

Analytic gradients for the spin-conserving and spin-flipping equation-of-motion coupled-cluster models with single and double substitutions

Sergey V. Levchenko, Tao Wang, and Anna I. Krylov

Department of Chemistry, University of Southern California, Los Angeles, California 90089-0482

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Analytic gradient expressions for the spin-conserving and spin-flipping equation-of-motion coupled-cluster models with single and double substitutions are derived using a Lagrangian approach for the restricted and unrestricted Hartree–Fock references, both for the case of all orbitals being active in correlated calculations and for the frozen core and/or virtual orbitals. Details of the implementation within the Q-CHEM electronic structure package are discussed. The capabilities of the new code are demonstrated by application to cyclobutadiene. © 2005 American Institute of Physics. [DOI: 10.1063/1.1877072]

I. INTRODUCTION

The importance of calculating energy derivatives analytically has been recognized several decades ago.^{1,2} Since calculations of global potential energy surfaces (PESs) with a subsequent interpolation are feasible only for very small systems,³ practical computational studies of spectroscopic and dynamical properties often focus on stationary points of PESs and thus require energy derivatives. For example, first derivatives allow one to characterize molecular equilibrium geometries, transition structures, and to calculate minimum energy paths and intrinsic reaction coordinates.

In principle, derivatives of any order can be computed numerically from total energies by a finite difference procedure. Since such calculations require only total energies, they can be performed for any electronic structure method. However, this universality of the numerical derivatives is their only advantage. The numerical evaluation of energy gradient for a system with N degrees of freedom requires $2N$ single point energy calculations (in the absence of symmetry). Moreover, the finite difference procedure often encounters numerical problems, such as poor convergence, numerical noise, etc. Calculation of analytic gradients is free of numerical instabilities and can be performed approximately at a cost of a single-point energy calculation, which results in significant time savings for polyatomic molecules.

Conceptually, derivation of analytic gradient expressions is nothing but differentiation of an energy expression with respect to (w.r.t.) nuclear coordinates. However, this seemingly simple procedure becomes rather cumbersome for wave functions that are not fully variationally optimized and thus do not satisfy the Hellmann–Feynman theorem. In these cases, the energy derivative w.r.t. perturbation ξ includes, in addition to the expectation value of the derivative of the Hamiltonian, terms that contain derivatives of the wave function $\Psi(\alpha)$ w.r.t. nonvariational parameters α :

$$\frac{dE}{d\xi} = \langle \Psi | \frac{\partial H}{\partial \xi} | \Psi \rangle + 2 \langle \Psi | H | \frac{\partial \Psi}{\partial \alpha} \rangle \frac{\partial \alpha}{\partial \xi}, \quad (1)$$

where $E = \langle \Psi | H | \Psi \rangle$ and $\langle \Psi | \Psi \rangle = 1$. The efficiency of analytic derivatives calculation stems from the realization of Handy and Schaefer² that the latter term in Eq. (1) does not require evaluation of the derivatives of the nonvariational parameters α w.r.t. all degrees of freedom, rather solving only one perturbation-independent linear equation for each type of the parameters (the Z -vector approach).² Thus, $(2n)$ th and $(2n + 1)$ th energy derivatives require solving only n th order coupled-perturbed (and some related) equations.

Alternatively, the terms due to nonvariational parameters can be evaluated by using the Lagrangian approach (see, for example, Refs. 4–8). In this method, instead of the energy functional, one introduces a new functional

$$L(\alpha, \lambda) = E + \lambda f(\alpha), \quad (2)$$

where λ denotes an undetermined Lagrange multiplier and $f(\alpha) = 0$ is an equation that defines values of the parameters α . This new functional, a Lagrangian, is stationary w.r.t. α , and multipliers λ are defined such that $\partial L / \partial \alpha = 0$. Thus, the Hellmann–Feynman theorem is satisfied for the new functional. Since the value of the Lagrangian is equal to that of the original energy functional when the optimal values of all the parameters are used, the gradient of the new functional is equal to that of the energy. This approach allows one to incorporate all the equations determining the nonvariational parameters in the energy functional in a general way. Note that the very existence of the Lagrangian implies the possibility to avoid evaluation of the derivatives of the nonvariational parameters w.r.t. all degrees of freedom, as shown by Handy and Schaefer.²

This paper presents general theory and implementation of analytic gradients for the equation-of-motion coupled-cluster models with single and double substitutions (EOM-CCSD) for excitation energies (EOM-EE-CCSD) (Refs. 9–11) and its spin-flip counterpart (EOM-SF-CCSD).^{12,13} EOM approach^{9,11,13–17} is a very powerful and versatile elec-

tronic structure tool that allows one to describe many multi-configurational wave functions within a single-reference formalism. EOM-EE-CCSD accurately describes electronically excited states that are dominated by a single electron promotion in a single-step computational procedure that simultaneously calculates several electronic states and provides a balanced account of both dynamical and nondynamical correlations. This results in a robust and efficient computational scheme that does not require an arbitrary active space selection for each state of interest and is free from root flipping, intruder states, size-consistency errors, and other problems associated with multireference models. For example, no special treatment of near-degenerate excited states or states with strong Rydberg-valence mixing is required within EOM-CC formalism, whereas these situations pose a challenge for multireference methods.^{8,18} However, EOM-EE-CCSD would fail when the reference state acquires significant multiconfigurational character due to a small highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) gap, e.g., at the dissociation limit or in diradicals. This problem can be cured by employing high-spin reference state and solving the EOM equations in the $M_s = -1$ subspace, as it is done in the EOM-SF-CCSD (Refs. 12 and 13) method. Thus, EOM-SF-CCSD extends single-reference EOM-CC methodology to such chemically important cases as diradicals, triradicals, and single-bond-breaking processes.

A general theory of analytic gradients for the EOM-CCSD methods was developed by Stanton and Gauss^{19–22} using direct differentiation of energy functional and the Z-vector technique of Handy and Schaefer.² The alternative derivations, which employed the Lagrangian approach, have also been reported.^{5,6} Reduced orbital space EOM-CC optimized geometries have been presented in Ref. 23, although no details of derivation/implementation were given. In this work, we employ the Lagrangian approach (see, for example, Refs. 4–8) to derive programmable gradient expressions for the EOM-EE-CCSD and EOM-SF-CCSD models for unrestricted Hartree–Fock (UHF) and restricted Hartree–Fock (RHF) references, including the case of frozen core/virtual orbitals. In the spin-orbital formulation, the EOM-SF-CCSD analytic gradient expressions are identical to the EOM-EE-CCSD ones; however, the spin symmetry of the EOM amplitudes and implementation are different, as discussed below. The new code for analytic gradients is implemented in the Q-CHEM electronic structure package.²⁴

The paper is organized as follows: Sec. II A presents EOM-CC equations and the energy functional, in Sec. II B we derive a general expression for the EOM-CC energy gradient in terms of fully relaxed density matrices, and Secs. II C and II D present derivation of programmable expressions for amplitude and orbital response equations, respectively. The capabilities of the EOM-SF-CCSD gradients are demonstrated by application to cyclobutadiene in Sec. III. Our conclusions are given in Sec. IV.

II. GENERAL THEORY

A. EOM-CCSD equations

In the EOM-CC theory, the target state wave functions are parametrized as:^{9,11,13}

$$|\Psi_R\rangle = \text{Re}^T |\Phi_0\rangle, \quad (3)$$

$$\langle \Psi_L | = \langle \Phi_0 | e^{-T} L, \quad (4)$$

where $|\Phi_0\rangle$ is a reference Slater determinant²⁵ and T is a spin-conserving and fully symmetric excitation operator from this reference:

$$T = \sum_{\mu} t_{\mu} \hat{\mu} = T_1 + \cdots + T_n, \quad T_1 = \sum_{ia} t_i^a a^+ i, \quad (5)$$

$$T_2 = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} a^+ b^+ j i, \quad \cdots, \quad (6)$$

and the amplitudes $\{t_{\mu}\}$, $\mu = 1, 2, \dots, n$, are determined by the CC equations for the reference state:

$$\langle \Phi_{\mu} | \bar{H} - E^{CC} | \Phi_0 \rangle = 0, \quad \bar{H} = e^{-T} H e^T, \quad E^{CC} = \langle \Phi_0 | \bar{H} | \Phi_0 \rangle. \quad (7)$$

In the above equation and further on, $\hat{\mu}$ is an excitation operator and Φ_{μ} denotes all μ -tuple excited determinants, e.g., $\Phi_1 = \{\Phi_i^a\}$, $\Phi_2 = \{\Phi_{ij}^{ab}\}$, etc.

The operators R and L^+ are general excitation operators:

$$R = R_0 + R_1 + \cdots + R_n,$$

$$L = L_0 + L_1 + \cdots + L_n,$$

where n is the highest excitation level, $R_0 = r_0 \hat{1}$, and the forms of R_k and L_k (as well as a definition of the excitation level k) depend upon the nature of the reference and final states; for example, when both the reference and the final state are states of a N -electron system, operators R_k conserve the number of electrons, i.e., contain equal number of creation and annihilation operators. When the reference and the final state differ by number of electrons, operators R_k/L_k^+ are ionizing or electron attaching. In EOM-EE and EOM-SF, operators R_k/L_k^+ conserve the total number of electrons:

$$R_1 = \sum_{ia} r_i^a a^+ i, \quad L_1 = \sum_{ia} l_i^a i^+ a, \quad \cdots. \quad (8)$$

The EOM-EE excitation operators also conserve the total number of α and β electrons and are therefore spin conserving ($M_s = 0$), while the EOM-SF operators include spin flip, i.e., have different number of annihilation and creation operators for each spin ($M_s \neq 0$).

Amplitudes $\{r_{\mu}, l_{\mu}\}$ are found as stationary points of the EOM energy functional:^{11,13}

$$E = \frac{\langle \Psi_L | H | \Psi_R \rangle}{\langle \Psi_L | \Psi_R \rangle} = \frac{\langle \Phi_0 | L | \bar{H} | R | \Phi_0 \rangle}{\langle \Phi_0 | L | R | \Phi_0 \rangle}. \quad (9)$$

By applying the bivariational principle, one arrives at a familiar EOM-CC non-Hermitian eigenproblem:

$$\langle \Phi_{\mu} | \bar{H} - E | R | \Phi_0 \rangle = 0, \quad (10)$$

$$\langle \Phi_0 L | \bar{H} - E | \Phi_\mu \rangle = 0, \quad (11)$$

$$\mu = 1, 2, \dots, n, \quad (12)$$

$$\langle \Phi_0 L^j | R^j \Phi_0 \rangle = \delta_{IJ}. \quad (13)$$

In the present work, we consider EOM-CC models in which the maximum excitation level is 2, and excitation operators R, L conserve the total number of electrons (EOM-EE-CCSD and EOM-SF-CCSD).

For a normalized Ψ_L, Ψ_R —see Eq. (13)—the EOM energy of Eq. (9) can conveniently be expressed by using symmetrized one- and two-particle density matrices:

$$E = \langle \Psi_L | H | \Psi_R \rangle = \sum_{pq} h_{pq} \gamma'_{pq} + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \Gamma'_{pqrs}, \quad (14)$$

$$\gamma'_{pq} = \frac{1}{2} \langle \Psi_L | p^+ q + q^+ p | \Psi_R \rangle, \quad (15)$$

$$\Gamma'_{pqrs} = \frac{1}{2} \langle \Psi_L | p^+ q^+ s r + s^+ r^+ p q | \Psi_R \rangle. \quad (16)$$

The EOM-CCSD programmable expressions for different blocks of γ'_{pq} and Γ'_{pqrs} are presented in Table I.

B. The analytic EOM-CCSD energy derivative and Lagrangian

As it follows from the preceding section, the EOM-CCSD energy depends upon the following set of parameters: $E = E(L, R, T, C)$ where L, R , and T are described above, and C is a molecular orbital matrix which defines transformation from atomic orbitals $\{\chi_\mu\}$ to molecular orbitals $\{\phi_p\}$:

$$\phi_p = \sum_{\mu} C_{\mu p} \chi_{\mu}. \quad (17)$$

Therefore the full energy derivative w.r.t. a perturbation ξ is:

$$\frac{dE}{d\xi} = \frac{\partial E}{\partial \xi} + \frac{\partial E}{\partial L} \frac{dL}{d\xi} + \frac{\partial E}{\partial R} \frac{dR}{d\xi} + \frac{\partial E}{\partial T} \frac{dT}{d\xi} + \frac{\partial E}{\partial C} \frac{dC}{d\xi}, \quad (18)$$

where the first term is a Hellmann–Feynman contribution that describes explicit ξ dependence of the Hamiltonian:

$$\frac{\partial E}{\partial \xi} = \sum_{pq} h_{pq}^{\xi} \gamma'_{pq} + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle^{\xi} \Gamma'_{pqrs}, \quad (19)$$

$$h_{pq}^{\xi} = \frac{\partial h_{pq}}{\partial \xi} = \sum_{\mu\nu} C_{\mu p} h_{\mu\nu}^{\xi} C_{\nu q}, \quad (20)$$

$$h_{\mu\nu}^{\xi} = \langle \chi_{\mu} | \frac{\partial \hat{h}}{\partial \xi} | \chi_{\nu} \rangle + \langle \frac{\partial \chi_{\mu}}{\partial \xi} | \hat{h} | \chi_{\nu} \rangle + \langle \chi_{\mu} | \hat{h} | \frac{\partial \chi_{\nu}}{\partial \xi} \rangle, \quad (21)$$

$$\langle pq || rs \rangle^{\xi} = \frac{\partial \langle pq || rs \rangle}{\partial \xi} = \sum_{\mu\nu\lambda\sigma} C_{\mu p} C_{\nu q} \langle \chi_{\mu} \chi_{\nu} || \chi_{\lambda} \chi_{\sigma} \rangle^{\xi} C_{\lambda r} C_{\sigma s}, \quad (22)$$

$$\begin{aligned} \langle \chi_{\mu} \chi_{\nu} || \chi_{\lambda} \chi_{\sigma} \rangle^{\xi} = & \langle \frac{\partial \chi_{\mu}}{\partial \xi} \chi_{\nu} || \chi_{\lambda} \chi_{\sigma} \rangle + \langle \chi_{\mu} \frac{\partial \chi_{\nu}}{\partial \xi} || \chi_{\lambda} \chi_{\sigma} \rangle \\ & + \langle \chi_{\mu} \chi_{\nu} || \frac{\partial \chi_{\lambda}}{\partial \xi} \chi_{\sigma} \rangle + \langle \chi_{\mu} \chi_{\nu} || \chi_{\lambda} \frac{\partial \chi_{\sigma}}{\partial \xi} \rangle. \end{aligned} \quad (23)$$

Since the EOM energy is stationary w.r.t. R, L^+ , the $\partial E / \partial L$ and $\partial E / \partial R$ terms are zero (see the Appendix). The evaluation of the so-called amplitude and orbital response terms, $dT/d\xi$ and $dC/d\xi$, respectively, is straightforward but tedious.^{19,26} As outlined in the Introduction, it can be simplified by employing the Lagrangian approach.^{4–8} If the UHF/RHF reference is used, the EOM-CC Lagrangian is

$$\begin{aligned} \mathcal{L}(L, R, T, C, Z, \Lambda, \Omega) = & \frac{\langle \Phi_0 L | \bar{H} | R \Phi_0 \rangle}{\langle \Phi_0 L | R \Phi_0 \rangle} \\ & + \sum_{\mu=1}^n z_{\mu} \langle \Phi_{\mu} | \bar{H} - E | \Phi_0 \rangle \\ & + \frac{1}{2} \sum_{pq} \lambda_{pq} (f_{pq} - \delta_{pq}) \\ & + \sum_{pq} \omega_{pq} (S_{pq} - \delta_{pq}), \end{aligned} \quad (24)$$

where $Z \equiv \{z_{\mu}\}$, $\Lambda \equiv \{\lambda_{pq}\}$, and $\Omega \equiv \{\omega_{pq}\}$ are undetermined Lagrange multipliers, and f and S are the Fock and molecular orbital (MO) overlap matrices, respectively:

$$f_{pq} = \langle p | h | q \rangle + \sum_j \langle p j | | q j \rangle, \quad (25)$$

$$S_{pq} = \langle \phi_p | \phi_q \rangle. \quad (26)$$

The first term in Eq. (24) is simply the energy functional of Eq. (9) and, since other terms of Eq. (24) do not depend on the EOM-amplitudes R and L , the Lagrangian is stationary w.r.t. L and R :

$$\frac{\partial \mathcal{L}}{\partial L} = \frac{\partial \mathcal{L}}{\partial R} = 0. \quad (27)$$

The second, third, and fourth terms in Eq. (24) are zero when the CC amplitude equations and the Hartree–Fock equations for the reference Φ_0 (i.e., orbital equations) are satisfied, which renders the Lagrangian as stationary w.r.t. the corresponding Lagrange multipliers. Alternatively, the amplitude and orbital equations can be retrieved by requesting the Lagrangian to be stationary w.r.t. the corresponding Lagrange multipliers:

$$\frac{\partial \mathcal{L}}{\partial Z_{\mu}} = \langle \Phi_{\mu} | \bar{H} - E | \Phi_0 \rangle = 0, \quad (28)$$

$$\frac{\partial \mathcal{L}}{\partial \lambda_{pq}} = f_{pq} - \delta_{pq} = 0, \quad (29)$$

$$\frac{\partial \mathcal{L}}{\partial \omega_{pq}} = S_{pq} - \delta_{pq} = 0. \quad (30)$$

The first equation above is simply Eq. (7), whereas the second and third are equivalent to the Hartree–Fock equations.

TABLE I. Excited states' effective one- and two-electron density matrices defined by Eqs. (15) and (16). Here it is assumed that left and right excited states are biorthogonalized such that $\sum_{ia} l_i^a l_i^a + \frac{1}{4} \sum_{ijab} l_{ij}^{ab} l_{ij}^{ab} = 1$, and the factor r_0 ensures orthogonality of the right excited states to the left ground state. Excited left states do not mix with the reference, thus $l_0 = 0$. Intermediates are summarized in Table II.

$$\begin{aligned} \gamma'_{ij} &= \tilde{\gamma}_{ij} + \delta_{ij} \\ \tilde{\gamma}_{ij} &= \frac{1}{2} P_+(ij) \left(- \sum_a l_i^a \tilde{r}_{ja}^a - \tilde{l}_{ij} - \sum_a Y_{ia}^1 t_{ij}^a \right) \\ \gamma'_{ia} &= \frac{1}{2} \left[r_0 l_i^a + Y_{ia}^1 + \sum_{jb} l_j^b (\tilde{r}_{ij}^{ab} - \tilde{r}_{ib} t_j^a - \tilde{r}_{ja} t_i^b) + \sum_{jb} Y_{jb}^1 (t_{ij}^{ab} - t_j^a t_i^b) - \sum_k \tilde{l}_{ki} r_k^a - \sum_c \tilde{l}^c r_i^c - \sum_j \tilde{l}_{ji} t_j^a - \sum_b \tilde{l}^{ba} t_i^b + t_i^a \right] \\ \gamma'_{ab} &= \frac{1}{2} P_+(ab) \left(\sum_i l_i^a \tilde{r}_{ib}^a + \tilde{l}^{ab} + \sum_i Y_{ia}^1 t_i^b \right) \\ \Gamma'_{ijkl} &= \tilde{\Gamma}_{ijkl} - \delta_{il} \delta_{kj} + \delta_{ki} \delta_{lj} - \delta_{li} \tilde{\gamma}_{jk} + \delta_{ki} \tilde{\gamma}_{jl} + \delta_{lj} \tilde{\gamma}_{ik} - \delta_{kj} \tilde{\gamma}_{il} \\ \tilde{\Gamma}_{ijkl} &= \frac{1}{4} \sum_{ab} (l_k^{ab} r_{ij}^{ab} + l_{ij}^{ab} r_{kl}^{ab}) \\ \Gamma'_{abcd} &= \frac{1}{4} \sum_{ij} (l_{ij}^{ab} r_{ij}^{cd} + l_{ij}^{cd} r_{ij}^{ab}) \\ \Gamma'_{ijka} &= \tilde{\Gamma}_{ijka} - \delta_{kj} \gamma'_{ia} + \delta_{ki} \gamma'_{ja} \\ \tilde{\Gamma}_{ijka} &= \frac{1}{2} \left[\sum_b l_{ij}^{ab} \tilde{r}_{kb}^a + \sum_b l_{ij}^{ba} \tilde{r}_{ij}^b + \sum_b Y_{kb}^1 \tilde{r}_{ij}^{ab} + \tilde{l}_{kj} t_i^a - \tilde{l}_{ki} t_j^a - \tilde{l}_{kj} r_i^a + \tilde{l}_{ki} r_j^a + \sum_{lbc} l_{kl}^{bc} \left(\frac{1}{2} r_{ij}^{bc} t_i^a - t_i^b \tilde{r}_{jl}^{ac} + t_j^b \tilde{r}_{il}^{ac} + t_{jl}^{ab} r_i^c - t_{il}^{ab} r_j^c + \frac{1}{2} t_{ij}^{bc} r_i^a \right) \right] \\ \Gamma'_{ijab} &= \frac{1}{2} \left[\tilde{r}_{ij}^{ab} + r_0 l_{ij}^{ab} - \sum_{kc} l_k^c (r_{kij}^{bac} - r_{kij}^{abc}) - \sum_{kc} l_k^c (-t_{ik}^{ac} r_j^b + t_{jk}^{bc} r_i^a + l_{ik}^{bc} r_j^a - t_{jk}^{bc} r_i^a + t_{ik}^{bc} r_j^c - t_{jk}^{bc} r_i^c - \tilde{r}_{jk}^{ab} t_i^c + \tilde{r}_{ik}^{ab} t_j^c + \tilde{r}_{ij}^{bc} r_k^a - \tilde{r}_{ij}^{bc} r_k^a + l_i^b \tilde{r}_{jk}^{ac} - t_j^b \tilde{r}_{ik}^{ac} - t_i^b \tilde{r}_{jk}^{ac} + t_j^b \tilde{r}_{ik}^{ac}) \right. \\ &\quad + \sum_k (\tilde{l}_{ki} \tilde{r}_{jk}^{ab} - \tilde{l}_{kj} \tilde{r}_{ik}^{ab}) + \sum_c (\tilde{l}^{ca} \tilde{r}_{ij}^{bc} - \tilde{l}^{cb} \tilde{r}_{ij}^{ac}) - \sum_{klcd} l_{kl}^{cd} \left(-\frac{1}{4} t_{ij}^{cd} r_{kl}^{ab} - t_{ik}^{cd} r_{jl}^{ab} + t_{jk}^{cd} r_{il}^{ab} + \frac{1}{2} t_{ij}^{ac} r_{kl}^{bd} + t_{ik}^{bc} r_{jl}^{ad} - t_{jk}^{bc} r_{il}^{ad} - \frac{1}{2} t_{ij}^{bc} r_{kl}^{ad} - \frac{1}{4} t_{ik}^{ab} r_{jl}^{cd} + \frac{1}{2} t_{jk}^{ab} r_{il}^{cd} \right. \\ &\quad + t_{kl}^{bc} r_{ij}^{ad} - l_{kl}^{bc} r_{ij}^{ad} - t_{kl}^{bc} r_{ij}^{ad} + t_{kl}^{bc} r_{ij}^{ad} - \frac{1}{2} t_{kl}^{bc} r_{ij}^{ad} + \frac{1}{2} t_{kl}^{bc} r_{ij}^{ad} + \frac{1}{2} t_{kl}^{bc} r_{ij}^{ad} - \frac{1}{2} t_{kl}^{bc} r_{ij}^{ad} + t_{kl}^{bc} r_{ij}^{ad} - t_{kl}^{bc} r_{ij}^{ad} - t_{kl}^{bc} r_{ij}^{ad} - \frac{1}{2} t_{kl}^{bc} r_{ij}^{ad} + t_{kl}^{bc} r_{ij}^{ad} - t_{kl}^{bc} r_{ij}^{ad} - t_{kl}^{bc} r_{ij}^{ad} \\ &\quad \left. + t_{kl}^{bc} r_{ij}^{ad} + \frac{1}{2} t_{kl}^{bc} r_{ij}^{ad} \right) \left. + \sum_{kc} Y_{kc}^1 (-t_{kij}^{bac} + t_{kij}^{abc} + t_i^c t_{jk}^{ab} - t_j^c t_{ik}^{ab} - t_i^b t_{jk}^{ac} + t_j^b t_{ik}^{ac} + t_i^a t_{jk}^{bc} - t_j^a t_{ik}^{bc}) + \sum_k [\tilde{l}_{ki} (t_{kj}^a r_i^b - t_k^a r_j^b - t_j^a r_k^b + t_k^a t_j^b - t_k^a t_j^b) + \tilde{l}_{kj} (t_k^a r_i^b - t_k^a r_j^b - t_j^a r_k^b + t_k^a t_j^b - t_k^a t_j^b) \right. \\ &\quad \left. + t_i^a r_k^b - t_i^a r_k^b - t_i^b r_k^a + t_i^b r_k^a \right] + \sum_c [\tilde{l}^{ca} (t_i^c r_j^b - t_i^c r_j^b + t_j^c r_i^a - t_j^c r_i^a) + \tilde{l}^{cb} (t_i^c r_j^a - t_i^c r_j^a - t_j^c r_i^b + t_j^c r_i^b)] \end{aligned}$$

$$\Gamma'_{iajb} = \tilde{\Gamma}_{iajb} + \delta_{ji} \gamma'_{ab}$$

$$\tilde{\Gamma}_{iajb} = -\frac{1}{2} \left[l_i^b \tilde{r}_{ja}^a + l_j^a \tilde{r}_{ib}^a - (Y_{ja}^1 l_i^b + Y_{ib}^1 l_j^a) + \sum_{kc} l_{jk}^{ac} (l_i^b \tilde{r}_{ic}^a + t_i^c \tilde{r}_{kb}^a - \tilde{r}_{ik}^{bc}) + \sum_{kc} l_{ik}^{bc} (t_j^a \tilde{r}_{jc}^a + t_j^c \tilde{r}_{ka}^a - \tilde{r}_{jk}^{ac}) \right]$$

$$\Gamma'_{iabc} = \frac{1}{2} \left[\sum_j l_{ij}^{bc} \tilde{r}_{ja}^a + \sum_j l_{ij}^{ca} \tilde{r}_{ij}^b + \sum_j Y_{ja}^1 \tilde{r}_{ij}^{bc} - r_i^a \tilde{l}^{ab} + l_i^a \tilde{l}^{bc} - t_i^a \tilde{l}^{ab} + l_i^a \tilde{l}^{bc} + \sum_{jkd} l_{jk}^{ad} \left(-l_{ij}^{bd} r_k^c + t_{ij}^{cd} r_k^d + \frac{1}{2} t_{ij}^{bc} r_i^d + t_j^c \tilde{r}_{ik}^{bd} - t_j^c \tilde{r}_{ik}^{bd} + \frac{1}{2} t_{ij}^{bc} r_i^d \right) \right]$$

If all orbitals are active in correlated calculations, the EOM-CC energy is invariant w.r.t. unitary transformations among occupied or among virtual orbitals, and λ_{ij} and λ_{ab} are therefore zero.

To make \mathcal{L} stationary w.r.t. all the parameters, we *define* the undetermined Lagrange multipliers $\{Z, \Lambda, \Omega\}$ such that $\partial\mathcal{L}/\partial T$ and $\partial\mathcal{L}/\partial C$ are zero. Thus, the *full* derivative of \mathcal{L} w.r.t. ξ becomes equal to the *partial* derivative:

$$\begin{aligned} \frac{dE}{d\xi} &= \frac{d\mathcal{L}(L^{opt}, R^{opt}, T^{opt}, C^{opt}, Z^{opt}, \Lambda^{opt}, \Omega^{opt})}{d\xi} \\ &= \frac{\partial\mathcal{L}(L^{opt}, R^{opt}, T^{opt}, C^{opt}, Z^{opt}, \Lambda^{opt}, \Omega^{opt})}{\partial\xi}, \end{aligned} \quad (31)$$

where superscript *opt* specifies that all the parameters satisfy the equations that ensure that \mathcal{L} is fully stationary w.r.t. all the parameters.

The Lagrangian derivative can be written as follows:

$$\begin{aligned} \frac{\partial\mathcal{L}(L, R, T, C, Z, \Lambda, \Omega)}{\partial\xi} &= \langle\Phi_0 L e^{-T} | \frac{\partial H}{\partial\xi} | e^T R \Phi_0\rangle \\ &\quad + \langle\Phi_0 Z e^{-T} | \frac{\partial H}{\partial\xi} | e^T \Phi_0\rangle \\ &\quad + \frac{1}{2} \sum_{pq} \lambda_{pq} \frac{\partial f_{pq}}{\partial\xi} + \sum_{pq} \omega_{pq} \frac{\partial S_{pq}}{\partial\xi} \\ &= \sum_{pq} h_{pq}^\xi \rho_{pq} + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle^\xi \Pi_{pqrs} \\ &\quad + \sum_{pq} \omega_{pq} S_{pq}^\xi, \end{aligned} \quad (32)$$

where h_{pq}^ξ and $\langle pq || rs \rangle^\xi$ are defined by Eqs. (20)–(23), S_{pq}^ξ is

$$S_{pq}^\xi = \sum_{\mu\nu} C_{\mu p} C_{\nu q} \left(\langle \frac{\partial \chi_\mu}{\partial\xi} | \chi_\nu \rangle + \langle \chi_\mu | \frac{\partial \chi_\nu}{\partial\xi} \rangle \right), \quad (33)$$

and effective density matrices ρ and Π are

$$\rho = \gamma' + \gamma'' + \gamma''', \quad (34)$$

$$\Pi = \Gamma' + \Gamma'' + \Gamma''', \quad (35)$$

where γ' and Γ' are the so-called nonrelaxed density matrices defined by Eqs. (15) and (16), γ'' and Γ'' are the amplitude response contributions:

$$\gamma''_{pq} = \frac{1}{2} \langle \Phi_0 Z e^{-T} | p^+ q + q^+ p | e^T \Phi_0 \rangle, \quad (36)$$

$$\Gamma''_{pqrs} = \frac{1}{2} \langle \Phi_0 Z e^{-T} | p^+ q^+ sr + s^+ r^+ pq | e^T \Phi_0 \rangle, \quad (37)$$

and γ''' and Γ''' are the orbital response contributions:

$$\gamma'''_{ij} = \frac{1}{2} \lambda_{ij}, \quad (38)$$

$$\gamma'''_{ia} = \frac{1}{2} \lambda_{ia}, \quad (39)$$

$$\gamma'''_{ab} = \frac{1}{2} \lambda_{ab}, \quad (40)$$

$$\Gamma'''_{ijkl} = -\delta_{ij} \gamma'''_{jk} + \delta_{ki} \gamma'''_{jl} + \delta_{ij} \gamma'''_{ik} - \delta_{kj} \gamma'''_{il}, \quad (41)$$

$$\Gamma'''_{ijka} = -\delta_{kj} \gamma'''_{ia} + \delta_{ki} \gamma'''_{ja}, \quad (42)$$

$$\Gamma'''_{iajb} = \delta_{ji} \gamma'''_{ab}. \quad (43)$$

The programmable expressions for the amplitude response contributions γ''_{pq} and Γ''_{pqrs} can be retrieved from the expressions in Table I by setting $r_0=1$, $r_i^a=0$, $r_{ij}^{ab}=0$, $l_i^a=z_i^a$, and $l_{ij}^{ab}=z_{ij}^{ab}$. When all occupied and/or virtual orbitals are active in correlated calculations, γ'''_{ij} and/or γ'''_{ab} are zero, respectively.

C. Amplitude response equations

The amplitude multipliers $\{Z\}$ are determined from the variational condition $\partial\mathcal{L}/\partial T=0$:

$$\frac{\partial\mathcal{L}}{\partial T_\mu} = \langle\Phi_0 L | [\bar{H}, \hat{\mu}] | R \Phi_0 \rangle + \langle\Phi_0 Z | [[\bar{H}, \hat{\mu}]] | \Phi_0 \rangle = 0. \quad (44)$$

This is a nonhomogeneous system of linear equations with respect to the $\{Z\}$ multipliers. It is convenient to rewrite Eq. (44) as:¹⁹

$$\begin{aligned} \langle\Phi_0 Z | \bar{H} | \Phi_\mu \rangle - \langle\Phi_0 Z | \hat{\mu} \bar{H} | \Phi_0 \rangle \\ = -\langle\Phi_0 L | [\bar{H}, \hat{\mu}] | R \Phi_0 \rangle, \\ \mu = 1, 2, \dots, n. \end{aligned} \quad (45)$$

By inserting the resolution of identity $\hat{1} = \sum_{\mu=0}^N (1/\mu!) |\Phi_\mu\rangle \langle\Phi_\mu|$ between $\hat{\mu}$ and \bar{H} in the left-hand side (lhs) of this equation, and using the reference state CC Eqs. (7), we arrive to:

$$\langle\Phi_0 Z | \bar{H} - E^{CC} | \Phi_\mu \rangle = -\Xi_\mu,$$

$$\Xi_\mu = \langle\Phi_0 L | [\bar{H}, \hat{\mu}] | R \Phi_0 \rangle, \quad \mu = 1, 2, \dots, n. \quad (46)$$

The lhs of this equation is identical to Eq. (11) for the left eigenstates of \bar{H} , upon the substitution of Z by L , and E^{CC} by E . Thus, the code for the left EOM eigenstates can be reused for solving amplitude response equations.

In order to derive programmable expressions for the right-hand side (rhs) of Eq. (46), Ξ_μ ,¹⁹ let us expand the commutator $[\bar{H}, \hat{\mu}]$,

$$\langle\Phi_0 L | [\bar{H}, \hat{\mu}] | R \Phi_0 \rangle = \langle\Phi_0 L | \bar{H} | R \Phi_\mu \rangle - \langle\Phi_0 L | \hat{\mu} \bar{H} | R \Phi_0 \rangle, \quad (47)$$

and insert the resolution of identity between \bar{H} and R in the first term and between $\hat{\mu}$ and \bar{H} in the second term. Using Eqs. (10) and (11), one can show that

$$\langle\Phi_0 L | [\bar{H}, \hat{\mu}] | R \Phi_0 \rangle = \sum_{\nu=n+1}^{n+\mu} \frac{1}{\nu!} \langle\Phi_0 L | \bar{H} | \Phi_\nu \rangle \langle\Phi_\nu | R \Phi_\mu \rangle. \quad (48)$$

The above derivation applies both to the case of all orbitals

being active in correlated calculations and to the case when some of the core and/or virtual orbitals are “frozen,” i.e., when the CC and EOM excitation operators T , R , L^+ operate only in the space of active orbitals. In the latter case, the excited determinants in Eq. (45) belong to the active-active excitation subspace, while the resolution of identity includes all the determinants. However, only the determinants that do not involve excitations from the frozen core or into frozen virtuals survive in Eq. (48).

For EOM-CCSD ($n=2$, $\mu=1, 2$), the elements of Ξ_μ assume the following form:

$$\xi_i^a = \frac{1}{4} \sum_{jkbc} r_{jk}^{bc} \langle \Phi_0 L | \bar{H} | \Phi_{ijk}^{abc} \rangle,$$

$$\xi_{ij}^{ab} = \sum_{kc} r_k^c \langle \Phi_0 L \bar{H} | \Phi_{ijk}^{abc} \rangle + \frac{1}{4} \sum_{klcd} r_{kl}^{cd} \langle \Phi_0 L \bar{H} | \Phi_{ijkl}^{abcd} \rangle;$$

and the programmable expressions are:

$$\begin{aligned} \xi_i^a = & F_{ia} \left(1 - \sum_{jb} r_{jj}^b l_j^b \right) - T_{ji}^3 l_j^a - T_{ba}^4 l_i^b + \sum_{jkbc} l_k^c r_{jk}^{bc} \langle ij || ab \rangle + \frac{1}{4} l_i^a \sum_{jkbc} r_{jk}^{bc} \langle jk || bc \rangle - \frac{1}{2} \sum_b Y_{ab}^2 F_{ib} - \frac{1}{2} \sum_{bc} Y_{bc}^2 l_{ibca}^7 - \frac{1}{2} \sum_j Y_{ij}^3 F_{ja} \\ & + \frac{1}{2} \sum_{jk} Y_{jk}^3 l_{ikja}^6 - \frac{1}{2} \sum_{jb} l_{ij}^{ab} \left(\sum_{klc} r_{kl}^{bc} l_{kljc}^6 - \sum_{kcd} r_{kj}^{cd} l_{kbc}^7 \right) + \sum_{jb} Y_{iajb}^4 F_{jb} - \sum_{jkb} Y_{jkb}^4 l_{ikjb}^6 - \sum_{jbc} Y_{icjb}^4 l_{jcab}^7 + \frac{1}{4} \sum_{jkl} Y_{ijkl}^5 l_{lkja}^6 \\ & - \frac{1}{4} \sum_{bcd} Y_{abcd}^6 l_{ibcd}^7, \end{aligned} \quad (49)$$

$$\begin{aligned} \xi_{ij}^{ab} = & \langle ij || ab \rangle + \omega r_0 l_{ij}^{ab} + Y_{ia}^1 F_{jb} - Y_{ja}^1 F_{ib} - Y_{ib}^1 F_{ja} + Y_{jb}^1 F_{ia} + \sum_c \left[\left(X_{ac}^1 + \frac{1}{2} Y_{ac}^2 \right) \langle ij || bc \rangle - \left(X_{bc}^1 + \frac{1}{2} Y_{bc}^2 \right) \langle ij || ac \rangle \right] + \sum_k \left[\left(X_{ik}^2 \right. \right. \\ & \left. \left. + \frac{1}{2} Y_{ik}^3 \right) \langle jk || ab \rangle - \left(X_{jk}^2 + \frac{1}{2} Y_{jk}^3 \right) \langle ik || ab \rangle \right] + \sum_{kc} r_k^c \left(l_i^a \langle jk || bc \rangle - l_j^a \langle ik || bc \rangle - l_i^b \langle jk || ac \rangle + l_j^b \langle ik || ac \rangle \right) - \sum_k \left(l_{ik}^{ab} T_{kj}^3 - l_{jk}^{ab} T_{ki}^3 \right) \\ & - \sum_c \left(l_{ij}^{ac} T_{cb}^4 - l_{ij}^{bc} T_{ca}^4 \right) + \frac{1}{4} \sum_{kl} Y_{ijkl}^5 \langle kl || ab \rangle + \frac{1}{4} \sum_{cd} Y_{abcd}^6 \langle ij || cd \rangle - \sum_{kc} r_k^c \left(l_{ik}^{ab} F_{jc} - l_{jk}^{ab} F_{ic} \right) - \sum_{kc} r_k^c \left(l_{ij}^{ac} F_{kb} - l_{ij}^{bc} F_{ka} \right) \\ & + \sum_{klc} r_k^c \left(l_{kl}^{ab} l_{ijkc}^6 + l_{ik}^{ac} l_{jlk}^6 - l_{jk}^{ac} l_{ilk}^6 - l_{ik}^{bc} l_{jlka}^6 + l_{jk}^{bc} l_{ilka}^6 + l_{jk}^{ab} l_{ilkc}^6 - l_{ik}^{ab} l_{jlkc}^6 \right) + \sum_{kcd} r_k^d \left(l_{ij}^{cd} l_{kcab}^7 + l_{ik}^{ac} l_{jcbd}^7 - l_{jk}^{ac} l_{icbd}^7 - l_{ik}^{bc} l_{jcad}^7 \right. \\ & \left. + l_{jk}^{bc} l_{icad}^7 - l_{ij}^{ac} l_{kcbd}^7 + l_{ij}^{bc} l_{kcad}^7 \right) + \sum_k \left(l_{ijka}^6 Y_{kb}^1 - l_{ijkb}^6 Y_{ka}^1 \right) + \sum_c \left(Y_{jc}^1 l_{icab}^7 - Y_{ic}^1 l_{jcab}^7 \right). \end{aligned} \quad (50)$$

The expressions for the intermediates are summarized in Table II. Intermediates F_{ia} , l_{ijka}^6 , and l_{iabc}^7 depend only on T amplitudes and integrals, and are already employed in solving the EOM equations.¹³ Other intermediates depend on the EOM amplitudes and therefore have to be recalculated for states of interest. Similarly to the EOM-amplitude equations, all the integrals and intermediates in the above equations are active space in the case of the frozen core/virtuals.

D. Orbital response equations

The orbital response multipliers $\{\Lambda, \Omega\}$ are determined from a variational condition $\partial \mathcal{L} / \partial C = 0$. In order to avoid half-transformed integrals, it is convenient to transform the resulting set of equations back to the MO basis, that is, to replace the original set of equations,

$$\frac{\partial \mathcal{L}}{\partial C_{\mu p}} = 0, \quad (51)$$

by the following:

$$\sum_{\mu} C_{\mu\mu} \frac{\partial \mathcal{L}}{\partial C_{\mu p}} = 0. \quad (52)$$

In order to derive equations, it is convenient to rewrite the Lagrangian as follows:

$$\begin{aligned} \mathcal{L} = & \sum_{pq} h_{pq} \gamma_{pq} + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \Gamma_{pqrs} + \frac{1}{2} \sum_{pq} \lambda_{pq} f_{pq} \\ & + \sum_{pq} \omega_{pq} (S_{pq} - \delta_{pq}), \end{aligned} \quad (53)$$

$$\gamma = \gamma' + \gamma'', \quad (54)$$

$$\Gamma = \Gamma' + \Gamma''. \quad (55)$$

The Lagrangian \mathcal{L} depends on the C matrix elements through the one- and two-electron integrals and the overlap matrix. After simple derivations (see the Appendix for more details)

TABLE II. Intermediates used in Eqs. (49) and (50) and in the excited states' effective one- and two-particle density matrices defined by Eqs. (15) and (16).

$$\begin{aligned}
 F_{ia} &= f_{ia} + \sum_{jb} t_j^b \langle ij || ab \rangle \\
 I_{ijka}^6 &= \langle ij || ka \rangle - \sum_c t_k^c \langle ij || ac \rangle \\
 I_{iabc}^7 &= \langle ia || bc \rangle - \sum_j t_j^a \langle ij || bc \rangle \\
 T_{ij}^3 &= \frac{1}{2} \sum_{kcd} r_{ik}^{cd} \langle jk || cd \rangle \\
 T_{ab}^4 &= \frac{1}{2} \sum_{klc} r_{kl}^{ac} \langle kl || bc \rangle \\
 X_{ab}^1 &= \sum_i t_i^a t_i^b \\
 X_{ij}^2 &= \sum_a t_i^a t_j^a \\
 Y_{ia}^1 &= \sum_{jb} t_{ij}^{ab} t_j^b \\
 Y_{ab}^2 &= \sum_{ijc} t_{ij}^{ac} t_{ij}^{bc} \\
 Y_{ij}^3 &= \sum_{kab} t_{ik}^{ab} t_{jk}^{ab} \\
 Y_{iajb}^4 &= \sum_{kc} t_{ia}^{ac} t_{jb}^{bc} \\
 Y_{ijkl}^5 &= \sum_{ab} t_{ij}^{ab} t_{kl}^{ab} \\
 Y_{abcd}^6 &= \sum_{ij} t_{ij}^{ab} t_{ij}^{cd} \\
 r_0 &= \frac{1}{\omega} \left(\sum_{ia} r_i^a F_{ia} + \frac{1}{4} \sum_{ijab} r_{ij}^{ab} \langle ij || ab \rangle \right) \\
 r_0 &= - \sum_{ia} r_i^a z_i^a - \frac{1}{4} \sum_{ijab} r_{ij}^{ab} z_{ij}^{ab} \\
 \tilde{r}_{ia} &= r_i^a + \frac{1}{2} r_0 t_i^a \\
 \tilde{\tilde{r}}_{ia} &= r_i^a + r_0 t_i^a \\
 \tilde{r}_{ij}^{ab} &= r_{ij}^{ab} + \frac{1}{2} r_0 t_{ij}^{ab} \\
 \tilde{\tilde{r}}_{ij}^{ab} &= r_{ij}^{ab} + r_0 t_{ij}^{ab} \\
 \tilde{\tilde{\tilde{r}}}_{ij}^{ab} &= t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a \\
 \tilde{\tilde{\tilde{\tilde{r}}}}_{ij}^{ab} &= \tilde{\tilde{r}}_{ij}^{ab} + \tilde{r}_{ia} t_j^b - \tilde{r}_{ib} t_j^a - \tilde{r}_{ja} t_i^b + \tilde{r}_{jb} t_i^a \\
 \tilde{\tilde{t}}_{ij} &= \frac{1}{2} \sum_{kab} t_{ik}^{ab} t_{jk}^{ab} \\
 \tilde{\tilde{\tilde{t}}}_{ij}^{ab} &= \frac{1}{2} \sum_{ijc} t_{ij}^{ac} t_{ij}^{bc} \\
 \tilde{\tilde{\tilde{\tilde{t}}}}_{ij} &= \frac{1}{2} \sum_{kab} t_{ik}^{ab} t_{jk}^{ab} \\
 \tilde{\tilde{\tilde{\tilde{\tilde{t}}}}}_{ij}^{ab} &= \frac{1}{2} \sum_{ijc} t_{ij}^{ac} t_{ij}^{bc}
 \end{aligned}$$

and assuming that the canonical Hartree–Fock orbitals are used (i.e., $f_{pq} = \delta_{pq} \epsilon_p$), as well as employing the Hermitian properties of Ω and Λ , one arrives at the following set of equations:

$$\begin{aligned}
 0 &= \sum_{\mu} C_{\mu i} \frac{\partial \mathcal{L}}{\partial C_{\mu j}} = 2 \sum_{ip} h_{ip} \gamma_{jp} + \sum_{pqr} \langle ip || qr \rangle \Gamma_{jpqr} + \epsilon_i \lambda_{ij} \\
 &+ \sum_{pq} \langle ip || jq \rangle \lambda_{pq} + 2 \omega_{ij}, \quad (56)
 \end{aligned}$$

$$\begin{aligned}
 0 &= \sum_{\mu} C_{\mu a} \frac{\partial \mathcal{L}}{\partial C_{\mu i}} = 2 \sum_p h_{ap} \gamma_{ip} + \sum_{pqr} \langle ap || qr \rangle \Gamma_{ipqr} + \lambda_{ia} \epsilon_a \\
 &+ \sum_{pq} \langle ip || ap \rangle \lambda_{pq} + 2 \omega_{ia}, \quad (57)
 \end{aligned}$$

$$\begin{aligned}
 0 &= \sum_{\mu} C_{\mu i} \frac{\partial \mathcal{L}}{\partial C_{\mu a}} = 2 \sum_p h_{ip} \gamma_{ap} + \sum_{pqr} \langle ip || qr \rangle \Gamma_{apqr} + \lambda_{ia} \epsilon_i \\
 &+ 2 \omega_{ia}, \quad (58)
 \end{aligned}$$

$$\begin{aligned}
 0 &= \sum_{\mu} C_{\mu a} \frac{\partial \mathcal{L}}{\partial C_{\mu b}} = 2 \sum_p h_{ap} \gamma_{bp} + \sum_{pqr} \langle ap || qr \rangle \Gamma_{bpqr} + \lambda_{ab} \epsilon_a \\
 &+ 2 \omega_{ab}. \quad (59)
 \end{aligned}$$

By subtracting Eq. (58) from Eq. (57), we obtain the equation that determines the multipliers λ_{pq} :

$$\begin{aligned}
 0 &= 2 \sum_p (h_{ap} \gamma_{ip} - h_{ip} \gamma_{ap}) + \sum_{pqr} (\langle ap || qr \rangle \Gamma_{ipqr} \\
 &- \langle ip || qr \rangle \Gamma_{apqr}) + \lambda_{ia} (\epsilon_a - \epsilon_i) + \sum_{pq} (\langle ip || aq \rangle \\
 &- \langle ip || pa \rangle) \lambda_{pq}. \quad (60)
 \end{aligned}$$

It is convenient to uncouple the equations for λ_{ij} and λ_{ab} from the above equation for λ_{ia} by using the conditions below, which follow from the Hermitian structure of Ω :

$$\sum_{\mu} C_{\mu i} \frac{\partial \mathcal{L}}{\partial C_{\mu j}} - \sum_{\mu} C_{\mu j} \frac{\partial \mathcal{L}}{\partial C_{\mu i}} = 0, \quad (61)$$

$$\sum_{\mu} C_{\mu a} \frac{\partial \mathcal{L}}{\partial C_{\mu b}} - \sum_{\mu} C_{\mu b} \frac{\partial \mathcal{L}}{\partial C_{\mu a}} = 0, \quad (62)$$

which yields:

$$\begin{aligned}
 0 &= 2 \sum_p (h_{ip} \gamma_{jp} - h_{jp} \gamma_{ip}) + \sum_{pqr} (\langle ip || qr \rangle \Gamma_{jpqr} \\
 &- \langle jp || qr \rangle \Gamma_{ipqr}) + \lambda_{ij} (\epsilon_i - \epsilon_j), \\
 0 &= 2 \sum_p (h_{ap} \gamma_{bp} - h_{bp} \gamma_{ap}) + \sum_{pqr} (\langle ap || qr \rangle \Gamma_{bpqr} \\
 &- \langle bp || qr \rangle \Gamma_{apqr}) + \lambda_{ab} (\epsilon_a - \epsilon_b). \quad (63)
 \end{aligned}$$

After Λ are determined, one can use Eqs. (56), (58), and (59) to compute occupied-occupied (OO), occupied-virtual (OV), and virtual-virtual (VV) blocks of Ω .

To obtain the final programmable form of the orbital response equations, we rewrite Eqs. (56), (58)–(60), and (63) by breaking the density matrices to the specific blocks, i.e., OO, OV, VV, etc., and by taking out the separable parts of OPDM and TPDMs from Table I:

$$\begin{aligned}
0 = & \lambda_{ia}(\epsilon_a - \epsilon_i) + \sum_{jk} \langle ik||ja \rangle \lambda_{jk} + \sum_{bc} \langle ib||ac \rangle \lambda_{bc} \\
& + \sum_{jb} (\langle ij||ab \rangle - \langle ib||ja \rangle) \lambda_{jb} + 2(\epsilon_a - \epsilon_i) \gamma_{ia} \\
& - 2 \sum_{jk} \langle ik||ja \rangle \tilde{\gamma}_{jk} - 2 \sum_{jb} \langle ib||ja \rangle \gamma_{jb} + 2 \sum_{jb} \langle ij||ab \rangle \gamma_{jb} \\
& + 2 \sum_{bc} \langle ib||ac \rangle \gamma_{bc} + \sum_{pqr} (\langle ap||qr \rangle \tilde{\Gamma}_{ipqr} - \langle ip||qr \rangle \tilde{\Gamma}_{apqr}),
\end{aligned} \tag{64}$$

$$\begin{aligned}
0 = & \lambda_{ij}(\epsilon_i - \epsilon_j) + 2\tilde{\gamma}_{ij}(\epsilon_i - \epsilon_j) + \sum_{pqr} (\langle ip||qr \rangle \tilde{\Gamma}_{jpqr} \\
& - \langle jp||qr \rangle \tilde{\Gamma}_{ipqr}),
\end{aligned} \tag{65}$$

$$\begin{aligned}
0 = & \lambda_{ab}(\epsilon_a - \epsilon_b) + 2\gamma_{ab}(\epsilon_a - \epsilon_b) + \sum_{pqr} (\langle ap||qr \rangle \tilde{\Gamma}_{bpqr} \\
& - \langle bp||qr \rangle \tilde{\Gamma}_{apqr}),
\end{aligned} \tag{66}$$

$$0 = \omega_{ia} + \frac{1}{2} \epsilon_i \lambda_{ia} + \epsilon_i \gamma_{ia} + \frac{1}{2} \sum_{pqr} \langle ip||qr \rangle \tilde{\Gamma}_{apqr}, \tag{67}$$

$$\begin{aligned}
0 = & \omega_{ij} + \delta_{ij} \epsilon_i + \frac{1}{2} \epsilon_i \lambda_{ij} + \epsilon_i \tilde{\gamma}_{ij} + \frac{1}{2} \sum_{pqr} \langle ip||qr \rangle \tilde{\Gamma}_{jpqr} \\
& + \frac{1}{2} \sum_{ka} (\langle ik||ja \rangle + \langle jk||ia \rangle) \lambda_{ka} + \frac{1}{2} \sum_{kl} \langle ik||jl \rangle \lambda_{kl} \\
& + \frac{1}{2} \sum_{ab} \langle ia||jb \rangle \lambda_{ab} + \sum_{kl} \langle ik||jl \rangle \tilde{\gamma}_{kl} + \sum_{ka} (\langle ik||ja \rangle \\
& + \langle jk||ia \rangle) \gamma_{ka} + \sum_{ab} \langle ia||jb \rangle \gamma_{ab},
\end{aligned} \tag{68}$$

$$0 = \omega_{ab} + \epsilon_a \gamma_{ab} + \frac{1}{2} \epsilon_a \lambda_{ab} + \frac{1}{2} \sum_{pqr} \langle ap||qr \rangle \tilde{\Gamma}_{bpqr}, \tag{69}$$

where $\tilde{\Gamma}_{pqrs}$ denotes nonseparable parts of Γ_{pqrs} , and

$$\begin{aligned}
\sum_{pqr} \langle ap||qr \rangle \tilde{\Gamma}_{ipqr} = & \sum_{jkl} \langle aj||kl \rangle \tilde{\Gamma}_{ijkl} + \sum_{bcd} \langle ab||cd \rangle \Gamma_{ibcd} \\
& + 2 \sum_{jkb} \langle aj||bk \rangle \tilde{\Gamma}_{ijbk} + \sum_{jkb} \langle ab||jk \rangle \tilde{\Gamma}_{ibjk} \\
& + 2 \sum_{jbc} \langle ab||jc \rangle \tilde{\Gamma}_{ibjc} + \sum_{jbc} \langle aj||bc \rangle \Gamma_{ijbc},
\end{aligned} \tag{70}$$

$$\begin{aligned}
\sum_{pqr} \langle ip||qr \rangle \tilde{\Gamma}_{apqr} = & \sum_{jkl} \langle ij||kl \rangle \tilde{\Gamma}_{ajkl} + \sum_{bcd} \langle ib||cd \rangle \Gamma_{abcd} \\
& + 2 \sum_{jkb} \langle ij||bk \rangle \tilde{\Gamma}_{ajbk} + \sum_{jkb} \langle ib||jk \rangle \Gamma_{abjk} \\
& + 2 \sum_{jbc} \langle ib||jc \rangle \tilde{\Gamma}_{abjc} + \sum_{jbc} \langle ij||bc \rangle \Gamma_{ajbc},
\end{aligned} \tag{71}$$

$$\begin{aligned}
\sum_{pqr} \langle ap||qr \rangle \tilde{\Gamma}_{bpqr} = & \sum_{ijk} \langle ai||jk \rangle \tilde{\Gamma}_{bijk} + \sum_{cde} \langle ac||de \rangle \Gamma_{bcde} \\
& + \sum_{ijc} (\langle ac||ij \rangle \Gamma_{bcij} + 2\langle ai||jc \rangle \tilde{\Gamma}_{bijc}) \\
& + \sum_{icd} (\langle ai||cd \rangle \Gamma_{bicd} + 2\langle ac||id \rangle \Gamma_{bcid})
\end{aligned} \tag{72}$$

$$\begin{aligned}
\sum_{pqr} \langle ip||qr \rangle \tilde{\Gamma}_{jpqr} = & \sum_{klm} \langle ik||lm \rangle \tilde{\Gamma}_{jklm} + \sum_{abc} \langle ia||bc \rangle \Gamma_{jabc} \\
& + \sum_{kla} (\langle ia||kl \rangle \tilde{\Gamma}_{jakl} + 2\langle ik||la \rangle \tilde{\Gamma}_{jkla}) \\
& + \sum_{kab} (\langle ik||ab \rangle \Gamma_{jkab} + 2\langle ia||kb \rangle \tilde{\Gamma}_{jabb}).
\end{aligned} \tag{73}$$

Equations (67)–(69) are straightforward to solve w.r.t. ω_{pq} . Equations (65) and (66) are solved only when frozen core or frozen virtual orbitals are present. Then the corresponding λ_{ij} and λ_{ab} are used in Eq. (64) which should be solved iteratively w.r.t. λ_{ia} . In the case of frozen core/virtual orbitals, all DMs from the above equations are defined only within the active space, while the integrals are full space. Thus, Λ and Ω have nonzero terms corresponding to frozen blocks. This is implemented using our general tensor library²⁷ developed for active space CC models.^{28–30}

III. RESULTS AND DISCUSSION

Recently, we presented the EOM-SF-CCSD vertical and adiabatic excitation energies of cyclobutadiene (CB).¹³ The present study employs the EOM-SF-CCSD analytic gradients to characterize equilibrium geometries and transition structures for the four low-lying valence states of CB, and the energy barrier for the interconversion between the two rectangular ground state structures.

Although the electronic structure of CB was subjected to exhaustive theoretical investigations (see Ref. 13 and Refs. 62–86 therein), no fully converged w.r.t. correlation treatment and one-electron basis set optimized geometries and transition structures have yet been reported. The difficulties originate in multiconfigurational character of the low-lying electronic states of CB, including the ground state, which results from the quasidegeneracy (or exact degeneracy at the square geometry) in the π system.^{13,31} Traditionally, this problem was treated by multireference (MR) methods.^{32–39} Due to the large computational costs of MR methods with proper account of dynamical correlation, previously reported

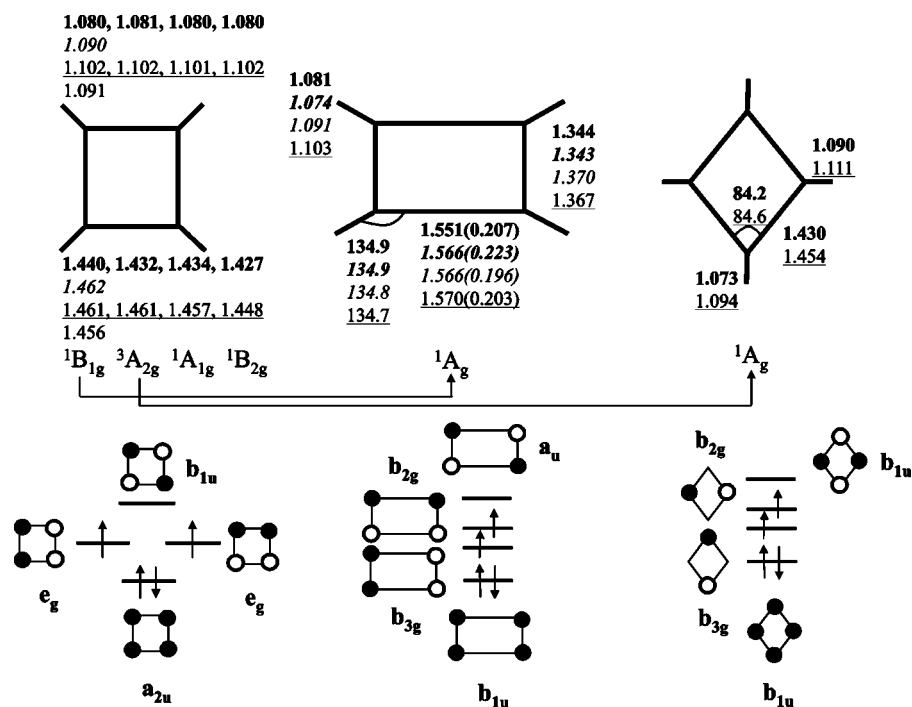


FIG. 1. Optimized geometries and transition structures of the four low-lying valence states of cyclobutadiene. For the square geometry, the values of C–H and C–C bond lengths, in angstroms, for different states are separated by commas. The results are shown for the following methods (from top to bottom): EOM-SF-CCSD/cc-pVTZ(mixed), EOM-SF-CCSD/[3s2p1d/2s], MR-CCSD/[3s2p1d/2s], and MR-BWCCSD/cc-pVDZ. The parameters for the rectangular ground state equilibrium geometry are shown for the following methods (starting from top): EOM-SF-CCSD/cc-pVTZ(mixed), CCSD(T)/cc-pVTZ, EOM-SF-CCSD/[3s2p1d/2s], and MR-CCSD/[3s2p1d/2s]. Only the second closed-shell singlet is stabilized by the rhombic distortion, and the corresponding equilibrium geometries are shown for EOM-SF-CCSD/cc-pVTZ(mixed) (upper number) and MR-CCSD/[3s2p1d/2s] (lower number). On the lower panel, π molecular orbitals and electronic configuration of triplet reference are shown.

results were obtained using relatively small bases. Alternatively, electronic structure of CB and other diradical systems can be described by starting from dication or dianion reference, and treating target states by diagonalizing the coupled-cluster similarity transformed Hamiltonian in the basis of configurations that contain the same number of electrons as the neutral system (EOM-DIP-CC and EOM-DEA-CC methods, respectively).^{40,41} These methods are single reference, and a large basis set can be employed for moderate systems when the CC amplitudes are truncated at double excitations. However, insufficient account of orbital relaxation upon ionization may result in large errors in optimized geometries.⁴² Finally, the EOM-SF-CCSD method provides balanced account of dynamical and nondynamical correlations for all low-lying states of CB (Ref. 13) and can be employed with large one-electron basis sets.

The optimized geometries and transition structures of CB are presented in Fig. 1. Molecular orbital picture for the four states is shown in Fig. 2. The largest basis set we employ is cc-pVTZ on carbon and cc-pVDZ on hydrogen,⁴³ with all orbitals being active. Additional calculation of the optimized geometry for the rectangular ground X^1A_g state with the full cc-pVTZ basis set on both carbon and hydrogen atoms yields at most 0.002 Å difference in the CC bond lengths relative to the mixed basis set.

As the results presented in Fig. 1 demonstrate, the increase in the basis set size leads to more compact structures for all the states considered: C–C bond lengths calculated with cc-pVTZ basis set are 0.02–0.03 Å shorter than those

calculated with the [3s2p1d/2s] basis set employed by Balkova and Bartlett.³⁷ This conclusion is confirmed by the EOM-SF-CCSD/[3s2p1d/2s] geometry optimization for the rectangular and square ground state CB, which gives at most 0.004 Å deviation from MR-CCSD/[3s2p1d/2s] C–C bond lengths.³⁷ Shortening of the equilibrium bond lengths upon increase of the basis set size is due to the increased number of polarization functions, which allows for more ionic character of the bonds.

Another interesting observation is that the multiconfigurational character of the rectangular ground state has small but noticeable effect on the equilibrium C–C bond lengths. Comparison between the CCSD(T) and EOM-SF-CCSD results (see Fig. 1) shows that CCSD(T) gives longer single

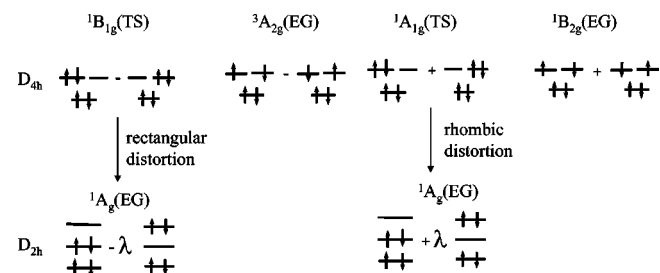


FIG. 2. Electronic configurations of the four low-lying states of CB at the square geometry and their change upon stabilizing distortions. In parentheses, the type of molecular geometry stationary points is indicated for each state: TS stands for a transition structure while EG denotes an equilibrium geometry.

C–C bond (1.566 Å vs 1.551 Å) but almost the same double C–C bond (1.343 Å vs 1.344 Å for EOM-SF-CCSD). This difference indicates that the single reference CCSD(T) method underestimates contribution of the second diradical configuration (see Fig. 2) in the overall wave function, because this configuration is doubly excited with respect to the first one. On the other hand, both configurations are single spin-flipping excitations from high-spin triplet reference and are correlated equally well in EOM-SF-CCSD.

The EOM-SF-CCSD/(cc-pVTZ/cc-pVDZ) energy difference between the optimized rectangular and square ground state structures (the automerization barrier) is 7.6 kcal/mol. This value does not include the zero-point vibrational energy. This result is very close to 7.4 kcal/mol obtained by the extrapolation of the MR-BWCCSD energies in the cc-pVDZ and cc-pVTZ bases to the basis set limit.³⁸

IV. CONCLUSIONS

General theory and programmable expressions for the analytic gradients for the EOM-EE-CCSD and EOM-SF-CCSD models are presented. The Lagrangian approach is employed to derive the orbital and amplitude response equations. The EOM-SF-CCSD analytic gradients are applied to calculate optimized geometries and transition structures of the four lowest valence states of cyclobutadiene. It is demonstrated that CC bond lengths are very sensitive to accurate account of dynamical and nondynamical correlations, and one-electron basis set. The calculated energy barrier for the automerization reaction is 7.6 kcal/mol.

The EOM-SF-CCSD analytic gradients enable quantitatively accurate and computationally affordable analysis of potential energy surfaces of diradicals and triradicals in the ground and low-lying excited states.

APPENDIX

1. Variational properties of the EOM functional

To differentiate the EOM energy functional w.r.t. R and L , we start from Eq. (9):

$$E = \frac{\langle \Phi_0 L | \bar{H} | R \Phi_0 \rangle}{\langle \Phi_0 L | R \Phi_0 \rangle} = \frac{\sum_{\mu=1}^2 L_{\mu} \langle \Phi_{\mu} | \bar{H} | R \Phi_0 \rangle}{\sum_{\mu=1}^2 L_{\mu} \langle \Phi_{\mu} | R \Phi_0 \rangle}. \quad (\text{A1})$$

By differentiating the energy w.r.t. the amplitudes L_{μ} and by using Eq. (9) we obtain

$$\begin{aligned} \frac{\partial E}{\partial L_{\mu}} &= \frac{\langle \Phi_{\mu} | \bar{H} | R \Phi_0 \rangle \langle \Phi_0 L | R \Phi_0 \rangle - \langle \Phi_0 L | \bar{H} | R \Phi_0 \rangle \langle \Phi_{\mu} | R \Phi_0 \rangle}{\langle \Phi_0 L | R \Phi_0 \rangle^2} \\ &= \frac{\langle \Phi_0 L | \bar{H} | R \Phi_0 \rangle - E \langle \Phi_{\mu} | R \Phi_0 \rangle}{\langle \Phi_0 L | R \Phi_0 \rangle} = \frac{\langle \Phi_{\mu} | \bar{H} - E | R \Phi_0 \rangle}{\langle \Phi_0 L | R \Phi_0 \rangle}, \end{aligned} \quad (\text{A2})$$

which is zero because equations for R are satisfied, see Eq. (10). Likewise, $\partial E / \partial R_{\mu} = 0$ by virtue of Eq. (11).

2. Derivation of orbital response equations

By combining Eqs. (52) and (53), we arrive at the following equation:

$$\begin{aligned} \sum_{\mu} C_{\mu\mu} \frac{\partial \mathcal{L}}{\partial C_{\mu t}} &= \sum_{pq} \left(\sum_{\mu} C_{\mu\mu} \frac{\partial h_{pq}}{\partial C_{\mu t}} \right) \gamma_{pq} \\ &+ \frac{1}{4} \sum_{pqrs} \left(\sum_{\mu} C_{\mu\mu} \frac{\partial \langle pq || rs \rangle}{\partial C_{\mu t}} \right) \Gamma_{pqrs} \\ &+ \frac{1}{2} \sum_{pq} \lambda_{pq} \left(\sum_{\mu} C_{\mu\mu} \frac{\partial f_{pq}}{\partial C_{\mu t}} \right) \\ &+ \sum_{pq} \omega_{pq} \left(\sum_{\mu} C_{\mu\mu} \frac{\partial S_{pq}}{\partial C_{\mu t}} \right). \end{aligned} \quad (\text{A3})$$

Thus, the evaluation of the derivative requires differentiation of the Hamiltonian and overlap matrix elements with respect to C , followed by contraction with C . The one-particle integral term is²⁸

$$\begin{aligned} \sum_{\mu} C_{\mu\mu} \frac{\partial h_{pq}}{\partial C_{\mu t}} &= \sum_{\mu} C_{\mu\mu} \frac{\partial (\sum_{\nu\lambda} C_{\nu p} h_{\nu\lambda} C_{\lambda q})}{\partial C_{\mu t}} \\ &= \sum_{\mu} C_{\mu\mu} (\delta_{pt} \sum_{\lambda} C_{\lambda q} h_{\mu\lambda} + \delta_{qt} \sum_{\nu} C_{\nu p} h_{\nu\mu}) \\ &= \delta_{pt} h_{uq} + \delta_{qt} h_{pu}. \end{aligned} \quad (\text{A4})$$

Similarly, the two-electron part yields:

$$\begin{aligned} \sum_{\mu} C_{\mu\mu} \frac{\partial \langle pq || rs \rangle}{\partial C_{\mu t}} &= \delta_{pt} \langle uq || rs \rangle + \delta_{qt} \langle pu || rs \rangle + \delta_{rt} \langle pq || us \rangle \\ &+ \delta_{st} \langle pq || ru \rangle. \end{aligned} \quad (\text{A5})$$

The Fock matrix derivatives are

$$\sum_{\mu} C_{\mu\mu} \frac{\partial f_{pq}}{\partial C_{\mu i}} = \delta_{ip} f_{uq} + \delta_{iq} f_{pu} + \langle pu || qi \rangle + \langle pi || qu \rangle, \quad (\text{A6})$$

$$\sum_{\mu} C_{\mu\mu} \frac{\partial f_{pq}}{\partial C_{\mu a}} = \delta_{ap} f_{uq} + \delta_{aq} f_{pu}. \quad (\text{A7})$$

And, finally, the overlap term is

$$\sum_{\mu} C_{\mu\mu} \frac{\partial S_{pq}}{\partial C_{\mu t}} = \delta_{pt} S_{uq} + \delta_{qt} S_{pu}. \quad (\text{A8})$$

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