MO}}^{pq} = - \sum_{B\alpha} \zeta_{\Delta E}^{B\alpha} [\langle B | E_{pp} | B \rangle \\ &\quad - \langle \alpha | E_{pp} | \alpha \rangle]_{X=X_0} + \frac{\partial W}{\partial \epsilon_p} \Big|_{X=X_0}. \end{aligned} \quad (35)$$

In the first term of the rhs, $\langle B | E_{pp} | B \rangle$ is the occupation number of orbital p in CSF B , and $\langle \alpha | E_{pp} | \alpha \rangle$ is an occupation number that is averaged over the reference functions. The information needed for Eq. (35) is obtained as by-products of the CASSCF calculation. As noted above for the multipliers for $\Delta E_{B\alpha}$, the second term in Eq. (35) has the same creation–annihilation operator structure as the effective Hamiltonian, so that the calculation is again straightforward,

$$\begin{aligned} \frac{\partial}{\partial \epsilon_m} W \Big|_{X=X_0} &\equiv \frac{1}{2} \sum_{\alpha\beta} D_{\alpha} D_{\beta} \left\{ - \sum_{pq,B} \langle \alpha | E_{pq} | B \rangle C_{B\beta} \right. \\ &\quad \times \sum_e (\delta_{mq} - \delta_{me}) \frac{u_{pe} u_{eq}}{(\epsilon_e - \epsilon_q + \Delta E_{B\alpha})^2} \\ &\quad \left. + (\alpha \leftrightarrow \beta) \right\} + (2\text{-} + 3\text{-body terms}). \end{aligned} \quad (36)$$

The full details are given in Eq. (A11) in the Appendix.

E. The multipliers for the MO rotations in the invariant doubly occupied, active, and external subspaces

The multipliers for the orbital rotations in the doubly occupied, active, and external subspaces may be obtained from the following equation,

$$\left(\frac{\partial}{\partial U_{ab}} - \frac{\partial}{\partial U_{ba}} \right) L \Big|_{X=X_0} = 0 \quad (a > b \in D), \quad (37)$$

where

$$c_{\mu i}(X) = \sum_m c_{\mu m}(X_0) U_{mi}. \quad (38)$$

We use U_{mi} rather than molecular coefficients themselves as in the conventional energy derivative methods. Rewriting Eq. (37) in matrix form as

$$\mathbf{A} \mathbf{x}_{\text{CAS,MO}}^D = \mathbf{b}, \quad (39)$$

we obtain

$$\begin{aligned} A^{ab,pq} &= \epsilon_a \delta_{pa} \delta_{qb} + 2 \sum_i D_{ib}^{\text{Ave}P} P_{pqia} - (a \leftrightarrow b) \\ &= \begin{cases} (\epsilon_a - \epsilon_b) \delta_{pa} \delta_{qb} & ((a,b) \in \text{doc,ext}) \\ (\epsilon_a - \epsilon_b) \delta_{pa} \delta_{qb} + 2 \sum_i (D_{ib}^{\text{Ave}P} P_{pqia} - D_{ia}^{\text{Ave}P} P_{pqib}) & ((a,b) \in \text{act}) \end{cases} \end{aligned} \quad (40)$$

as the matrix elements, and

$$b^{ab} = -2 \left\{ \sum_i \zeta_{\text{CAS,MO}}^{ii} \sum_j D_{jb}^{\text{Ave}} P_{iija} + \sum_i \zeta_u^{ib} u_{ia} + 2 \sum_{ijk} \zeta_g^{ijkb} (ij|ka) - (a \leftrightarrow b) \right\} \quad (41)$$

as the vector elements, where P_{pqrs} are the Roothaan–Bagus supermatrix integrals,¹⁷

$$P_{pqrs} = (pq|rs) - \frac{1}{4}(pr|qs) - \frac{1}{4}(ps|rq). \quad (42)$$

The $\zeta_{\text{CAS,MO}}^{pq}$ for the doubly occupied and external subspaces can be determined without having to solve linear equations, since the matrix is diagonal for doubly occupied and external subspaces. A small linear equation of dimension is $n_{\text{act}}(n_{\text{act}} - 1)/2$ must be solved to obtain $\zeta_{\text{CAS,MO}}^{pq}$ for the active subspace.

F. The multipliers for the MO rotations mixing different subspaces (doc-act, doc-ext, and act-ext subspaces) and the CI coefficients

The multipliers for the orbital rotation mixing among different subspaces and for the CI coefficients are obtained by solving coupled linear equations corresponding to the state-averaged CASSCF equation. The dimension of these linear equations is large, so their solution represents the most time-consuming part of the problem:

$$\begin{cases} (\partial/\partial U_{ab} - \partial/\partial U_{ba})L|_{X=X_0} = 0 & (a > b \in O) \\ \partial L/\partial C_A(\gamma)|_{X=X_0} = 0 \\ \partial L/\partial E_{\text{CAS}}(\gamma)|_{X=X_0} = 0 \end{cases}, \quad (43)$$

where $a > b \in O$ means that orbitals a and b are in different orbital subspaces (doubly occupied, active, or external). Equation (39) may be written in matrix form as,

$$\begin{pmatrix} \mathbf{A}_{\text{MO,MO}} & \mathbf{A}_{\text{MO,CI}} & \mathbf{0} \\ \mathbf{A}_{\text{CI,MO}} & \mathbf{A}_{\text{CI,CI}} & \mathbf{A}_{\text{CI,E}} \\ \mathbf{0} & \mathbf{A}_{\text{E,CI}} & \mathbf{0} \end{pmatrix} \begin{pmatrix} \mathbf{x}_{\text{CAS,MO}}^O \\ \mathbf{x}_{\text{CAS,CI}} \\ \mathbf{x}_{\text{CAS,E}} \end{pmatrix} = \begin{pmatrix} \mathbf{b}_{\text{CAS,MO}}^O \\ \mathbf{b}_{\text{CAS,CI}} \\ \mathbf{0} \end{pmatrix}. \quad (44)$$

The coefficient matrix \mathbf{A} consists of six nonzero parts,

$$A_{\text{MO,MO}}^{ab,pq} = (\delta_{bp}x_{aq} + Y_{pqab} - (p \leftrightarrow q)) - (a \leftrightarrow b), \quad (45)$$

$$A_{\text{MO,CI}}^{ab,A\alpha} = \sum_B X_{ab}^{AB} C_B(\alpha) - (a \leftrightarrow b) \quad (a > b; p > q \in O), \quad (46)$$

$$A_{\text{CI,MO}}^{A\alpha,pq} = w(\alpha) \sum_B C_B(\alpha) (X_{pq}^{AB} - X_{qp}^{AB}), \quad (47)$$

$$A_{\text{CI,CI}}^{A\alpha,B\beta} = [H_{BA} - \delta_{BA} E^{\text{CAS}}(\alpha)] \delta_{\alpha\beta}, \quad (48)$$

$$A_{\text{CI,E}}^{A\alpha,\beta} = -2C_A(\alpha) \delta_{\alpha\beta}, \quad (49)$$

$$A_{\text{E,CI}}^{\alpha,B\beta} = -C_B(\alpha) \delta_{\alpha\beta}, \quad (50)$$

where X_{ab}^{AB} and Y_{pqab} are defined in Eqs. (A12) and (A13) in the Appendix, respectively. The vector \mathbf{b} on the rhs of Eq. (39) has two nonzero parts, given in Eqs. (51) and (52):

$$b_{\text{CAS,MO}}^{ab} = - \sum_{p \geq q \in D} \zeta_{\text{CAS,MO}}^{pq} \left(\delta_{bp} F_{aq} + \delta_{bq} F_{ap} + 2 \sum_i D_{ib} P_{pqia} - (a \leftrightarrow b) \right) - 2 \left\{ \sum_i \zeta_u^{ib} u_{ia} + 2 \sum_{ijk} \zeta_g^{ijkb} (ij|ka) - (a \leftrightarrow b) \right\} \quad (51)$$

$$b_{\text{CAS,CI}}^{A\alpha} = -w(\alpha) \sum_{p \geq q \in D} \zeta_{\text{CAS,MO}}^{pq} \sum_{rs} \langle \alpha | E_{rs} + E_{sr} | A \rangle \times P_{pqrs} + 2C_A(\alpha) E_A^{(0)} \sum_B \zeta_{\Delta E}^{B\alpha} - \frac{\partial}{\partial C_A(\alpha)} W. \quad (52)$$

The last term in the rhs of $b_{\text{CAS,CI}}^{A\alpha}$ is

$$\frac{\partial}{\partial C_A(\alpha)} W \equiv 2D_\alpha^2 E^{\text{CAS}}(\alpha) C_A(\alpha) + D_\alpha \sum_\beta D_\beta \times \left\{ - \sum_{pq} \langle \beta | E_{pq} | A \rangle \sum_e \left[\frac{u_{pe} u_{eq}}{\epsilon_e - \epsilon_q + \Delta E_{A\beta}} + (\beta \rightarrow \alpha) \right] \right\} + (2- + 3\text{-body terms}), \quad (53)$$

where the 2- and 3-body terms are given in Eq. (A15) in the Appendix. The coefficient matrices $\mathbf{A}_{\text{MO,MO}}$, $\mathbf{A}_{\text{MO,CI}}$, $\mathbf{A}_{\text{CI,MO}}$, and $\mathbf{A}_{\text{CI,CI}}$ are very similar to those in the coupled perturbed state-averaged CASSCF equations,^{18,19} except that the terms corresponding to the normalization of the CI vectors are missing. These normalization conditions are included in $\mathbf{A}_{\text{CI,E}}$ and $\mathbf{A}_{\text{E,CI}}$ instead.

G. The multipliers for the MO orthonormalization conditions

The final step in solving the linear equations for the multipliers is the computation of the multipliers for the orthonormalization conditions of the orbitals,

$$\left(\frac{\partial}{\partial U_{ab}} + \frac{\partial}{\partial U_{ba}} \right) L \Big|_{X=X_0} = 0, \quad (a \geq b) \quad (54)$$

which reduces to

$$\zeta_S^{ab} = -2^{-1} (1 + \delta_{ab})^{-1} \xi_{ab}. \quad (55)$$

The ξ_{ab} are obtained by changing the sign from minus to plus in subsections IV D–F and collecting them,

$$\begin{aligned} \xi_{ab} = & \sum_\alpha \sum_A \zeta_{\text{CAS,CI}}^{A\alpha} \sum_B X_{ab}^{AB} C_B(\alpha) \\ & + \sum_{p > q \in O} \zeta_{\text{CAS,MO}}^{pq} (\delta_{bp} x_{aq} + Y_{pqab} - (p \leftrightarrow q)) \\ & + \sum_{p \geq q \in D} \zeta_{\text{CAS,MO}}^{pq} \left(\delta_{bp} F_{aq} + \delta_{bq} F_{ap} + 2 \sum_i D_{ib} P_{pqia} \right) + 2 \left(\sum_i \zeta_u^{ib} u_{ia} + 2 \sum_{ijk} \zeta_g^{ijkb} (ij|ka) \right) + (a \leftrightarrow b). \end{aligned} \quad (56)$$

V. MOLECULAR ENERGY GRADIENT

The Lagrangian multipliers obtained in the previous section may now be combined with the molecular integrals to compute the molecular energy gradients:

$$\begin{aligned}
 \left. \frac{dL}{dX} \right|_{X=X_0} &= \left[\frac{\partial W}{\partial X} + \zeta \frac{\partial e}{\partial X} \right]_{X=X_0} \\
 &= \left[\zeta \frac{\partial e}{\partial X} \right]_{X=X_0} \\
 &= \sum_{\alpha} \sum_A \zeta_{\text{CAS,CI}}^{A\alpha} \sum_B \frac{\partial H_{AB}}{\partial X} C_B(\alpha) \\
 &\quad + \sum_{p>q \in O} \zeta_{\text{CAS,MO}}^{pq} \frac{\partial}{\partial X} (x_{pq} - x_{qp}) \\
 &\quad + \sum_{p \geq q \in D} \zeta_{\text{CAS,MO}}^{pq} \frac{\partial F_{pq}}{\partial X} + \sum_{p \geq q} \zeta_S^{pq} (p|q)^X \\
 &\quad + \sum_{pq} \zeta_u^{pq} (p|h|q)^X + \sum_{pqrs} \zeta_g^{pqrs} (pq|rs)^X \\
 &= \sum_{pq} d_h^{pq} (p|h|q)^X + \sum_{pw} d_S^{pq} (p|q)^X \\
 &\quad + \sum_{pqrs} D_g^{pqrs} (pq|rs)^X, \tag{57}
 \end{aligned}$$

where $(p|h|q)^X$, $(p|q)^X$, and $(pq|rs)^X$ are transformed integral derivatives in the MO basis defined by Eqs. (6), (7), and (8), respectively, and d_h^{pq} , d_S^{pq} , and D_g^{pqrs} are effective densities for the Lagrangian in the MO basis. The densities are given by

$$\begin{aligned}
 d_h^{pq} &= \sum_{\alpha} \sum_A \zeta_{\text{CAS,CI}}^{A\alpha} \langle A | E_{pq} | \alpha \rangle \\
 &\quad + \sum_{i>j \in O} \zeta_{\text{CAS,MO}}^{ij} \text{Ave}(\delta_{pi} \langle \alpha | E_{jq} | \alpha \rangle - (i \leftrightarrow j)) \\
 &\quad + \zeta_u^{pq} + \left\{ \begin{array}{l} \zeta_{\text{CAS,MO}}^{pq} \quad (p > q \in D) \\ 0 \quad (\text{otherwise}) \end{array} \right\}, \tag{58}
 \end{aligned}$$

$$d_S^{pq} = \zeta_S^{pq}, \tag{59}$$

and

$$\begin{aligned}
 D_g^{pqrs} &= \sum_{\alpha} \sum_A \zeta_{\text{CAS,CI}}^{A\alpha} \langle A | E_{pq,rs} | \alpha \rangle / 2 \\
 &\quad + \sum_{i>j \in O} \zeta_{\text{CAS,MO}}^{ij} \text{Ave}(\delta_{pi} \langle \alpha | E_{jq,rs} | \alpha \rangle - (i \leftrightarrow j)) \\
 &\quad + \zeta_g^{pqrs} + \sum_{i>j \in D} \zeta_{\text{CAS,MO}}^{ij} (\delta_{pi} \delta_{qj} D_{rs}^{\text{Ave}} \\
 &\quad + \delta_{pi} \delta_{sj} D_{qr}^{\text{Ave}}). \tag{60}
 \end{aligned}$$

These densities are transformed back into the atomic orbital (AO) basis, and the energy gradients may be obtained by multiplying the densities in the AO basis by the first-derivative integrals,

$$\begin{aligned}
 \left. \frac{dL}{dX} \right|_{X=X_0} &= \sum_{\mu\nu} d_h^{\mu\nu} \frac{d}{dX} (\mu|h|\nu) + \sum_{\mu\nu} d_S^{\mu\nu} \frac{d}{dX} (\mu|\nu) \\
 &\quad + \sum_{\mu\nu\rho\sigma} D_g^{\mu\nu\rho\sigma} \frac{d}{dX} (\mu\nu|\rho\sigma). \tag{61}
 \end{aligned}$$

The following is the summary of the computational steps:

- (1) *In step 1*, the wave function is determined: (a). Compute the CASSCF wave functions; (b). Canonicalize the CASSCF MOs and transform the integrals to the MO basis. Then, recompute the CASSCF wave functions for the canonical Fock MOs; (c). Compute the MC-QDPT effective Hamiltonian and obtain the final energy by diagonalizing it.
- (2) *In step 2*, the zeroth-order Lagrangian multipliers are determined by solving the appropriate linear equations: (a). Compute the ζ_K ; (b). Compute the diagonal $\zeta_{\text{CAS,MO}}$ ($= \zeta_{\text{CAS,MO}}^{pp}$); (c). Compute the block-diagonal part of the $\zeta_{\text{CAS,MO}}$; (d). Solve the linear equation for the $\zeta_{\text{CAS,CI}}$ and the off-diagonal part of the $\zeta_{\text{CAS,MO}}$; (e). Compute the ζ_S .
- (3) *In the final step 3*, energy gradients are computed: (a). Compute the effective densities of the Lagrangian for the overlap, one-, and two-electron integrals on the MO basis; (b). Transform the densities back to the AO basis; (c). Multiply the densities and the derivative integrals to obtain the gradient, which is looped over all the nuclear coordinates.

VI. DISCUSSION AND CONCLUDING REMARKS

We have derived an analytic gradient method for the second-order MC-QDPT energy along the lines of the response function formalism without using a second-quantization form of the energy expression and constraining conditions or an exponential form of parameter relaxation. In the present derivation, we have not used the independent set of variables to describe the orbital rotations and CSF rotations. The use of exponential parameter relaxation introduces more than 100 terms (156 Goldstone diagrams versus only 25 diagrams in our derivation!) in the orbital relaxation of the energy expression. Therefore, though some redundant variables and relevant constraining conditions were necessary in the present derivation, the formulas are more compact. This suggests that one might expect better performance in the actual computations. The equations presented here are currently being implemented into the electronic structure codes GAMESS²⁰ and MR2D.²¹

In the present work, we put some limitations on the derivations to simplify the presentation. First, we have omitted the contributions from doubly occupied orbitals in the energy expression. To include those contributions, one introduces a

change in the definition of the one-particle perturbation matrix (14), making the equations more complex,

$$(p|v|q) = (p|h|q) + \sum_i^{\text{doc}} [2(pq|ii) - (pi|i q)], \quad (62)$$

since they now depend on two-electron integrals as well as the one-electron perturbation integral. This, of course, affects ζ_g^{pqrs} and the effective two-electron density D_g^{pqrs} in Eqs. (32) and (60), respectively. Furthermore, the one- and two-particle coupling constants $\langle A|E_{pq}|B\rangle$ and $\langle A|E_{pq,rs}|B\rangle$ which include doubly occupied orbital labels should be replaced by those not including doubly occupied orbital labels according to the well-known formulae,

$$\langle A|E_{pq}|B\rangle = \begin{cases} \langle A|E_{pq}|B\rangle & (p,q:\text{act}) \\ 2\delta_{pq}\delta_{AB} & (p,q:\text{doc}) \end{cases} \quad (63)$$

and

$$\langle A|E_{pq,rs}|B\rangle = \begin{cases} \langle A|E_{pq,rs}|B\rangle & (p,q,r,s:\text{act}) \\ 2\delta_{rs}\langle A|E_{pq}|B\rangle & (p,q:\text{act};r,s:\text{doc}) \\ 2\delta_{pq}\langle A|E_{rs}|B\rangle & (p,q:\text{doc};r,s:\text{act}) \\ -\delta_{rq}\langle A|E_{ps}|B\rangle & (p,s:\text{act};r,q:\text{doc}) \\ -\delta_{ps}\langle A|E_{rq}|B\rangle & (p,s:\text{doc};r,q:\text{act}) \\ 2(2\delta_{pq}\delta_{rs} - \delta_{ps}\delta_{rq})\delta_{AB} & (p,q,r,s:\text{doc}) \end{cases} \quad (64)$$

in practical implementation.

Another limitation placed on the derivation is that the reference functions of the perturbation are the same as that used for the CASSCF functions. However, we also perform calculations for which this is not the case. For example, we might use just one of the state-averaged CASSCF wave functions as a reference function for a perturbation calculation. To treat such a case introduces one more constraining CI equation in the Lagrangian, giving rise to two kinds of CI equations: one for CASSCF solutions coupled with the generalized Brillouin condition, and the other for determining reference functions. Although this makes formulas a little more complicated, the extension is straightforward.

The present formulation is not applicable to conventional QDPT based on a single configuration wave function,

since the reference functions and orbital energies are different from those described in Sec. III B. However, the effective Hamiltonian (10) and the energy expression (16) may also be used to express the QDPT energy. Thus, the derivation of the formulas for QDPT may be performed in the same manner described in the present article, and they will be presented in the forthcoming paper.

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APPENDIX: NOTATION

In the text of the present article, some definitions are omitted to avoid being filled with long equations. The following are the complete definitions of notations omitted in the text.

$$V = \sum_{pq} (h_{pq} - \epsilon_p \delta_{pq}) E_{pq} + \frac{1}{2} \sum_{pqrs} (pq|rs) E_{pq,rs} \\ = \sum_{pq} v_{pq} E_{pq} + \frac{1}{2} \sum_{pqrs} (pq|rs) E_{pq,rs}, \quad (A1)$$

$$x_{pq} = \text{Ave } x_{pq}(\alpha) = \sum_{\alpha} w(\alpha) x_{pq}(\alpha), \quad (A2)$$

$$x_{pq}(\alpha) = \sum_i h_{pi} \langle \alpha | E_{qi} | \alpha \rangle + \sum_{ijk} (pi|jk) \langle \alpha | E_{qi,jk} | \alpha \rangle, \\ [w(\alpha) \text{ is the weight of the } \alpha \text{th state.}] \quad (A3)$$

$$|\alpha\rangle = \sum_A C_A(\alpha) |A\rangle, \quad (A4)$$

$$D_{rs}^{\text{Ave}} = \text{Ave} \langle \alpha | E_{rs} | \alpha \rangle = \sum_{\alpha} w(\alpha) \langle \alpha | E_{rs} | \alpha \rangle, \quad (A5)$$

$$d_{ab}^{E(2)} = \frac{\partial}{\partial u_{ab}} E^{(2)} \Big|_{X=X_0} = \frac{1}{4} \sum_{\alpha\beta} D_{\alpha} D_{\beta} \left\{ - \sum_{pq,B} \langle \alpha | E_{pq} | B \rangle C_{B\beta} \sum_e \frac{\delta_{pa} \delta_{eb} u_{eq} + u_{pe} \delta_{ea} \delta_{qb}}{\epsilon_e - \epsilon_q + \Delta E_{B\alpha}} - \sum_{pqrs,B} \langle \alpha | E_{pq,rs} | B \rangle C_{B\beta} \right. \\ \left. \times \left[\sum_e \frac{\delta_{pa} \delta_{eb} g_{eqrs}}{\epsilon_e - \epsilon_q + \epsilon_r - \epsilon_s + \Delta E_{B\alpha}} + \sum_e \frac{g_{pers} \delta_{ea} \delta_{qb}}{\epsilon_e - \epsilon_q + \Delta E_{B\alpha}} \right] + (\alpha \leftrightarrow \beta) \right\}, \quad (A6)$$

$$D_{abcd}^{E(2)} = \frac{\partial}{\partial g_{abcd}} E^{(2)} \Big|_{X=X_0} = \frac{1}{4} \sum_{\alpha\beta} D_{\alpha} D_{\beta} \left\{ - \sum_{pqrs,B} \langle \alpha | E_{pq,rs} | B \rangle C_{B\beta} \left[\sum_e \frac{u_{pe} \delta_{ea} \delta_{qb} \delta_{rc} \delta_{sd}}{\epsilon_e - \epsilon_q + \epsilon_r - \epsilon_s + \Delta E_{B\alpha}} \right. \right. \\ \left. \left. + \sum_e \frac{\delta_{pa} \delta_{eb} \delta_{rc} \delta_{sa} \delta_{eq}}{\epsilon_e - \epsilon_q + \Delta E_{B\alpha}} + \frac{1}{2} \sum_{(a',b')} \frac{\delta_{pa} \delta_{a'b} \delta_{rc} \delta_{b'd} \delta_{a'qb's} + g_{pa'r'b'} \delta_{a'a} \delta_{qb} \delta_{b'c} \delta_{sd}}{\epsilon_{a'} - \epsilon_q + \epsilon_{b'} - \epsilon_s + \Delta E_{B\alpha}} \right] \right. \\ \left. + \sum_{pqrstu,B} \langle \alpha | E_{pq,rs,tu} | B \rangle C_{B\beta} \sum_e \frac{\delta_{pa} \delta_{eb} \delta_{rc} \delta_{sd} g_{eqtu} + g_{pers} \delta_{ea} \delta_{qb} \delta_{tc} \delta_{ud}}{\epsilon_e - \epsilon_q + \epsilon_t - \epsilon_u + \Delta E_{B\alpha}} + (\alpha \leftrightarrow \beta) \right\}. \quad (A7)$$

It is convenient to employ the symmetrized effective densities:

$$d_{ab}^{E(2)} \leftarrow \frac{1}{2}(d_{ab}^{E(2)} + d_{ba}^{E(2)}), \quad (\text{A8})$$

$$D_{abcd}^{E(2)} \leftarrow \frac{1}{8}(D_{abcd}^{E(2)} + D_{abdc}^{E(2)} + D_{bacd}^{E(2)} + D_{badc}^{E(2)} + D_{cdab}^{E(2)} + D_{cdba}^{E(2)} + D_{dcab}^{E(2)} + D_{dcba}^{E(2)}), \quad (\text{A9})$$

to simplify the following equations.

$$\begin{aligned} \zeta_{\Delta E}^{B\alpha} = \frac{\partial}{\partial \Delta E_{B\alpha}} E \Big|_{X=X_0} &= \frac{1}{2} \sum_{\alpha\beta} D_{\alpha} D_{\beta} \left\{ \sum_{pq,B} \langle \alpha | E_{pq} | B \rangle C_{B\beta} \sum_e \frac{u_{pe} u_{eq}}{(\epsilon_e - \epsilon_q + \Delta E_{B\alpha})^2} \right. \\ &+ \sum_{pqrs,B} \langle \alpha | E_{pq,rs} | B \rangle C_{B\beta} \left[\sum_e \frac{u_{pe} g_{eqrs}}{(\epsilon_e - \epsilon_q + \epsilon_r - \epsilon_s + \Delta E_{B\alpha})^2} + \sum_e \frac{g_{pers} u_{eq}}{(\epsilon_e - \epsilon_q + \Delta E_{B\alpha})^2} \right. \\ &+ \left. \left. \frac{1}{2} \sum_{(a,b)} \frac{g_{parb} g_{aqbs}}{(\epsilon_a - \epsilon_q + \epsilon_b - \epsilon_s + \Delta E_{B\alpha})^2} \right] + \sum_{pqrstu,B} \langle \alpha | E_{pq,rs,tu} | B \rangle \right. \\ &\left. \times C_{B\beta} \sum_e \frac{g_{pers} g_{eqtu}}{(\epsilon_e - \epsilon_q + \epsilon_t - \epsilon_u + \Delta E_{B\alpha})^2} + (\alpha \leftrightarrow \beta) \right\}, \quad (\text{A10}) \end{aligned}$$

$$\begin{aligned} \frac{\partial}{\partial \epsilon_m} W \Big|_{X=X_0} &= \frac{1}{2} \sum_{\alpha\beta} D_{\alpha} D_{\beta} \left\{ - \sum_{pq,B} \langle \alpha | E_{pq} | B \rangle C_{B\beta} \sum_e (\delta_{mq} - \delta_{me}) \frac{u_{pe} u_{eq}}{(\epsilon_e - \epsilon_q + \Delta E_{B\alpha})^2} - \sum_{pqrs,B} \langle \alpha | E_{pq,rs} | B \rangle C_{B\beta} \right. \\ &\times \left[\sum_e (\delta_{mq} - \delta_{me} + \delta_{ms} - \delta_{mr}) \frac{u_{pe} g_{eqrs}}{(\epsilon_e - \epsilon_q + \epsilon_r - \epsilon_s + \Delta E_{B\alpha})^2} + \sum_e (\delta_{mq} - \delta_{me}) \frac{g_{pers} u_{eq}}{(\epsilon_e - \epsilon_q + \Delta E_{B\alpha})^2} \right. \\ &+ \left. \left. \frac{1}{2} \sum_{(a,b)} (\delta_{mq} - \delta_{ma} + \delta_{ms} - \delta_{mb}) \frac{g_{parb} g_{aqbs}}{(\epsilon_a - \epsilon_q + \epsilon_b - \epsilon_s + \Delta E_{B\alpha})^2} \right] - \sum_{pqrstu,B} \langle \alpha | E_{pq,rs,tu} | B \rangle C_{B\beta} \right. \\ &\left. \times \sum_e (\delta_{mq} - \delta_{me} + \delta_{mu} - \delta_{mu}) \frac{g_{pers} g_{eqtu}}{(\epsilon_e - \epsilon_q + \epsilon_t - \epsilon_u + \Delta E_{B\alpha})^2} + (\alpha \leftrightarrow \beta) \right\}, \quad (\text{A11}) \end{aligned}$$

$$X_{pq}^{AB} = \sum_i (p|h|i)[\langle A | E_{qi} | B \rangle + \langle B | E_{qi} | A \rangle] + \sum_{ijk} (pi|jk)[\langle A | E_{qi,jk} | B \rangle + \langle B | E_{qi,jk} | A \rangle], \quad (\text{A12})$$

$$Y_{pqab} = \sum_{\alpha} w(\alpha) Y_{pqab}(\alpha), \quad (\text{A13})$$

$$Y_{pqab}(\alpha) = (p|h|a)\langle \alpha | E_{qb} | \alpha \rangle + \sum_{mn} [(p|a|mn)\langle \alpha | E_{qb,mn} | \alpha \rangle + (p|a|mn)\langle \alpha | E_{qm,bn} | \alpha \rangle + (p|m|an)\langle \alpha | E_{qm,nb} | \alpha \rangle], \quad (\text{A14})$$

$$\begin{aligned} \frac{\partial}{\partial C_A(\alpha)} W &= 2D_{\alpha}^2 E^{\text{CAS}}(\alpha) C_A(\alpha) + D_{\alpha} \sum_{\beta} D_{\beta} \left\{ - \sum_{pq} \langle \beta | E_{pq} | A \rangle \sum_e \left[\frac{u_{pe} u_{eq}}{\epsilon_e - \epsilon_q + \Delta E_{A\beta}} + (\beta \rightarrow \alpha) \right] - \sum_{pqrs} \langle \beta | E_{pq,rs} | A \rangle \right. \\ &\times \left[\sum_e \frac{u_{pe} g_{eqrs}}{\epsilon_e - \epsilon_q + \epsilon_r - \epsilon_s + \Delta E_{A\beta}} + \sum_e \frac{g_{pers} u_{eq}}{\epsilon_e - \epsilon_q + \Delta E_{A\beta}} + \frac{1}{2} \sum_{(a,b)} \frac{g_{parb} g_{aqbs}}{\epsilon_a - \epsilon_q + \epsilon_b - \epsilon_s + \Delta E_{A\beta}} + (\beta \rightarrow \alpha) \right] \\ &\left. - \sum_{pqrstu} \langle \beta | E_{pq,rs,tu} | A \rangle \sum_e \left[\frac{g_{pers} g_{eqtu}}{\epsilon_e - \epsilon_q + \epsilon_t - \epsilon_u + \Delta E_{A\beta}} + (\beta \rightarrow \alpha) \right] \right\}. \quad (\text{A15}) \end{aligned}$$

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