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Equation-of-motion spin-flip coupled-cluster model with single and double substitutions: Theory and application to cyclobutadiene

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While the equation-of-motion coupled-cluster (EOM-CC) method is capable of describing certain multiconfigurational wave functions within a single-reference framework (e.g., open-shell type excited states, doublet radicals, etc.), it may fail in cases of more extensive degeneracy, e.g., bond breaking and polyradicals. This work presents an extension of the EOM-CC approach to these chemically important situations. In our approach, target multiconfigurational wave functions are described as spin-flipping excitations from the high-spin reference state. This enables a balanced treatment of nearly degenerate electronic configurations present in the target low-spin wave functions. The relations between the traditional spin-conserving EOM models and the EOM spin-flip method is discussed. The presentation of the formalism emphasizes the variational properties of the theory and shows that the killer condition is rigorously satisfied in single-reference EOM-CC theories. The capabilities and advantages of the new approach are demonstrated by its application to cyclobutadiene. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1630018]

I. INTRODUCTION

The equation-of-motion (EOM) formalism is one of the approaches used in quantum mechanics for the direct calculation of energy differences rather than total energies.[1] It is always energy differences between the states of the system which are observed experimentally. Chemistry and spectroscopy are often concerned about energy differences that are many orders of magnitude smaller than total energies. This is the crux of a major challenge faced by the electronic structure theory—tiny errors in total energies may result in very large errors in energy differences. For example, 1 percent of the ethylene total energy is about 21 eV, which exceeds even the ionization potential of the molecule! That is why EOM as well as other approaches formulated for energy differences (e.g., electron propagator or Green function, and response techniques) are potentially more accurate than approximate methods of the similar complexity formulated for the states' total energies. However, this potential can be fulfilled only if the realization ensures a balanced treatment of the states of interest.

Different formalisms often yield very similar working equations[1]—for example, the linear response coupled-cluster (CC) model[2–4] is identical to EOM-CC.[2,5–10] However, each of the approaches offers certain advantages. The most appealing property of the linear response formalism is that it mimics optical spectroscopy, e.g., an excited state energy is obtained as a pole of the first-order response function.[4,11] The strength of EOM theory is that it makes a very clear distinction between the reference and target states. In the context of coupled-cluster methods, this freedom in the reference state choice has enabled extension of EOM-CC models from treating electronically excited closed-shell molecules towards ionized and open-shell systems[12–15] (for detailed reviews, see Refs. 16, 17).

The focus of this work is on the EOM spin-flip (SF) CC model, which targets bond breaking, diradicals, and triradicals. The next section reviews the general EOM formalism and explains the importance of the reference state choice. Our derivation of EOM-CC emphasizes the variational properties of the theory and does not invoke the projective approach. We demonstrate for the first time that the killer condition is rigorously satisfied in single-reference EOM-CC theories, although, in Surján terms, "for the wrong reason."[18] The presentation employs operator algebra—see Refs. 19, 20 for a very compact and practical summary. The general formalism is followed by the presentation of working equations and the implementation of the EOM-SF-CC model with single and double excitations (EOM-SF-CCSD). Section III presents application of the new method to cyclobutadiene. Concluding remarks are given in Sec. IV.

II. THEORY

A. Equation-of-motion formalism

Consider a general (not necessarily Hermitian) operator $\bar{H}$ and two of its eigenstates, $|0\rangle$ and $|f\rangle$, with eigenvalues E_0 and E_f, respectively

$$\bar{H}|0\rangle = E_0|0\rangle, \tag{1}$$

$$\bar{H}|f\rangle = E_f|f\rangle. \tag{2}$$

For a non-Hermitian operator, bra eigenstates are not Hermitian conjugates of ket eigenstates: $\langle k| \neq (|k\rangle)^+$). Moreover, neither bra nor ket eigenstates form an orthonormal set. However, bra's and ket's form a biorthogonal set, $\langle k|l\rangle = \delta_{kl}$, provided that the corresponding eigenvalues are non-

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zero. A general excitation operator $R(f)$ is defined such that it promotes a system from the initial (or reference) state $|0\rangle$ into the final state $|f\rangle$

$$R(f)|0\rangle=|f\rangle. \tag{3}$$

No assumptions are made about the nature of the initial and final states: they can be the ground and electronically excited states (or any two electronic states) of an N-electron system, or states of an N-electron and an ionized or detached system, etc. It is convenient to represent the excitation operator R from Eq. (3) by the following bra-ket form:

$$R(f)\equiv|f\rangle\langle 0|. \tag{4}$$

The so-defined operator is of rank one[21] and can act on any reference state $|\tilde{0}\rangle$

$$R(f)|\tilde{0}\rangle=|f\rangle\langle 0|\tilde{0}\rangle. \tag{5}$$

Therefore, for any state $|\tilde{0}\rangle$ which has a nonzero overlap with the exact reference state $\langle 0|$

$$[\bar{H},R(f)]|\tilde{0}\rangle=\omega_{0f}R(f)|\tilde{0}\rangle, \tag{6}$$

where $[\bar{H},R(f)]=\bar{H}R(f)-R(f)\bar{H}$, and $\omega_{0f}=E_f-E_0$. The above equation shows that if no approximations have been made for the excitation operator $R(f)$, the exact energy difference ω_{0f} can be computed without an explicit calculation of the initial and final states.

By introducing the de-excitation operator[22] $L(f)=|0\rangle\langle f|$, the transition energy ω_{0f} can be written as a general expectation value of the non-Hermitian operator $\bar{H}$

$$\omega_{0f}=\frac{\langle\tilde{0}|L(f)[\bar{H},R(f)]|\tilde{0}\rangle}{\langle\tilde{0}|L(f)R(f)|\tilde{0}\rangle}. \tag{7}$$

In expression (7) (as well as in the subsequent presentation), the bra reference state $\langle\tilde{0}|$ can be chosen to be a Hermitian conjugate of the ket reference state. Form (7) provides a useful functional whose stationary values will coincide with the eigenvalues of (6) when operator $R(f)$ is represented in a complete operator basis set. However, the corresponding ω's do not provide upper bounds of the exact energy differences, even when a Hermitian operator (i.e., the bare Hamiltonian H) is used in Eq. (7), and the de-excitation operator is a Hermitian conjugate of the excitation operator (in this case the corresponding total energies are upper bounds of the exact total energies given that a linear parametrization of the excitation operator $R(f)$ is used[23]).

Alternatively, one can consider functionals based on the so-called commutator metric[1,19,20]

$$\omega_{0f}=\frac{\langle\tilde{0}|[L(f),[\bar{H},R(f)]]_{\pm}|\tilde{0}\rangle}{\langle\tilde{0}|[L(f),R(f)]_{\pm}|\tilde{0}\rangle}. \tag{8}$$

All three functionals yield identical results in the complete operator basis set limit, or when the so-called killer condition is satisfied[1]

$$L(f)|\tilde{0}\rangle=0. \tag{9}$$

The killer condition means that the reference state $|\tilde{0}\rangle$ cannot be de-excited (i.e., that the reference can be regarded as a vacuum). Alternatively, (9) can be interpreted as orthogonality of the reference and final states

$$L(f)|\tilde{0}\rangle=|0\rangle\langle f|\tilde{0}\rangle=0. \tag{10}$$

Note that the killer condition (10) is satisfied when the exact initial state is used as the reference, and the operator basis is complete with respect to the final states. Another simple case when the killer condition is easily satisfied is when the single Slater determinant is used as the reference $|\tilde{0}\rangle$, and the operator L is pure de-excitation operators with respect to the reference $|\tilde{0}\rangle$ (i.e., does not annihilate electrons from the occupied orbitals and does not create electrons in the virtual orbitals). For an excellent presentation of the different derivations of the EOM equations, and the role of the killer condition, see the recent work of Surján and co-workers.[18]

One of the disturbing consequences of the violation of killer condition is that functionals (7) and (8) become nonequivalent. Indeed, which of the three functionals should be employed in the derivation of working equations? All of them give the exact result in the limit of the complete operator basis set; however, the choice between them in the case of an approximate theory is rather arbitrary.

At this point, we depart from the textbook EOM presentation.[1] Instead of general excitation operators $R(f),L^{+}(f)$ which generate the *exact* final state $|f\rangle$ when acting on *any* reference state provided that $\langle 0|\tilde{0}\rangle\neq 0$, we introduce less general operators $\tilde{R}(f),\tilde{L}^{+}(f)$ defined with respect to the specific reference $|\tilde{0}\rangle$

$$\begin{aligned}\tilde{R}(f)&=|f\rangle\langle\tilde{0}|,\\ \tilde{L}(f)&=|\tilde{0}\rangle\langle f|.\end{aligned} \tag{11}$$

Unlike $R(f)$, $\tilde{R}(f)$ will not yield the exact final state when acting on a state $|g\rangle$ with nonzero overlap with $|0\rangle$ if $\langle\tilde{0}|g\rangle=0$: $\tilde{R}(f)|g\rangle=|f\rangle\langle\tilde{0}|g\rangle=0$. Because commutator equation (6) is no longer valid for $\tilde{R}$ (unless, of course, the reference $|\tilde{0}\rangle$ happens to be the exact eigenstate $|0\rangle$), functionals (7) and (8) will not yield the exact ω_{0f} even when the operators $\tilde{R}(f),\tilde{L}^{+}(f)$ are expanded over the complete basis. However, the *difference* between the resulting ω_{0f} and the exact one assumes the same constant value for all the target states $|f\rangle$.[24] Therefore, for an arbitrary reference $|\tilde{0}\rangle$, the exact energy gap between any two target states $|f\rangle$ and $|i\rangle$ will be retrieved from functionals (7) and (8) in the limit when the operators $\tilde{R}(f),\tilde{L}^{+}(f)$ are expanded over the complete basis.

In practice, excitation and de-excitation operators are expanded over a finite basis set. In the case of a linear parametrization, it is convenient to expand the excitation and de-excitation operators over a set of operators ρ_k and λ_k

$$\tilde{R}(f)=\sum_k r_k^f\rho_k, \tag{12}$$

$$\tilde{L}(f)=\sum_k l_k^f \lambda_k . \tag{13}$$

When acting on the reference $|\tilde{0}\rangle$, these operators generate a biorthogonal set of basis functions

$$\rho_k|\tilde{0}\rangle=|\tilde{k}\rangle, \tag{14}$$

$$\langle\tilde{0}|\lambda_l=\langle\tilde{l}|, \tag{15}$$

$$\langle\tilde{l}|\tilde{k}\rangle=\delta_{lk}, \quad \langle\tilde{k}|\neq(|\tilde{k}\rangle)^+. \tag{16}$$

The completeness of the operator basis set $\{\rho_k,\lambda_l\}$ is derived from the completeness of the Hilbert space $\{|\tilde{k}\rangle,\langle\tilde{l}|\}$. Note that only the completeness with respect to the target states $|f\rangle$ is required for the EOM functionals to yield the exact energy differences between the target states, while the Hilbert space can be incomplete with respect to other groups of eigenstates, provided that the target states are not interacting across the Hamiltonian with these groups (e.g., states of different point group or spin symmetry, or with different number of electrons).

It is convenient (although not necessary) to choose operators ρ_k,λ_k to be of rank one

$$\begin{aligned}\rho_k&=|\tilde{k}\rangle\langle\tilde{0}|,\\ \lambda_k&=|\tilde{0}\rangle\langle\tilde{l}|.\end{aligned} \tag{17}$$

By considering the first variation of functional (7) with respect to the right $\tilde{R}$ and left $\tilde{L}$ vectors, and by assuming that variations $\delta\tilde{R}$ and $\delta\tilde{L}$ are independent (see Ref. 20 for the discussion of bivariational principle, an extension of variational principle to the case of non-Hermitian Hamiltonians), we arrive at a non-Hermitian secular problem for the expansion coefficients $\{r_k\}$ and $\{l_k\}$

$$(\bar{H}-E_0)\boldsymbol{R}=\boldsymbol{R}\boldsymbol{\Omega}, \tag{18}$$

$$\boldsymbol{L}(\bar{H}-E_0)=\boldsymbol{\Omega}\boldsymbol{L}, \tag{19}$$

$$E_0=\langle\tilde{0}|\bar{H}|\tilde{0}\rangle, \tag{20}$$

where matrices $\boldsymbol{R}$ and $\boldsymbol{L}$ are constructed from the expansion coefficients (12) and (13), e.g., $\boldsymbol{R}_{if}=r_i^f$; diagonal matrix $\boldsymbol{\Omega}$ contains the transition energies: $\boldsymbol{\Omega}_{kk}=\omega_{0k}$; and $\bar{\boldsymbol{H}}$ is the matrix of the Hamiltonian operator $\bar{H}$ in the basis of (14) and (15): $\bar{\boldsymbol{H}}_{lk}=\langle\tilde{l}|\bar{H}|\tilde{k}\rangle$.

At this point, we can discuss choices of the reference $|\tilde{0}\rangle$, the Hamiltonian $\bar{H}$, and the operator basis ρ_k,λ_k. The first applications of the EOM formalism used the bare Hamiltonian H, and employed correlated (e.g., multireference) wave functions as the reference state $|\tilde{0}\rangle$.[25,26] By analogy, the first applications of the EOM formalism to the CC models also used the bare Hamiltonian (e.g., see Ref. 2 and references therein), and the CC wave function[27,28] as the reference $|\tilde{0}\rangle$. In this approach, the killer condition (9) is not satisfied. Moreover, a straightforward application of functional (7) *does not yield* EOM-CC equations even if one replaces the bra reference by $\langle\Phi_0|\exp(-T)$ as opposed to $\langle\Phi_0|\exp(T^+)$. That is why a projective approach has been traditionally used to derive the EOM equations,[29,2,6] although variational properties of the EOM-CC theory have been recognized.[6,7]

Alternatively, in a single-reference coupled-cluster EOM theory, one can consider a single Slater determinant $|\Phi_0\rangle$ as the reference state $|\tilde{0}\rangle$ which greatly simplifies the choice of the excitation operators $\tilde{R},\tilde{L}^+$,[30] and easily satisfies the killer condition (9). Correlation effects are folded in $\bar{H}$ through the similarity transformation[31]

$$\bar{H}\equiv e^{-T}He^T, \tag{21}$$

$$T=T_1+\cdots+T_m, \tag{22}$$

where T_k are k-fold excitations from $|\Phi_0\rangle$. Regardless of the nature of T, similarity transformation does not change the eigenvalues of the Hamiltonian—therefore stationary values of functionals (7)–(8) yield exact energy differences between the target states when the excitation operators $\tilde{R},\tilde{L}^+$ are expanded over the complete operator basis set. However, the exact ω_{0f} can only be obtained when both the operator set is complete and $|\tilde{0}\rangle\equiv|0\rangle$. The latter can be achieved by an appropriate choice of T from the similarity transformation, i.e., when T is not truncated and satisfies the CC equations for the reference $|\tilde{0}\rangle$, the single determinant $|\tilde{0}\rangle$ becomes an eigenstate of $\bar{H}$.

Even in the case of the exact $\tilde{R}$, $\tilde{L}^+$, and $|\tilde{0}\rangle$, the corresponding left and right eigenvectors of $\bar{H}$ are not Hermitian conjugates. Eigenstates of the bare Hamiltonian H can be obtained from the eigenstates of $\bar{H}$ as follows:

$$|\Psi\rangle=\tilde{\mathrm{R}}\mathrm{e}^T|\Phi_0\rangle. \tag{23}$$

In the EOM-CC approach, amplitudes T are defined by the coupled-cluster equations[27,28,32] for the reference state

$$E_{\mathrm{CC}}=\langle\Phi_0|\bar{H}|\Phi_0\rangle, \tag{24}$$

$$\langle\Phi_i^a|\bar{H}|\Phi_0\rangle=0, \quad \langle\Phi_{ij}^{ab}|\bar{H}|\Phi_0\rangle=0, \quad \cdots, \tag{25}$$

where E_{CC} is the total coupled-cluster energy for the reference state, and the so-called projective equations (25) define amplitudes of the cluster operators T_k. Usually[2,6,10] but not necessarily,[33] the cluster operator T is truncated at the same level as the EOM operators $\tilde{R}$ and $\tilde{L}^+$. When this is the case, or when T is truncated at the higher excitation level than $\tilde{R}$, the reference determinant $|\Phi_0\rangle$ is an eigenstate of $\bar{H}$ in the subspace of up to n-tuple excited determinants, the corresponding eigenvalue being E_{CC} from Eq. (24).

B. Choice of the reference state

A subtle issue for discussion is the choice of the reference state $|\tilde{0}\rangle$. Formally, any reference state can be used in Eqs. (6)–(8) without affecting the ability of the theory to converge to the exact answer (for the energy differences between the target states). However, as can be seen from Eqs. (14) and (15), the operator basis sets $\{\rho_k\}$ and $\{\lambda_k\}$ are defined with respect to the reference state. The quality of the operator basis set can be judged by the quality of the basis of many-electron basis functions which are generated by the

basis operators from the reference [see Eqs. (14) and (15)]. Therefore, the choice of the reference is directly related to the choice of the operator basis: *for different references, the same ansatz for the excitation operators*[30] *would result in a different set of many-electron basis functions*. Thus, one can consider the reference as one of the model's parameters subject for optimization. Unlike many state-by-state approaches where the reference is chosen such that it serves as the best zero-order wave function for the state of interest, the optimal reference in EOM is the one which results in the most balanced description of the EOM target states. Moreover, when one is interested in a single target state (e.g., the ground state of a molecule), the optimal reference is not necessarily the one which has the largest overlap with the target state's wave function, but rather the one which produces a more flexible and balanced set of many-electron basis functions.

One of the most popular applications of the EOM-CC theory is for calculating electronic excitation energies (EOM-EE).[5–10] The optimal reference for EOM-EE is often the closed-shell ground-state Hartree–Fock determinant, and operators $\tilde{R}$ and $\tilde{L}$ conserve the number of α and β electrons

$$R_1^{\mathrm{EE}}=\sum_{ia} r_i^a a^+ i,$$

$$L_1^{\mathrm{EE}}=\sum_{ia} l_i^a i^+ a,$$

$$\cdots. \tag{26}$$

Note that open-shell excited states whose zero-order description requires two-determinantal wave functions are well described by single-reference EOM models.[16] Identical equations can be derived within the linear response formalism.[2–4,34,35] The EOM-EE-CC excitation energies become exact when both the EOM operators $\tilde{R}$, $\tilde{L}$, and the operator T from the similarity transformation include up to n-tuple excitations, and T satisfies CC equations (25). Interestingly enough, accurate values of the excitation energies can be obtained with *different* truncation levels in $\tilde{R},\tilde{L}$, and T, with higher excitations being more important in the EOM part.[33]

More general excitations can change the number of electrons in the system. In order to calculate transition energies of such processes (i.e., ionization potentials or electron affinities), the EOM-IP or EOM-EA methods can be used.[12,13] The reference states for EOM-IP/EA are determinants for $N+1/N-1$ electron states, whereas the final states are N-electron ones. Another class of less obvious but very successful applications of the EOM-IP/EA methods is not concerned with electron ionization or attachment processes, but rather targets ground and excited states of problematic neutral systems. In these applications, an $N-1$ or $N+1$ electron reference state is used in order to generate a balanced set of configurations needed for a target N-electron system. For example, to avoid the troublesome symmetry breaking in doublet radicals (or to obtain spin-pure wave functions), EOM-IP/EA methods have been successfully applied.[12,36] In these models, the reference determinant is chosen to represent a *closed-shell* cation or anion, and the EOM operators $\tilde{R}$ and $\tilde{L}$ do not conserve the number of electrons.[12,13,37]

$$R_1^{\mathrm{IP}}=\sum_i r_i i,$$

$$R_1^{\mathrm{EA}}=\sum_a r_a a^+, \tag{27}$$

$$\cdots.$$

While EOM-IP/EA-CC yield the exact IP/EA only under the same conditions as EOM-EE-CC, the exact description of the target (ionized or attached) states can be achieved with only the EOM operators being expanded over the complete basis. For example, the EOM-IP-CC description of the lithium atom will be exact even with $T=0$, provided that $\tilde{R},\tilde{L}^+$ include up to triple electron excitations, e.g.,

$$\tilde{R}^{\mathrm{IP}}=\sum_i r_i i+\sum_{ija} r_{ij}^a a^+ ij+\tfrac{1}{4}\sum_{ijkab} r_{ijk}^{ab} a^+ b^+ jik + \tfrac{1}{6}\sum_{ijklabc} r_{ijkl}^{abc} a^+ b^+ c^+ kjil. \tag{28}$$

Doubly ionized/attached EOM models which target diradicals have also been presented[14]

$$R_1^{\mathrm{DIP}}=\sum_{ij} r_{ij} ji,$$

$$R_1^{\mathrm{DEA}}=\sum_{ab} r_{ab} a^+ b^+, \tag{29}$$

$$\cdots.$$

Similar approaches have been used in conjunction with propagator techniques.[38–42]

Last, in cases where target states are multiconfigurational due to orbital degeneracies, a high-spin reference state can be chosen. To obtain target low-spin states, the EOM operators $\tilde{R}$ and $\tilde{L}$ should include spin-flip (EOM-SF models)[15,43–46] So far, models based on a high-spin triplet and quartet references have been implemented and benchmarked;[15,43–49] however, extensions of the SF approach to the higher spin references are also very promising. An attractive feature of the triplet and quartet reference-based EOM-SF models is that only a single spin-flip is required to obtain target $M_s=0/M_s=\frac{1}{2}$ states. That is why the corresponding EOM-SF equations in a spin–orbital form are identical to those of the non-SF EOM theories. The following SF models have been implemented and benchmarked:[15,43–49] (i) the SF models based on the Hartree–Fock reference wave function, i.e., SF configuration interaction singles (SF-CIS), spin-complete SF-CIS, and SF-CI model with single and double substitutions (SF-CISD); (ii) the perturbatively corrected SF-CIS model, SF-CIS(D); (iii) the SF optimized orbitals CCD model (EOM-SF-OOCCD, or EOM-SF-OD). Recently, the SF variant of density functional theory has been introduced.[46] In this work, we introduce the EOM-SF-CCSD model. As in the non-SF ground[50] and excited[51] states variants, EOM-CCSD performs very similarly to EOM-OD.

Computationally, however, EOM-CCSD is more efficient since it does not involve integral transformation at each CC iteration.

C. EOM-SF-CCSD model

This work considers EOM-CCSD models in which T, $\tilde{R}$, and $\tilde{L}^+$ are truncated to the single and double excitations, and operators $\tilde{R}$ and $\tilde{L}^+$ conserve the total number of electrons in the system. Thus, the transformed Hamiltonian (21) is diagonalized in the subspace of the reference determinant (O), and the determinants generated by single (S) and double (D) electron excitations from the reference. Relative to the reference, all possible singly excited determinants can be divided into the three groups: (i) those which are generated by the $\alpha\rightarrow\alpha$ and $\beta\rightarrow\beta$ excitations, and thus having the same number of α and β electrons as the reference, i.e. (N_α,N_β); (ii) those which are generated by the $\alpha\rightarrow\beta$ excitations—these have one α-electron less and one β-electron more than the reference, i.e. $(N_\alpha-1,N_\beta+1)$; (iii) those which are generated by the $\beta\rightarrow\alpha$ excitations—these have one β-electron less and one α-electron more than the reference, i.e. $(N_\alpha+1,N_\beta-1)$. Likewise, one can split the R_1 operator into the three components: $M_s=0$, $M_s=-1$, and $M_s=+1$, respectively. In a similar fashion, doubly excited determinants (and, respectively, the R_2 operator) can be divided into the following groups: $(N_\alpha,N_\beta)/M_s=0$, $(N_\alpha-1,N_\beta+1)/M_s=-1$, $(N_\alpha+1,N_\beta-1)/M_s=+1$, $(N_\alpha-2,N_\beta+2)/M_s=-2$, $(N_\alpha+2,N_\beta-2)/M_s=+2$. The M_s of the corresponding determinants is defined by the M_s of the excitation operator $\tilde{R}$ and the M_s of the reference determinant and is simply their sum. For example, when the $M_s=0$ reference is used, the M_s of the excitation operator $\tilde{R}$ is equal to the M_s of the determinants generated by $\tilde{R}$ acting on the reference.

Since the nonrelativistic Hamiltonian H does not include spin, the matrix of $\bar{H}$ is block diagonal in the basis of the so-generated determinants. Therefore, one can diagonalize each M_s block of $\bar{H}$ independently. In the traditional implementation of EOM-CCSD, only the $M_s=0$ block is diagonalized, which yields singlets and $M_s=0$ components of triplet states (in the case of a singlet reference state).[52]

In the SF variant of EOM-CCSD, we consider spin-flipping (e.g., $M_s=1$ or $M_s=-1$) parts of $\tilde{R}$. In the case of a singlet reference, the diagonalization of the $M_s=\pm1$ blocks yields $M_s=\pm1$ components of triplet states which are exactly degenerate with the $M_s=0$ counterparts calculated by the traditional approach outlined above.[53] However, when the high spin $M_s=1$ triplet reference is used, the $M_s=-1$ excitations yield the $M_s=0$ determinants. Therefore, the diagonalization of $\bar{H}$ produces $M_s=0$ final states (both singlets and triplets).

In the basis of the reference, and the singly and doubly excited determinants, $\bar{H}$ assumes the following form:

$$\bar{H}=\begin{pmatrix} E_{\mathrm{CC}} & \bar{H}_{\mathrm{OS}} & \bar{H}_{\mathrm{OD}} \\ 0 & \bar{H}_{\mathrm{SS}} & \bar{H}_{\mathrm{SD}} \\ 0 & \bar{H}_{\mathrm{DS}} & \bar{H}_{\mathrm{DD}} \end{pmatrix}, \tag{30}$$

where E_{CC} is the reference CC energy from Eq. (24), and $\bar{H}_{\mathrm{SO}}=\bar{H}_{\mathrm{DO}}=0$ due to Eq. (25). It immediately follows from Eq. (30) that: (i) the reference CCSD wave function is an eigenvector of $\bar{H}$ with $R_0=\hat{1}$ and $R_1=R_2=0$, the corresponding eigenvalue being E_{CC}; (ii) the reference state left eigenvector has $L_0=\hat{1}$, and all other left eigenvectors have $L_0=0$ due to the biorthogonality condition. Since right eigenvectors do not form an orthonormal set, the reference also can be present in final EOM states (i.e, $R_0=r_0\hat{1}$, $r_0\neq0$). However, excitation energies can be calculated by diagonalizing $\bar{H}$ in the basis of single and double excitations only.[7] Values of the so-calculated R_1 and R_2 define the weight of the reference determinant in the right EOM-CC eigenvector

$$r_0=\frac{1}{\omega}(\bar{H}_{\mathrm{OS}}R_1+\bar{H}_{\mathrm{OD}}R_2). \tag{31}$$

Alternatively, r_0 can be calculated from the biorthogonality condition by using the reference state left eigenvector (also known as the Z- or Λ-vector from the CC gradient theory)

$$r_0=-(Z_1\cdot R_1+Z_2\cdot R_2). \tag{32}$$

In the SF variant (when the reference and excited determinants have a different number of α and β electrons), the reference is not present in final EOM states (i.e., $r_0=0$ for all the EOM-SF states).

After subtracting the reference energy from $\bar{H}$, the EOM-CCSD left and right eigenproblem reads as follows:

$$\begin{pmatrix} \bar{H}_{\mathrm{SS}}-E_{\mathrm{CC}} & \bar{H}_{\mathrm{SD}} \\ \bar{H}_{\mathrm{DS}} & \bar{H}_{\mathrm{DD}}-E_{\mathrm{CC}} \end{pmatrix}\begin{pmatrix} R_1 \\ R_2 \end{pmatrix}=\omega\begin{pmatrix} R_1 \\ R_2 \end{pmatrix}, \tag{33}$$

$$(L_1\ \ L_2)\begin{pmatrix} \bar{H}_{\mathrm{SS}}-E_{\mathrm{CC}} & \bar{H}_{\mathrm{SD}} \\ \bar{H}_{\mathrm{DS}} & \bar{H}_{\mathrm{DD}}-E_{\mathrm{CC}} \end{pmatrix}=\omega(L_1\ \ L_2), \tag{34}$$

where ω is the energy difference relative the reference state: $\omega=E-E_{\mathrm{CC}}$. We present working equations and discuss details of the implementation in the Appendix.

III. RESULTS AND DISCUSSION

In the first set of benchmark calculations, we compared EOM-SF-CCSD against EOM-SF-OD. As in the non-SF variant, the performance of the SF-CCSD model is very similar to that of SF-OD. We compared both models by using some of the benchmark systems from Ref. 47. We have found that differences in equilibrium geometries and frequencies do not exceed 10^{-4} Å and 10 cm^{-1}, respectively. Differences in excitation energies are about thousandths of eV.

In order to demonstrate capabilities and advantages of the SF-CCSD model, we apply it to calculate vertical and adiabatic electronic excitation energies in cyclobutadiene. As explained below, the degree of orbital degeneracy and, consequently, the character of the low-lying valence states of cyclobutadiene depend strongly on nuclear positions—while at the lowest triplet state equilibrium geometry the lowest singlet state is two-configurational, it becomes predominantly single-configurational at its own equilibrium geom-

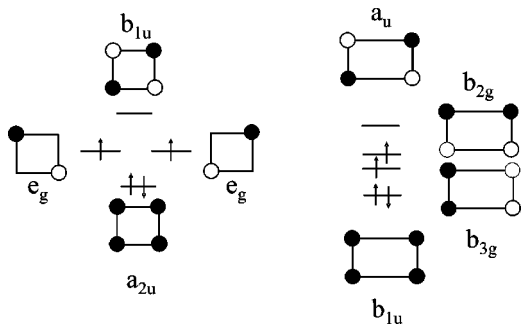

FIG. 1. Molecular π-orbitals derived from carbons' p orbitals at the $1\,^3A_{2g}$ equilibrium geometry (left panel), and at the $X\,^1A_g$ equilibrium geometry (right panel). Electronic configuration of the triplet state is shown.

etry. We will demonstrate that although advanced single reference techniques (e.g., EOM-EE-CCSD) give reasonable description of the cyclobutadiene excited states in the latter case, they fail in the former. EOM-SF-CCSD, however, treats both limits well, and therefore yields accurate results for both vertical and adiabatic energies.

Calculations are performed using the Q-CHEM[54] *ab initio* package, to which our programs for the EOM-SF-CCSD and EOM-EE-CCSD methods are linked. Additional results are obtained using the ACES II *ab initio* program.[55] Most of the calculations are performed in the cc-pVTZ basis set.[56] The performance of the less expensive basis set composed of the cc-pVTZ basis on carbon atoms and cc-pVDZ on hydrogens is also investigated. Equilibrium geometries of the $X\,^1A_g$ ground state and the $1\,^3A_{2g}$ excited state are optimized by the CCSD(T)[57] and SF-DFT[46,58] methods. Vertical and adiabatic excitation energies are calculated at these geometries. All electrons are active in the CCSD(T) and the EOM-CCSD calculations. Both UHF and ROHF references are used in the EOM-SF-CCSD calculations.

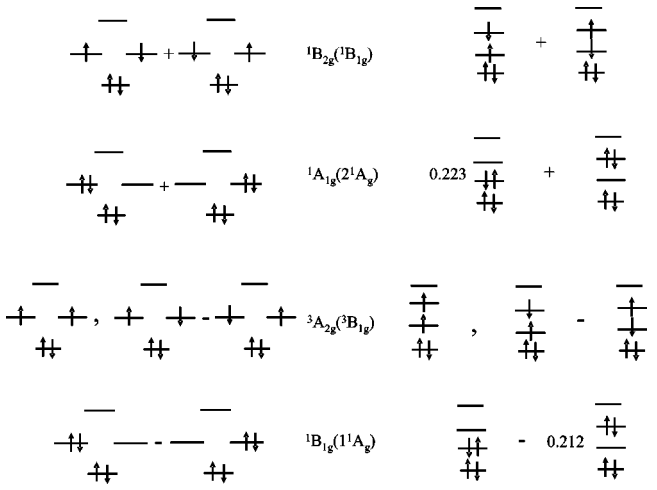

FIG. 2. Leading electronic configurations in the EOM-SF-CCSD wave functions of the valence states of cyclobutadiene at the square (left panel) and rectangular (right panel) geometries. For the D_{4h} geometries (left panel), D_{2h} symmetry labels are given in parentheses.

TABLE I. Optimized geometries of the rectangular ground $X\,^1A_g$ state of cyclobutadiene. The bond length alternation, Δ_{CC}, is also shown. Bond lengths are in angstrom, angles in degrees.

	C–C	C=C	Δ_{CC}	CH	HCC[a]
SCF/cc-pVDZ[b]	1.569	1.323	0.25	1.079	134.9
B3LYP/cc-pVDZ[c]	1.581	1.339	0.24	1.090	134.9
CCSD/[3s2p1d/2s][d]	1.609	1.383	0.23	1.092	134.6
CCSD(T)/cc-pVDZ[b]	1.583	1.364	0.22	1.095	134.9
MCSCF/6-31G[e]	1.553	1.366	0.22	1.068	134.8
MPJ5(GVB)/cc-pVDZ[c]	1.580	1.336	0.24	1.068	134.9
MR-CCSD/[3s2p1d/1s][f]	1.570	1.367	0.20	1.103	134.7
SF-DFT/6-311G**[g]	1.56	1.33	0.23	1.07	134.9
CCSD(T)/cc-pVTZ[g]	1.566	1.343	0.22	1.074	134.9

[a]The angle between the CH bond and the longer CC bond.
[b]References 85, 86.
[c]Reference 86.
[d]This work, basis from Ref. 77.
[e]CAS within the π system, Ref. 78.
[f]Reference 82.
[g]This work, see also Fig. 3.

A. Molecular orbitals and low-lying valence states of cyclobutadiene

Figure 1 shows the π system of cyclobutadiene—molecular orbitals derived from the four atomic p_z orbitals of carbons (Z axis is perpendicular to the molecular plane). At the square (D_{4h}) geometry (Fig. 1, left panel), two of the four π orbitals are exactly degenerate. This degeneracy is lifted by a rectangular distortion (Fig. 1, right panel). The leading electronic configurations of the lowest valence states are shown in Fig. 2. At both D_{4h} and D_{2h} structures, the lowest four states are derived by distributing two electrons in two (nearly) degenerate molecular orbitals. Therefore, these states are best described as diradical states.[47,48,59–61] Note that at the D_{4h} geometry, all the electronic states are exactly two-configurational, while at the D_{2h} structure the wave function of the ground $X\,^1A_g$ state is dominated by a single determinant. As it follows from the molecular orbital picture, D_{2h} distortions are energetically favorable for the ground $X\,^1A_g$ state.[62]

The experimental structure of cyclobutadiene is not available; however, there is a host of theoretical calculations.[62–86] Table I summarizes some of the previously reported structures of the $X\,^1A_g$ state calculated by single-reference (SR) and multireference (MR) SCF, CC, and DFT methods. Figure 3 presents the equilibrium geometries of the $^3A_{2g}$ and $X\,^1A_g$ states optimized at the CCSD(T)/cc-pVTZ level. For the well-behaved triplet state, the errors in the

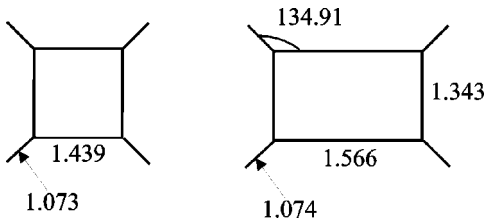

FIG. 3. Equilibrium geometries of the $1\,^3A_{2g}$ (left) and $X\,^1A_g$ (right) references, optimized at the CCSD(T)/cc-pVTZ level of theory. Bond lengths are in angstroms, angles in degrees.

TABLE II. Total energies (hartree) of the ground $X\ ^1A_g$ state of cyclobutadiene, and vertical excitation energies (eV) at the $X\ ^1A_g$ equilibrium geometry. D_{2h} symmetry, optimized at the CCSD(T)/cc-pVTZ level of theory.

	$E_{tot}(X\ ^1A_g)$[a]	$1\ ^3B_{1g}$	$2\ ^1A_g$	$1\ ^1B_{1g}$
EOM-CCSD[b]	−154.393 46	1.353	n/a	3.326
EOM-CCSD[c]	−154.416 93	1.351	n/a	3.319
UHF-EOM-SF-CCSD[b]	−154.401 52	1.661	4.376	3.426
UHF-EOM-SF-CCSD[c]	−154.424 95	1.659	4.369	3.420
ROHF-EOM-SF-CCSD[c]	−154.442 54	1.661	4.363	3.417

[a]For EOM-CCSD, the total CCSD energy of the $X\ ^1A_g$ reference; for EOM-SF-CCSD, the total energy of the EOM $1\ ^1A_g$ target state. The $1\ ^3B_{1g}$ reference is employed in the SF calculations.
[b]Mixed basis: cc-pVTZ on carbons and cc-pVDZ on hydrogens.
[c]Full cc-pVTZ basis.

TABLE III. Total energies (hartree) of the ground $X\ ^1B_{1g}$ state of cyclobutadiene, and vertical excitation energies (eV) at the $1\ ^3A_{2g}$ equilibrium geometry. D_{4h} symmetry, optimized at the CCSD(T)/cc-pVTZ level of theory.

	$E_{tot}(X\ ^1B_{1g})$[a]	$1\ ^3A_{2g}$	$2\ ^1A_{1g}$	$1\ ^1B_{2g}$
EOM-CCSD[b]	−154.357 12	−0.592	n/a	1.539
EOM-CCSD[c]	−154.380 58	−0.590	n/a	1.534
UHF-EOM-SF-CCSD[b]	−154.389 52	0.369	1.826	2.145
UHF-EOM-SF-CCSD[c]	−154.413 01	0.369	1.824	2.143
ROHF-EOM-SF-CCSD[c]	−154.413 42	0.369	1.814	2.137

[a]For EOM-CCSD, the total CCSD energy of the $X\ ^1B_{1g}$ reference; for EOM-SF-CCSD, the total energy of the EOM $X\ ^1B_{1g}$ target state. The $1\ ^3A_{2g}$ reference is employed in the SF calculations.
[b]Mixed basis: cc-pVTZ on carbons and cc-pVDZ on hydrogens.
[c]Full cc-pVTZ basis.

CCSD(T)/cc-pVTZ geometry should not exceed 0.002 Å.[87] However, the accuracy of the CCSD(T) model for the $X\ ^1A_g$ state may deteriorate due to the anticipated multiconfigurational character of this state. To clarify this, we performed geometry optimization with the SF-DFT method which was shown to yield very accurate structures for diradicals and triradicals.[46,48,49] An excellent agreement between the SF-DFT and CCSD(T) geometries suggests relatively minor multiconfigurational character in the $X\ ^1A_g$ state. This is also confirmed by the EOM-SF-CCSD amplitudes (see Fig. 2).

As it follows from Table I, the ground-state structure is rather sensitive to the theoretical method employed. First, including dynamical correlation effects results in longer CC and CH bonds—compare, for example, the SCF/cc-pVDZ and CCSD(T)/cc-pVDZ results. Second, a basis set of a better than cc-pVDZ quality is required for accurate geometries—comparison between the CCSD(T)/cc-pVDZ and CCSD(T)/cc-pVTZ results shows that the increase in the basis set size results in considerably shorter bond lengths. Finally, nondynamical correlation leads to more square structures, e.g., compare the bond alternation for the SCF and MCSCF methods, or for CCSD and MR-CCSD. Overall, we conclude that the CCSD(T)/cc-pVTZ geometries present the best estimates of the equilibrium structures, and we employ these geometries in our calculations of vertical and adiabatic excitation energies. Of course, the lowest singlet at square geometries is multiconfigurational, and would not be correctly described by the traditional single-reference methods.

B. Vertical and adiabatic excitation energies of cyclobutadiene

Calculated vertical excitation energies at the singlet and triplet geometries are presented in Tables II and III, respectively. The EOM-SF-CCSD results are also shown in Fig. 4. One of the many nontrivial features of cyclobutadiene is the violation of Hund's rule—the singlet state is below the triplet even at the triplet equilibrium geometry, when HOMO and LUMO are exactly degenerate.[60,65] Although Hund's rule always works for atoms, it can be violated in molecules through the effect of dynamic spin-polarization.[60]

Since the HOMO–LUMO degeneracy is lifted by the rectangular distortion from the square geometry (Fig. 2, right panel), the EOM-CCSD provides qualitatively correct description of the excited states, i.e., singlet–triplet ordering at the singlet geometry. Quantitatively, however, the difference between the EOM-EE-CCSD and the EOM-SF-CCSD excitation energies equals 0.308 eV, which is beyond the EOM-CCSD error bars of 0.1–0.3 eV.[88] Therefore, even at the distorted geometry the ground state is sufficiently multiconfigurational for the EOM-CCSD to fail (see Fig. 2, right panel). The EOM-CCSD errors for the second closed-shell singlet are much larger due to substantial doubly excited character.

At the square geometry, where HOMO and LUMO are exactly degenerate, the EOM-CCSD model fails more dramatically, e.g., singlet–triplet ordering is reversed due to the unbalanced treatment of the two leading determinants (see Fig. 2, left panel). The EOM-SF-CCSD model, however, gives the correct singlet–triplet ordering because both degenerate configurations are formally single excitations (with a spin-flip) from the high-spin triplet reference, and therefore are treated on an equal footing by the SF methods.

Finally, the EOM-EE-CCSD and EOM-SF-CCSD adiabatic excitation energies for the $^3A_{2g} \leftarrow X\ ^1A_g$ transition are 0.399 and 0.694 eV, respectively.

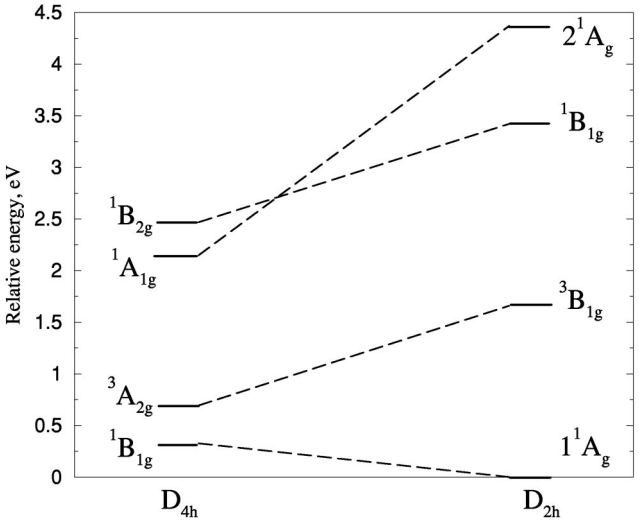

FIG. 4. Excitation energies of the valence states of cyclobutadiene relative to the ground $X\ ^1A_g$ state at the CCSD(T)/cc-pVTZ optimized geometries.

TABLE IV. Vertical excitation energies (eV) at rectangular singlet (RS) and square triplet (ST) geometries. The geometries are specified in the footnotes. D_{4h} symmetry labels are shown in parentheses. The $X\ ^1A_g(X\ ^1B_{1g})$ is the lowest state at both geometries.

	$1\ ^3B_{1g}(^3A_{2g})$	$2\ ^1A_g(^1A_{1g})$	$1\ ^1B_{1g}(^1B_{2g})$
RS (D_{2h}) geometry			
PPP-CI/[a]		4.351	3.523
SCF-CI/[5s5p/5s][b]	1.622	4.767	5.984
SCF-CI/3-21(+)G[c]	1.12	4.90	3.46
MCSCF/SVP[d]	1.274	3.715	4.138
H^ν/(4s5p1d/2s1p)[e]	1.44	4.06	3.39
EOM-CCSD/4-31G[f]	1.12	5.36	3.67
EOM-CCSD/cc-pVTZ[g]	1.351	n/a	3.319
EOM-SF-CCSD/cc-pVTZ[g]	1.659	4.369	3.420
ST (D_{4h}) geometry			
SCF-CI/[5s5p/5s][h]	0.590	2.754	4.914
ROKS(BLYP)/TZ2P[i]	−0.208	1.040	0.797
EOM-CCSD/cc-pVTZ[g]	−0.590	n/a	1.534
EOM-SF-CCSD/cc-pVTZ[g]	0.369	1.824	2.143

[a]Reference 89; at the geometry from Ref. 70: $R_{C-C}=1.57$ Å, $R_{C=C}=1.34$ Å, $R_{CH}=1.085$ Å, $\theta_{HCC}=135°$.
[b]Reference 65; $R_{C-C}=1.514$ Å, $R_{C=C}=1.338$ Å, $R_{CH}=1.059$ Å, $\theta_{HCC}=130°$.
[c]Reference 73; $R_{C-C}=1.526$ Å, $R_{C=C}=1.316$ Å, $R_{CH}=1.08$ Å, $\theta_{HCC}=135°$.
[d]Reference 75; $R_{C-C}=1.548$ Å, $R_{C=C}=1.375$ Å, $R_{CH}=1.085$ Å, $\theta_{HCC}=135°$.
[e]Reference 98; at the geometry from Ref. 77: $R_{C-C}=1.567$ Å, $R_{C=C}=1.346$ Å, $R_{CH}=1.084$ Å, $\theta_{HCC}=134.9°$.
[f]Reference 67; $R_{C-C}=1.581$ Å, $R_{C=C}=1.323$ Å, $R_{CH}=1.067$ Å, $\theta_{HCC}=134.7°$.
[g]This work; geometry is shown in Fig. 3.
[h]Reference 65; $R_{CC}=1.424$ Å, $R_{CH}=1.059$ Å.
[i]Reference 99; unspecified triplet geometry.

We found that the EOM-SF-CCSD excitation and total energies are rather insensitive to the reference employed; for example, the difference between the UHF and ROHF excitation energies does not exceed 0.01 eV. This is consistent with the recent study of Sears *et al.*[45] On a more technical side, Tables II and III demonstrate that the excitation energies calculated with the full cc-pVTZ basis and a smaller basis composed of the cc-pVTZ basis on carbons and the cc-pVDZ basis on hydrogen are very close.

The experimental data on the electronic spectrum of C_4H_4 are scarce and contradictory.[89–93] The most recent measurement of the UV absorption spectrum of argon-matrix isolated cyclobutadiene was reported by Michl's group.[93] It shows only one intense peak around 200 nm (6.2 eV); however, a weak absorption tail extends up to about 500 nm (2.5 eV). Note that the only spin- and symmetry-allowed transition from Table II is $^1B_{1g}\leftarrow X\ ^1A_g$ at 3.42 eV.

The electronic spectrum of cyclobutadiene has been serving as a sharpening stone for electronic structure methodology.[63–67,69,71,73,75,78,82,94–99] For a comprehensive review of earlier results, see Ref. 89. Table IV summarizes some of the theoretical results for the vertical excitation energies of cyclobutadiene at the singlet and triplet equilibrium geometries. The best agreement between the EOM-SF-CCSD valence transitions is with the semiempirical Parr–Pariser–Pople (PPP) model with the full CI in the π system,[89] as well as with the effective valence shell Hamiltonian (H^ν) method.[98] Note that the geometries employed in these calculations are very close to the geometries used in this work. While the PPP-CI method is not an accurate structural tool because only π electrons are considered, it may still yield reasonably accurate excitation energies within π systems due to the high degree of parametrization.

There is an interesting relation between the H^ν method and EOM-SF-CCSD. In both cases, the effective Hamiltonian which includes dynamical correlation effects is diagonalized in a smaller configurational subspace. While in EOM-SF-CCSD the reference and excited state spaces are separated by their spin-projection values ($M_s=1$ for the triplet reference, and $M_s=0$ for target states), in the H^ν approach total configuration space is divided to valence subspace and its orthogonal compliment.[98] This allows us to separate the degenerate configurations (π system) from the rest of the configurational space (σ system) and treat them in a reasonably balanced fashion without sacrificing π–σ and σ–σ dynamical correlation. This explains the fairly good agreement between the H^ν and EOM-SF-CCSD results.

The importance of the π–σ correlation is confirmed by the comparison of SCF-CI results for the open-shell singlet $^1B_{1g}$ state obtained by Buenker and Peyerimhoff,[65] and by Fratev *et al.*[73] (see Table IV). Buenker and Peyerimhoff included in their CI all configurations derived from distributing the four π electrons among the eight π spin-orbitals. The resulting energy of the $^1B_{1g}\leftarrow X\ ^1A_g$ transition (5.984 eV) is 2.56 eV higher than the corresponding EOM-SF-CCSD value. Moreover, contrary to the EOM-SF-CCSD results, this state is placed above the $2\ ^1A_g$ state. The CI space employed by Fratev *et al.* included only single excitations from HOMO, but these excitations were not limited to the π system. Inclusion of the excitations to σ-antibonding orbitals results in much better agreement between SCF-CI and EOM-SF-CCSD (3.46 and 3.42 eV, respectively).

To conclude, a large basis set and a high level of correlation is required for a proper description of cyclobutadiene. High degeneracy in the π system, along with strong dynamical π–σ and σ–σ correlation, require well-balanced treatment of all electrons. This is easily achieved in the presented SF variant of EOM-CCSD. Despite the fact that degeneracy is lifted by rectangular distortions, the ground $X\ ^1A_g$ state is still considerably multiconfigurational. This causes traditional single-configurational approaches to fail for transition energies, although it has only a minor effect on the geometry of the ground state.

IV. CONCLUSIONS

The EOM formalism is a versatile tool for treating a wide range of chemically important situations. When combined with the single-reference coupled-cluster approach, it yields a hierarchy of size-consistent models of increasing accuracy. The EOM-CC models for excitation energies (EOM-EE) and ionized states (EOM-EA/IP) have been extensively used over the last decade, and it is now well recognized that EOM-CC is capable of describing certain multiconfigurational wave functions within a single-reference framework (e.g., open-shell type excited states, doublet radi-

cals, etc.).[16,17] This work presents an extension of the EOM-CC methods to situations with more extensive degeneracy, i.e., bond breaking, and di- and triradicals. In our approach, target multiconfigurational wave functions are described as spin-flipping excitations from the high spin reference. The relations between the EOM-SF, EOM-EE, and EOM-IP/EA models are discussed. The capabilities and advantages of the new approach are demonstrated by its application to cyclobutadiene.

ACKNOWLEDGMENTS

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APPENDIX: PROGRAMMABLE EOM-CCSD EQUATIONS

We solve Eqs. (33) and (34) by using a generalized Davidson's iterative diagonalization procedure,[100–102] which requires calculation of products of the transformed Hamiltonian matrix with trial vectors

$$\sigma_i^a=([\bar{H}_{\mathrm{SS}}-E_{\mathrm{CC}}]R_1)_i^a+(\bar{H}_{\mathrm{SD}}R_2)_i^a \tag{A1}$$

$$\sigma_{ij}^{ab}=(\bar{H}_{\mathrm{DS}}R_1)_{ij}^{ab}+([\bar{H}_{\mathrm{DD}}-E_{\mathrm{CC}}]R_2)_{ij}^{ab}$$

$$\tilde{\sigma}_i^a=(\bar{L}_1[H_{\mathrm{SS}}-E_{\mathrm{CC}}])_i^a+(L_2\bar{H}_{\mathrm{DS}})_i^a \tag{A2}$$

$$\tilde{\sigma}_{ij}^{ab}=(L_1\bar{H}_{\mathrm{SD}})_{ij}^{ab}+(L_2[\bar{H}_{\mathrm{DD}}-E_{\mathrm{CC}}])_{ij}^{ab} \tag{A3}$$

Programmable expressions for right σ and left $\tilde{\sigma}$ are

$$([\bar{H}_{\mathrm{SS}}-E_{\mathrm{CC}}]R_1)_i^a=\langle\Phi_i^a|\bar{H}-E_{\mathrm{CC}}|R_1\Phi_0\rangle=\sum_b r_i^b F_{ab}-\sum_j r_j^a F_{ij}-\sum_{jb} r_j^b I_{ibja}^1, \tag{A4}$$

$$(\bar{H}_{\mathrm{SD}}R_2)_i^a=\langle\Phi_i^a|\bar{H}|R_2\Phi_0\rangle=\sum_{jb} r_{ij}^{ab}F_{jb}-\tfrac{1}{2}\left(\sum_{jkb} r_{jk}^{ab}I_{ibjk}^6+\sum_{jbc} r_{ij}^{bc}I_{jabc}^7\right), \tag{A5}$$

$$(\bar{H}_{\mathrm{DS}}R_1)_{ij}^{ab}=\langle\Phi_{ij}^{ab}|\bar{H}|R_1\Phi_0\rangle=\sum_k (r_k^a I_{ijkb}^2-r_k^b I_{ijka}^2)+\sum_c (r_i^c I_{jcab}^3-r_j^c I_{icab}^3)+\sum_l (T_{il}^1 t_{jl}^{ab}-T_{jl}^1 t_{il}^{ab})+\sum_d (T_{ad}^2 t_{ij}^{bd}-T_{bd}^2 t_{ij}^{ad}), \tag{A6}$$

TABLE V. Intermediates used in Eqs. (A4)–(A11). To avoid storage of large 6-index quantities, intermediates which have to be updated at each iteration of diagonalization procedure were introduced.

$$F_{ia}=f_{ia}+\Sigma_{jb}t_j^b\langle ij||ab\rangle$$
$$F_{ij}=f_{ij}+\Sigma_a t_i^a f_{ja}+\Sigma_{ka}t_k^a\langle jk||ia\rangle+\Sigma_{kab}t_i^a t_k^b\langle jk||ab\rangle+\tfrac{1}{2}\Sigma_{kbc}t_{ik}^{bc}\langle jk||bc\rangle$$
$$F_{ab}=f_{ab}-\Sigma_i t_i^a f_{ib}-\Sigma_{ic}t_i^c\langle ia||bc\rangle+\Sigma_{ijc}t_i^c t_j^a\langle ij||bc\rangle-\tfrac{1}{2}\Sigma_{jkc}t_{jk}^{ac}\langle jk||bc\rangle$$
$$I_{iajb}^1=\langle ia||jb\rangle-\Sigma_k t_k^b\langle jk||ia\rangle-\Sigma_c t_i^c\langle jb||ac\rangle+\Sigma_{kc}t_i^c t_k^b\langle jk||ac\rangle-\Sigma_{kc}t_{ik}^{bc}\langle jk||ac\rangle$$
$$I_{ijka}^2=-\langle ij||ka\rangle+2\Sigma_l t_l^a I_{ijkl}^4+\Sigma_b(t_i^b(\langle jb||ka\rangle-\Sigma_{lc}t_{jl}^{ac}\langle kl||bc\rangle))-t_j^b(\langle ib||ka\rangle$$
$$-\Sigma_{lc}t_{il}^{ac}\langle kl||bc\rangle))-\Sigma_{bc}t_i^b t_j^c\langle ka||bc\rangle-\Sigma_{lbc}t_l^b t_{ij}^{ac}\langle kl||bc\rangle+\Sigma_c t_{ij}^{bc}f_{kc}-\tfrac{1}{2}\Sigma_{cd}t_{ij}^{cd}\langle kb||cd\rangle+\Sigma_{lc}(t_{il}^{bc}\langle jc||kl\rangle-t_{jl}^{bc}\langle ic||kl\rangle)$$
$$I_{icab}^3=-\langle ic||ab\rangle+2\Sigma_d t_i^d)I_{bcad}^5+\Sigma_j(t_j^b(\langle ia||jc\rangle-\Sigma_{kd}t_{ik}^{cd}\langle jk||ad\rangle)-t_j^c(\langle ia||jb\rangle$$
$$-\Sigma_{kd}t_{ik}^{bd}\langle jk||ad\rangle))-\Sigma_{jk}t_j^b t_k^c\langle jk||ia\rangle-\Sigma_{jkd}t_j^d t_{ik}^{bc}\langle jk||ad\rangle+\Sigma_k t_{ik}^{ab}f_{kc}-\tfrac{1}{2}\Sigma_{kl}t_{kl}^{ab}\langle ic||kl\rangle+\Sigma_{kd}(t_{ik}^{ad}\langle kb||cd\rangle-t_{ik}^{bd}\langle ka||cd\rangle)$$
$$I_{ijkl}^4=\tfrac{1}{2}\langle ij||kl\rangle+\tfrac{1}{2}\Sigma_a(t_j^a\langle kl||ia\rangle-t_i^a\langle kl||ja\rangle)+\tfrac{1}{2}\Sigma_{ab}t_i^a t_j^b\langle kl||ab\rangle+\tfrac{1}{4}\Sigma_{cd}t_{ij}^{cd}\langle kl||cd\rangle$$
$$I_{abcd}^5=\tfrac{1}{2}\langle ab||cd\rangle-\tfrac{1}{2}\Sigma_i(t_i^a\langle ib||cd\rangle-t_i^b\langle ia||cd\rangle)+\tfrac{1}{2}\Sigma_{ij}t_i^a t_j^b\langle ij||cd\rangle+\tfrac{1}{4}\Sigma_{kl}t_{kl}^{ab}\langle kl||cd\rangle$$
$$I_{ijka}^6=\langle ij||ka\rangle-\Sigma_c t_k^c\langle ij||ac\rangle$$
$$I_{iabc}^7=\langle ia||bc\rangle-\Sigma_j t_j^a\langle ij||bc\rangle$$

$$T_{ij}^1=\Sigma_{kc}r_k^c I_{jkic}^6$$
$$T_{ab}^2=\Sigma_{kc}r_k^c I_{kabc}^7$$
$$T_{ij}^3=\tfrac{1}{2}\Sigma_{kcd}r_{ik}^{cd}\langle jk||cd\rangle$$
$$T_{ab}^4=\tfrac{1}{2}\Sigma_{klc}r_{kl}^{ac}\langle kl||bc\rangle$$
$$T_{ij}^5=\tfrac{1}{2}\Sigma_{kab}l_{ik}^{ab}t_{jk}^{ab}$$
$$T_{ab}^6=\tfrac{1}{2}\Sigma_{ijc}l_{ij}^{ac}t_{ij}^{bc}$$

$$r_0=\frac{1}{\omega}(\Sigma_{ia}r_i^a f_i^a+\Sigma_{ijab}r_i^a t_j^b\langle ij||ab\rangle+\tfrac{1}{4}\Sigma_{ijab}r_{ij}^{ab}\langle ij||ab\rangle)$$
$$r_0=-\Sigma_{ia}r_i^a z_i^a-\tfrac{1}{4}\Sigma_{ijab}r_{ij}^{ab}z_{ij}^{ab}$$

$$A_{iaia}=F_{aa}-F_{ii}-I_{iaia}^1$$
$$D_{ijab,ijab}=-F_{ii}-F_{jj}+F_{aa}+F_{bb}-(I_{ibib}^1+I_{jbjb}^1+I_{iaia}^1+I_{jaja}^1)+I_{ijij}^4+I_{abab}^5-\tfrac{1}{2}\Sigma_l(\langle jl||ab\rangle t_{jl}^{ab}+\langle il||ab\rangle t_{il}^{ab})-\tfrac{1}{2}\Sigma_d(\langle ij||bd\rangle t_{ij}^{bd}+\langle ij||ad\rangle t_{ij}^{ad})$$

$$
\begin{aligned}
([\bar{H}_{\mathrm{DD}}-E_{\mathrm{CC}}]R_2)_{ij}^{ab} &= \langle \Phi_{ij}^{ab}|\bar{H}-E_{\mathrm{CC}}|R_2\Phi_0\rangle \\
&= \sum_k (r_{jk}^{ab}F_{ik}-r_{ik}^{ab}F_{jk}) + \sum_c (r_{ij}^{ac}F_{bc}-r_{ij}^{bc}F_{ac}) \\
&\quad + \sum_{kc} (r_{jk}^{ac}I_{ickb}^1 - r_{ik}^{ac}I_{jckb}^1 + r_{ik}^{bc}I_{jcka}^1 - r_{jk}^{bc}I_{icka}^1) \\
&\quad + \sum_{kl} r_{kl}^{ab}I_{ijkl}^4 + \sum_{cd} r_{ij}^{cd}I_{abcd}^5 + \sum_l (T_{il}^3 t_{jl}^{ab} - T_{jl}^3 t_{il}^{ab}) \\
&\quad + \sum_d (T_{ad}^4 t_{ij}^{bd} - T_{bd}^4 t_{ij}^{ad}), \qquad \text{(A7)}
\end{aligned}
$$

$$
\begin{aligned}
(L_1[\bar{H}_{\mathrm{SS}}-E_{\mathrm{CC}}])_i^a &= \langle \Phi_0 L_1|\bar{H}-E_{\mathrm{CC}}|\Phi_i^a\rangle \\
&= \sum_b l_i^b F_{ba} - \sum_j l_j^a F_{ji} - \sum_{jb} l_j^b I_{jaib}^1, \qquad \text{(A8)}
\end{aligned}
$$

$$
\begin{aligned}
(L_2\bar{H}_{\mathrm{DS}})_i^a &= \langle \Phi_0 L_2|\bar{H}|\Phi_i^a\rangle \\
&= \tfrac{1}{2}\sum_{jkb} l_{jk}^{ab}I_{jkib}^2 + \tfrac{1}{2}\sum_{jbc} l_{ij}^{bc}I_{jabc}^3 \\
&\quad + \sum_{lk} T_{lk}^5 I_{ikla}^6 + \sum_{dc} T_{dc}^6 I_{idac}^7, \qquad \text{(A9)}
\end{aligned}
$$

$$
\begin{aligned}
(L_1\bar{H}_{\mathrm{SD}})_{ij}^{ab} &= \langle \Phi_0 L_1|\bar{H}|\Phi_{ij}^{ab}\rangle \\
&= l_i^a F_{jb} - l_j^a F_{ib} + l_j^b F_{ia} - l_i^b F_{ja} \\
&\quad + \sum_k (l_k^b I_{ijka}^6 - l_k^a I_{ijkb}^6) + \sum_c (l_j^c I_{icab}^7 - l_i^c I_{jcab}^7), \qquad \text{(A10)}
\end{aligned}
$$

$$
\begin{aligned}
(L_2[\bar{H}_{\mathrm{DD}}-E_{\mathrm{CC}}])_{ij}^{ab} &= \langle \Phi_0 L_2|\bar{H}-E_{\mathrm{CC}}|\Phi_{ij}^{ab}\rangle \\
&= \sum_k (l_{jk}^{ab}F_{ki} - l_{ik}^{ab}F_{kj}) + \sum_c (l_{ij}^{ac}F_{cb} - l_{ij}^{bc}F_{ca}) \\
&\quad + \sum_{kl} l_{kl}^{ab}I_{klij}^4 + \sum_{cd} l_{ij}^{cd}I_{cdab}^5 + \sum_{kc} (-l_{ik}^{ac}I_{kbjc}^1 + l_{jk}^{ac}I_{kbic}^1 \\
&\quad + l_{ik}^{bc}I_{kajc}^1 - l_{jk}^{bc}I_{kaic}^1) + \sum_l (T_{il}^5\langle jl||ab\rangle - T_{jl}^5\langle il||ab\rangle) \\
&\quad + \sum_d (T_{ad}^6\langle ij||bd\rangle - T_{bd}^6\langle ij||ad\rangle). \qquad \text{(A11)}
\end{aligned}
$$

Intermediates used in Eqs. (A4)–(A11) are given in Table V.

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[21] The rank of a linear operator A acting in a carrier space S equals to the dimensionality of the image space $span\{Ax\}$, $x \in S$. Note that the following alternative representation of the excitation operator from Eq. (3): $R'(f) \equiv |f\rangle\langle 0| + A(\hat{1} - |0\rangle\langle 0|)$, where A is any operator, does not ensure the unit rank of the operator $R(f)|g\rangle = |f\rangle\langle 0|g\rangle = 0$, $R'(f)|g\rangle = |f\rangle\langle 0|g\rangle + A(\hat{1}|g\rangle - |0\rangle\langle 0|g\rangle) = A|g\rangle$ for any state $|g\rangle \neq |0\rangle$. Note that the operators $R(f)$ and $R'(f)$ act differently on $|\tilde{0}\rangle$, and that $R'(f)$ does not satisfy Eqs. (5) and (6).
[22] In the case of a Hermitian $\bar{H}$, $L(f)$ is simply the adjoint of $R(f)$: $L(f) = R(f)^+$. In the general case: $L(f)R(f') = \delta_{ff'}|0\rangle\langle 0|$.
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[24] The operator $\tilde{R}(f)$ is no longer an eigenoperator of the superoperator $\bar{H}$, $[\tilde{H}, \tilde{R}(f)]|\tilde{0}\rangle = E_f\tilde{R}(f)|\tilde{0}\rangle - |f\rangle\Sigma_k E_k\langle\tilde{0}|k\rangle^2$, where the sum runs over all eigenstates of $\bar{H}$. Consequently, the expectation value ω_{0f} from Eq. (7) becomes $\omega_{0f} = \langle\tilde{0}|L(f)[\bar{H}, \tilde{R}(f)]|\tilde{0}\rangle = E_f - \Sigma_k E_k\langle\tilde{0}|k\rangle^2$. Note that the second term in the right-hand side of the above equation depends only upon the reference, and is therefore the same for all the target $|f\rangle$. Therefore, for an arbitrary reference $|\tilde{0}\rangle$, the exact energy gap between any two target states $|f\rangle$ and $|i\rangle$ will be retrieved from functionals (7) and (8) in the limit when the operators $\tilde{R}(f), \tilde{L}^+(f)$ are expanded over the complete basis, $\omega_{if} = \omega_{0f} - \omega_{0i} = E_f - E_i$.
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[30] The reference determinant $|\Phi_0\rangle$ defines a separation of the orbital space into a subspace of orbitals occupied in $|\Phi_0\rangle$ and a complementary subspace of virtual orbitals. We will adhere to the convention when indexes $i,j,k,\ldots$, are reserved for the orbitals occupied in the reference determinant $|\Phi_0\rangle$, indexes $a,b,c,\ldots$—to unoccupied orbitals, and $p,q,r,s,\ldots$ are used in a general case, i.e., when an orbital can be either occupied or virtual. Then, excitation and de-excitation operators can be represented as $\tilde{R} = R_0 + R_1 + \cdots + R_n$, $\tilde{L} = L_0 + L_1 + \cdots + L_n$, where n is the highest excitation level, $R_0 = r_0\hat{1}$, and the form 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 the 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.
[31] If the bare Hamiltonian H and the single-determinantal reference is used in Eq. (7), familiar CI equations are recovered. For example, by truncating the excitation operators up to double excitations, transition energies are found by the diagonalization of the bare Hamiltonian matrix in the basis of the reference, and the singly and doubly excited determinants.

Thus, EOM-CC and CI methods are very similar both conceptually and technically. Technically, Davidson iterative diagonalization procedure for the Hermitian matrices (Ref. 100) should be appropriately modified (Refs. 101, 102) for the case of non-Hermitian matrices ($\bar{H}$ in the EOM-CC theory). The computational cost of the diagonalization step is approximately the same for the CI and CC models truncated at the same level of excitation (e.g., N^6 for the CISD and the CCSD models). Practically, however, the truncated EOM-CC model is superior to the CI truncated at the same level because effects of higher excitations are "folded in" through the similarity transformation (21) into the effective Hamiltonian $\bar{H}$. The role of the similarity transformation is to achieve more compact representation of vectors $\tilde{R},\tilde{L}$. For example, if T is not truncated and is a solution of CC equations in a full multielectron space, the reference determinant $|\tilde{0}\rangle$ is an eigenstate of $\bar{H}$ with the exact eigenvalue.

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