Gradients for the similarity transformed equation-of-motion coupled-cluster method

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A derivation of gradients for the similarity transformed equation-of-motion coupled-cluster singles and doubles method is presented. Algebraic operator equations for all of the terms which appear in the equations are given, with a discussion about the procedure for solving the equations. © *1999 American Institute of Physics.* [S0021-9606(99)30722-4]

I. INTRODUCTION

The equation-of-motion coupled-cluster (EOM-CC) method,[1,2] which is related to coupled-cluster linear response theory,[3–8] offers an attractive and unified formalism to extend single-reference coupled-cluster theory to excitation energies, ionization potentials, and electron affinities. When based on a coupled-cluster singles and doubles (CCSD)[9] ground state, the resulting methods are EE-EOM-CCSD for excitation energies,[10,11] IP-EOM-CCSD for ionization potentials,[12] and EA-EOM-CCSD for electron affinities.[13] These methods are conceptually single reference in that the entire calculation is built upon one reference determinant. Therefore, the only choices necessary in the method are the choice of basis set, the choice of reference determinant, usually the Hartree–Fock solution, and the choice of excitation level to include in the ground and excited state operators.

Several applications[10,14–18] of EE-EOM-CCSD and coupled-cluster singles and doubles linear response[19,20] have been made. The method has also been extended to include various effects of triple excitations.[21–24] But EOM-CCSD, and especially EE-EOM-CCSD, has some drawbacks. The first is the cost of the method. Every EE-EOM-CCSD excited state is approximately as expensive as a ground state CCSD calculation. Approximations can be made to reduce the cost,[25–27] with varying degrees of success. The second drawback is the accuracy of the method. For ethylene, butadiene, and cyclopentadiene, the average error in an EOM-CCSD calculation for the Rydberg states was 0.17 eV, but the average error for the valence states was 0.26 eV.[18]

The key to EOM-CC theory is the similarity transformation of the Hamiltonian. After the ground state coupled-cluster equations have been solved, the cluster amplitudes are used to transform the Hamiltonian. A similarity transformation changes the eigenfunctions of an operator without changing its eigenvalues. Hence, the energies of the excited states, electron attached states, and ionized states, which are all eigenvalues of the full, untruncated Hamiltonian matrix in terms of the appropriate bases, have not changed.

This transformation does, however, serve to reduce the coupling between excitation levels in the Hamiltonian matrix. Specifically, the coupling between single excitations and triples excitations (along with the coupling between double and quadruple excitations, etc.) has been reduced. Therefore, it now becomes reasonable to introduce approximations where only a subset of all possible excitations is included in the Hamiltonian matrix. In EE-EOM-CCSD the matrix is limited to only single and double excitations, i.e., determinants where one or two virtual orbitals replace one or two occupied orbitals. For EA-EOM-CCSD the space is limited to determinants where an electron has been added to a single virtual orbital and determinants where along with the electron being added to a virtual orbital, an occupied orbital is replaced with a virtual orbital. These are the so-called $1p$ and $2p1h$ states. For IP-EOM-CCSD the space consists of the $1h$ and $2h1p$ determinants, which are those determinants with one electron removed from an occupied orbital and those determinants with one electron removed and one electron excited.

In the similarity transformed equation-of-motion coupled-cluster (STEOM-CC) theory[28–30] the blocking of the matrix by similarity transformations is carried one step farther. Starting with the EOM-CC transformed Hamiltonian, a second similarity transformation[31] is performed in order to minimize the coupling between single excitations and doubles excitations.

Since the second similarity transformation is done in such a way as to preserve the reduction of the singles–triples coupling from the first similarity transformation, the eigenvectors for states dominated by single excitations are almost exclusively composed of only single excitations, meaning that the truncation needs to leave only the space of singles. Now the final diagonalization to get the eigenvalues and eigenvectors only scales as the fourth power of the basis set, as opposed to the sixth power scaling for EOM-CCSD. The trade-off is having to perform the second similarity transformation. Calculation of the amplitudes that define the second transformation scales as the fifth power of the basis set. The actual transformation presents a negligible step in a full

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STEOM-CC calculation. In practice the CCSD calculation of the parent state dominates the overall expense of the calculation.

If the final diagonalization is over the space where an electron has been removed from an occupied orbital and placed in an unoccupied orbital, then excited states are calculated, and the method is known as excitation energy STEOM-CC (EE-STEOM-CC).[28,30] If the final space is over states with two electrons removed, the method is the double ionization potential STEOM-CC (DIP-STEOM-CC).[30] Finally, if the space is over determinants with two electrons added, the method is the double electron attachment STEOM-CC (DEA-STEOM-CC).[30] Each of these methods provides an important tool for describing interesting chemistry, and although we will focus on the EE-STEOM-CC variant, everything said can be applied to the other two with simple modifications.

II. AN OVERVIEW OF STEOM-CCSD

In STEOM-CC theory, the orbital space is divided into occupied and virtual spin–orbitals, sometimes referred to as holes and particles, based on the orbital's occupancy in the reference determinant. The orbital space is then subdivided into active and inactive occupied spin–orbitals and active and inactive virtual spin–orbitals. To distinguish the sets, the labels *i, j, k,* and *l* will refer to generic occupied orbitals, and *a, b, c,* and *d* will refer to generic virtual orbitals. Active occupied orbitals will be *m* and *n* while active virtuals will be *e* and *f*. Explicitly inactive orbitals will be indicated with a prime, such as i' and a'. The labels *p, q, r,* and *s* can refer to any orbital.

Although a STEOM-CC calculation could be based on any coupled-cluster or many-body perturbation theory treatment of the ground state, so far only CCSD and MBPT(2) have been used.[28] This discussion will focus on STEOM-CC with a CCSD[9] ground state, giving the STEOM-CCSD method.[28] In coupled-cluster theory, the ground state of the molecule is represented as

$$|\Psi_0\rangle = e^T|0\rangle, \tag{1}$$

where $|0\rangle$ is a single determinant. In this paper it will be the Hartree–Fock determinant. For CCSD the operator T consists of pure excitation operators of the form

$$T = T_1 + T_2 = \sum_{i,a} t_i^a\{a^\dagger i\} + \frac{1}{4}\sum_{\substack{i,j\\a,b}} t_{ij}^{ab}\{a^\dagger i b^\dagger j\}. \tag{2}$$

The curly brackets mean that the operator is normal ordered with respect to $|0\rangle$.

The normal-ordered Hamiltonian, in second quantization, is

$$H = h_0 + \sum_{p,q} f_{pq}\{p^\dagger q\} + \frac{1}{4}\sum_{\substack{p,q\\r,s}} W_{pqrs}\{p^\dagger r q^\dagger s\}. \tag{3}$$

The constant term, h_0, is the energy of the reference determinant. The f_{pq} refer to the appropriate parts of the Fock operator. The W_{pqrs} are antisymmetrized two electron integrals.

After the first transformation the Hamiltonian becomes

$$\begin{aligned}\bar{H} &= e^{-T}He^T\\ &= \bar{h}_0 + \sum_{p,q} \bar{h}_{pq}\{p^\dagger q\} + \frac{1}{4}\sum_{\substack{p,q\\r,s}} \bar{h}_{pqrs}\{p^\dagger r q^\dagger s\}\\ &\quad + \frac{1}{36}\sum_{\substack{p,q,r\\s,t,u}} \bar{h}_{pqrstu}\{p^\dagger s q^\dagger t r^\dagger u\} + \cdots .\end{aligned} \tag{4}$$

With a CCSD reference state, $\bar{H}$ will contain up to six-body terms, but the four- and higher-body terms do not appear in the EOM-CCSD or STEOM-CCSD equations. Explicit equations for these $\bar{H}$ elements can be found elsewhere.[32] In terms of $\bar{H}$, the CCSD equations can be written as

$$\begin{aligned}\langle \mathbf{\Phi}_i^a|\bar{H}|0\rangle &= \bar{\mathbf{h}}_{ai} = \mathbf{0},\\ \langle \mathbf{\Phi}_{ij}^{ab}|\bar{H}|0\rangle &= \bar{\mathbf{h}}_{abij} = \mathbf{0}.\end{aligned} \tag{5}$$

The CCSD energy is

$$E_{\text{CCSD}} = \langle 0|\bar{H}|0\rangle = \bar{h}_0. \tag{6}$$

Thus, solving the CCSD equations is equivalent to setting the one- and two-body pure excitation parts of $\bar{H}$ to zero.

In STEOM-CC, a second many-body similarity transformation[31] is performed in order to also set to zero selected remaining terms which increase the net excitation level by one. But since, in diagrammatic language, the necessary operators have a line at the bottom, they do not commute and can connect to each other. Thus a normal ordered exponential operator $\{e^S\}$ is used. The normal ordered exponential, introduced by Lindgren,[33] excludes terms inside the normal ordering from connecting to each other.

The S operator used in the transformation consists of two parts $S = S^+ + S^-$, where

$$S^+ = S_1^+ + S_2^+ = \sum_{a',e} s_e^{a'}\{a'^\dagger e\} + \frac{1}{2}\sum_{\substack{a,b\\j,e}} s_{ej}^{ab}\{a^\dagger e b^\dagger j\}, \tag{7}$$

and

$$S^- = S_1^- + S_2^- = \sum_{i',m} s_{i'}^{m}\{m^\dagger i'\} + \frac{1}{2}\sum_{\substack{i,m\\b,j}} s_{ij}^{mb}\{m^\dagger i b^\dagger j\}. \tag{8}$$

It is the presence of the active q-annihilation operators which cause the components of S to, in general, not commute.[30]

The double similarity transformed Hamiltonian takes the form

$$\begin{aligned}G &= \{e^S\}^{-1}\bar{H}\{e^S\}\\ &= g_0 + \sum_{p,q} g_{pq}\{p^\dagger q\} + \sum_{\substack{p,q\\r,s}} g_{pqrs}\{p^\dagger r q^\dagger s\} + \cdots .\end{aligned} \tag{9}$$

The similarity transformation preserves the zeros for the one- and two-body pure excitation parts, so that[30]

$$\begin{aligned}\mathbf{g}_{ai} &= \bar{\mathbf{h}}_{ai} = \mathbf{0},\\ \mathbf{g}_{abij} &= \bar{\mathbf{h}}_{abij} = \mathbf{0}.\end{aligned} \tag{10}$$

Also,

$$g_0 = \overline{h}_0 = E_{\mathrm{CCSD}}. \tag{11}$$

In principle, like the CCSD equations for T above, the S equations could be derived by setting the appropriate parts of G to zero. These are[30]

$$\begin{aligned} \mathbf{g}_{mi'} &= \langle \mathbf{\Phi}_{i'} | G | \mathbf{\Phi}_m \rangle = \mathbf{0}, \\ \mathbf{g}_{a'e} &= \langle \mathbf{\Phi}^{d'} | G | \mathbf{\Phi}^e \rangle = \mathbf{0}, \\ \mathbf{g}_{mbij} &= \langle \mathbf{\Phi}_{ji}^{b} | G | \mathbf{\Phi}_m \rangle = \mathbf{0}, \\ \mathbf{g}_{abej} &= \langle \mathbf{\Phi}_{j}^{ba} | G | \mathbf{\Phi}^e \rangle = \mathbf{0}. \end{aligned} \tag{12}$$

Note that the second quantized matrix elements equated to zero in the second two equations provide the primary coupling terms between singly and doubly excited determinants. In practice, the S coefficients are not calculated this way. Doing so would lead to systems of nonlinear equations which in some situations can be numerically unstable.[28] Instead, the equivalence of IP-EOM-CC and EA-EOM-CC to Fock space coupled-cluster theory[34] is exploited to rewrite S in terms of IP-EOM-CCSD and EA-EOM-CCSD eigenvectors.

After the S coefficients are determined, the problem remains of how to determine the G coefficients. Instead of using Eq. (9) directly, the equation

$$\{e^S\} G = \overline{H} \{e^S\} \tag{13}$$

is used. It has been shown[31] that this equation is equivalent to

$$(\{e^S\} G)_c = (\overline{H} \{e^S\})_c \tag{14}$$

or

$$G = (\overline{H} \{e^S\})_c - (\{e^S - 1\} G)_c, \tag{15}$$

where the c means that the equations must be connected.

In practice, all terms involving S_1 are dropped from the matrix elements of G that enter the final diagonalization step.[30] Since S_1 does not change the net excitation level, it is not involved in the decoupling of excitation blocks. Ignoring all of the S_1 terms is equivalent to a simple rotation of the eigenvector, and since the G matrix is diagonalized over all singly excited determinants this ''rotation'' is automatically compensated for in the diagonalization. Therefore, including the S_1 terms does not change the final answer, and for convenience they are left out. Leaving out S_1 also simplifies Eq. (15).

Since only the singles–singles block of G is needed, the second term (the so-called renormalization contribution) does not contribute.[30] The transformed matrix elements that enter the final step in a STEOM-CC calculation are obtained straightforwardly from

$$G = (\overline{H} e^{S_2})_c. \tag{16}$$

The orbital form of the equations that define G can be found in Ref. 30.

Finally, the G matrix is diagonalized over the space of single excitations to get the excited states. Since G is not Hermitian, it has different right- and left-hand eigenvectors. Given a right- and left-hand eigenvector for a specific state, the energy of the state can be represented as

$$E = \langle 0 | L G R | 0 \rangle, \tag{17}$$

where the defining equations for L and R are

$$\langle \mathbf{p} | G R | 0 \rangle = E \langle \mathbf{p} | R | 0 \rangle, \tag{18}$$

and

$$\langle 0 | L G | \mathbf{p} \rangle = E \langle 0 | L | \mathbf{p} \rangle. \tag{19}$$

The notation here is that the space of all possible n-electron determinants is divided into $|\mathbf{h}\rangle = |\mathbf{p}\rangle \oplus |\mathbf{q}\rangle$, as was done by Stanton for EOM-CCSD gradients.[35–37] The difference is that since the STEOM-CCSD eigenvector only consists of the reference determinant and single excitations, $|\mathbf{p}\rangle$ only includes the reference determinant ($|0\rangle$) and singly excited determinants ($|\mathbf{s}\rangle$). The double ($|\mathbf{d}\rangle$) excitations are a part of $|\mathbf{q}\rangle$.

III. STEOM-CCSD GRADIENTS

Gradients are most easily obtained by using the method of undetermined Lagrangian multipliers.[38,39] The expression for the energy is supplemented by all of the equations that define the various amplitudes which appear in the energy expression, each multiplied by an undetermined parameter. This constitutes the so-called energy functional (a scalar quantity). By construction, requiring the value of the functional to be stationary with respect to the variations of the Langrangian multipliers yields the amplitude equations. This is sufficient to determine the energy, which does not require knowledge of the numerical value of the Langrangian multipliers. In order to obtain energy derivatives, the value of the functional is also made stationary with respect to first-order variations in the amplitudes, and this provides equations that determine the values of the Lagrangian multipliers. The first-order change in energy upon applying a perturbation now only involves the change in the Hamiltonian matrix elements, which are multiplied by a group of coefficients (amplitudes and Langrangian multipliers) that define an effective density matrix.

This method of undetermined Lagrangian multipliers was used previously for EOM-CCSD and P-EOM-MBPT(2) gradients.[40] For EOM-CCSD gradients[35] the quantity zeta (Z) was introduced in order to guarantee the solution of the ground state coupled-cluster equations and to account for the response of the ground state T amplitudes to the perturbation, i.e., the role of lambda (Λ) for ground state coupled-cluster theory.[41,45] That operator is still needed for STEOM-CCSD, but now two more Z like quantities are needed in order to account for the response of the $S^{\pm}$ coefficients to the perturbation. These will be called Z^{+} and Z^{-}, and they have the form

$$Z^+ = Z_1^+ + Z_2^+ = \sum_{a',e} \zeta_{a'}^{e}\{e^\dagger a'\} + \frac{1}{2}\sum_{\substack{a,b\\e,j}} \zeta_{ab}^{ej}\{e^\dagger a j^\dagger b\},$$
$$Z^- = Z_1^- + Z_2^- = \sum_{i',m} \zeta_m^{i'}\{i'^\dagger m\} + \frac{1}{2}\sum_{\substack{m,b\\i,j}} \zeta_{mb}^{ij}\{i^\dagger m j^\dagger b\}. \tag{20}$$

Even though $S_1^{\pm}$ are not used in the final diagonalization over singly excited states, they appear in the equations for $S_2^{\pm}$[30] and therefore must appear in the functional. Since $S_1^{\pm}$ appear, $Z^{\pm}$ must also contain one-body components. The forms of $Z^{\pm}$ are the deexcitation analogs of S^+ and S^-, and $Z^{\pm}$ relate to $S^{\pm}$ just as Λ relates to T in coupled-cluster gradients.[41,45]

In order to be consistent with ground state coupled-cluster theory[41] and to distinguish it from the $Z^{\pm}$ above, what was called Z for EOM-CCSD gradients[35] will be called Λ here. It has the form

$$\Lambda = \sum_{a,i} \lambda_a^i\{i^\dagger a\} + \frac{1}{4}\sum_{\substack{a,b\\i,j}} \lambda_{ab}^{ij}\{i^\dagger a j^\dagger b\}. \tag{21}$$

The STEOM-CCSD functional therefore is

$$F = \langle 0|LGR|0\rangle + \sum_e \langle \Phi^e|Z^+G|\Phi^e\rangle + \sum_m \langle \Phi_m|Z^-G|\Phi_m\rangle + \langle 0|\Lambda\bar{H}|0\rangle + E(1-\langle 0|LR|0\rangle), \tag{22}$$

and at stationarity it has as its numerical value the total energy. The $|\Phi^e\rangle$ and $|\Phi_m\rangle$ are determinants where an electron has been added to an active virtual orbital and where an electron has been removed from an active occupied orbital, respectively.

The procedure for deriving gradient equations from the functional is that the derivative of the functional with respect to every quantity in the formula will be taken and set to zero. For the energy, which is a scalar, this is straightforward, but all of the other quantities are operators. In the case of an operator, the procedure is to take the derivative with respect to each coefficient in the operator and to set the resulting scalar equation to zero. This yields a vector of equations for each operator.[40]

By inspection it can be seen that taking the derivative of F with respect to L and R and setting them equal to zero give Eqs. (18) and (19), respectively. It also can be seen by inspection that taking the derivative with respect to Λ yields the ground state coupled-cluster equations. The derivative with respect to E gives the normalization condition for L and R. Therefore, by construction, the value of the functional is stationary with respect to variations of L, R, Λ, and E when the STEOM-CC amplitude equations are satisfied.

The result of taking the derivative with respect to Z^+ and Z^- is more difficult. For this two new spaces must be introduced. They are $|\mathbf{Q}^+\rangle$ and $|\mathbf{Q}^-\rangle$, and they are defined as the spaces into which $S^{\pm}$ project when acting on $|\mathbf{P}^+\rangle$ and $|\mathbf{P}^-\rangle$, respectively, and where $|\mathbf{P}^{\pm}\rangle$ are the space of all determinants with one electron added to an active virtual orbital or with one electron removed from an active occupied orbital.[30]

Using this notation, the result of taking the derivative of the functional with respect to the coefficients in Z^+ is, for all e,

$$\mathbf{0} = \frac{\partial F}{\partial \boldsymbol{\zeta}^+} = \langle \mathbf{Q}^+|G|\mathbf{\Phi}^e\rangle, \tag{23}$$

or equivalently

$$\mathbf{0} = \langle \mathbf{\Phi}^{a'}|G|\mathbf{\Phi}^e\rangle,$$
$$\mathbf{0} = \langle \mathbf{\Phi}_j^{ba}|G|\mathbf{\Phi}^e\rangle. \tag{24}$$

The derivative with respect to the coefficients in Z^- is, for all m,

$$\mathbf{0} = \frac{\partial F}{\partial \boldsymbol{\zeta}^-} = \langle \mathbf{Q}^-|G|\mathbf{\Phi}_m\rangle, \tag{25}$$

or

$$\mathbf{0} = \langle \mathbf{\Phi}_{i'}|G|\mathbf{\Phi}_m\rangle,$$
$$\mathbf{0} = \langle \mathbf{\Phi}_{ji}^{b}|G|\mathbf{\Phi}_m\rangle. \tag{26}$$

These equations are equivalent to Eq. (12), and they can be used as the defining equations for S. The fact that, in practice, S is calculated in a different manner does not matter. It is sufficient that these equations are equivalent to the ones used.

We are now left with making the functional stationary with respect to S^+, S^-, and T, which are hidden inside G. The first step is to note that, from Eq. (16),

$$\langle 0|LGR|0\rangle = \langle 0|L\bar{H}\{e^{S_2}\}R|0\rangle. \tag{27}$$

Note that the connected symbol has been dropped, since it is superfluous for the singles–singles block of G.

It has also been shown[30] that

$$\langle \mathbf{Q}^{\pm}|G|\mathbf{P}^{\pm}\rangle = \langle Q^{\pm}|\bar{H} + (\bar{H} - E_{\rm CC})S^{\pm}|\mathbf{P}^{\pm}\rangle - \langle \mathbf{Q}^{\pm}|S^{\pm}|\mathbf{P}^{\pm}\rangle\langle \mathbf{P}^{\pm}|\bar{H} + \bar{H}S^{\pm} - E_{\rm CC}|\mathbf{P}^{\pm}\rangle, \tag{28}$$

where $E_{\rm CC}$ stands for the ground state coupled-cluster energy. Here G contains both S_1 and S_2.

Substituting Eqs. (27) and (28) into Eq. (22) gives

$$F = \langle 0|L\bar{H}\{e^{S_2}\}R|0\rangle + \sum_e \langle \Phi^e|Z^+(\bar{H} + (\bar{H} - E_{\rm CC})S^+)|\Phi^e\rangle - \sum_e \langle \Phi^e|Z^+S^+|\mathbf{P}^+\rangle\langle \mathbf{P}^+|(\bar{H}(1+S^+) - E_{\rm CC})|\Phi^e\rangle + \sum_m \langle \Phi_m|Z^-(\bar{H} + (\bar{H} - E_{\rm CC})S^-)|\Phi^m\rangle - \sum_m \langle \Phi_m|Z^-S^-|\mathbf{P}^-\rangle\langle \mathbf{P}^-|(\bar{H}(1+S^-) - E_{\rm CC})|\Phi_m\rangle + \langle 0|\Lambda\bar{H}|0\rangle + E(1-\langle 0|LR|0\rangle). \tag{29}$$

It is now possible to continue taking derivatives of the functional with respect to the operators it contains, i.e., S^+, S^-, and T. The annihilation and creation portions of these operators will be called Ω_{S^+}, Ω_{S^-}, and Ω_T, respectively. These are the parts of the operators remaining after the derivative with respect to the coefficients in the operator has been taken.

The first term to consider is S^+. Taking the derivative of the functional with respect to the S^+ coefficients gives for all f and κ, where κ labels a generic $|\mathbf{Q}^+\rangle$ space determinant,

$$\begin{aligned}\mathbf{0}&=\frac{\partial F}{\partial \mathbf{s}^+}\\ &=\frac{\partial F}{\mathbf{s}^\kappa}=\langle 0|L\bar{H}\{e^{S_2}\Omega_{S_f^\kappa}\}R|0\rangle\,\delta_{\kappa,2h1p}\\ &\quad+\sum_e \langle\Phi^e|Z^+(\bar{H}-E_{\rm CC})\Omega_{S_f^\kappa}|\Phi^e\rangle\,\delta_{ef}\\ &\quad-\sum_e \langle\Phi^e|Z^+\Omega_{S_f^\kappa}|\mathbf{\Phi}^f\rangle\langle\mathbf{\Phi}^f|(\bar{H}(1+S^+)-E_{\rm CC})|\Phi^e\rangle\\ &\quad-\sum_e \langle\Phi^e|Z^+S^+|\mathbf{P}^+\rangle\langle\mathbf{P}^+|\bar{H}\Omega_{S_f^\kappa}|\Phi^e\rangle\,\delta_{ef},\end{aligned}\qquad(30)$$

or

$$\begin{aligned}\mathbf{0}&=\langle 0|L\bar{H}\{e^{S_2}\Omega_{S_f^\kappa}\}R|0\rangle\,\delta_{k,2h1p}+\langle\mathbf{\Phi}^f|Z^+(\bar{H}-E_{\rm CC})|\mathbf{\Phi}^\kappa\rangle\\ &\quad-\langle\mathbf{\Phi}^f|Z^+S^+|\mathbf{P}^+\rangle\langle\mathbf{P}^+|\bar{H}|\mathbf{\Phi}^\kappa\rangle\\ &\quad-\sum_e \langle\Phi^e|Z^+|\mathbf{\Phi}^\kappa\rangle\langle\mathbf{\Phi}^f|(\bar{H}(1+S^+)-E_{\rm CC})|\Phi^e\rangle.\end{aligned}\qquad(31)$$

Inserting a resolution of the $|\mathbf{Q}^+\rangle$ space into the second and third terms yields for all f and κ

$$\begin{aligned}\mathbf{0}&=\langle 0|L\bar{H}\{e^{S_2}\Omega_{S_f^\kappa}\}R|0\rangle\,\delta_{\kappa,2h1p}\\ &\quad+\sum_\eta \langle\mathbf{\Phi}^f|Z^+|\Phi^\eta\rangle\langle\Phi^\eta|\bar{H}|\mathbf{\Phi}^\kappa\rangle\\ &\quad-\sum_\eta \langle\mathbf{\Phi}^f|Z^+|\Phi^\eta\rangle\langle\Phi^\eta|S^+|\mathbf{P}^+\rangle\langle\mathbf{P}^+|\bar{H}|\mathbf{\Phi}^\kappa\rangle\\ &\quad-\sum_e \langle\mathbf{\Phi}^f|(\bar{H}(1+S^+)-E_{\rm CC})|\Phi^e\rangle\langle\Phi^e|Z^+|\mathbf{\Phi}^\kappa\rangle,\end{aligned}\qquad(32)$$

where η labels another generic $|\mathbf{Q}^+\rangle$ space determinant. Note that the first term on the right-hand side of Eq. (32) only appears when κ is a $2p1h$ excitation since the corresponding term in the functional does not contain S_1.

In order to solve for Z^+ in Eq. (32), it is useful to introduce some new quantities. These are

$$\mathbf{Y}_\kappa^f=\langle 0|L\bar{H}\{e^{S_2}\Omega_{S_f^\kappa}\}R|0\rangle\,\delta_{\kappa,2h1p},\qquad(33)$$

$$\mathbf{A}_\kappa^\eta=\langle\Phi^\eta|S^+|\mathbf{P}^+\rangle\langle\mathbf{P}^+|\bar{H}|\Phi^\kappa\rangle-\langle\Phi^\eta|\bar{H}|\Phi^\kappa\rangle,\qquad(34)$$

$$\mathbf{B}_e^f=\langle\Phi^f|(\bar{H}(1+S^+)-E_{\rm CC})|\Phi^e\rangle,\qquad(35)$$

and

$$\mathbf{Z}_\kappa^f=\langle\Phi^f|Z^+|\Phi^\kappa\rangle.\qquad(36)$$

Again, $\mathbf{Y}_\kappa^f$ only appears when κ is a $2p1h$ excitation. Using these definitions, Eq. (32) becomes

$$\sum_\eta \mathbf{Z}_\eta^f\mathbf{A}_\kappa^\eta+\sum_e \mathbf{B}_e^f\mathbf{Z}_\kappa^e=\mathbf{Y}_\kappa^f.\qquad(37)$$

In a typical calculation, the active space has of the order of ten orbitals; the largest active space used to date had only eleven occupied and fifty virtual spatial orbitals.[42] Therefore, because of its small size, the matrix $\mathbf{B}$ can be explicitly diagonalized, yielding the EA-EOMCC eigenvalues. Then, assuming that $\mathbf{UB}=\boldsymbol{\epsilon}\mathbf{U}$ with $\boldsymbol{\epsilon}$ diagonal, we can left multiply Eq. (37) by $\mathbf{U}$ to get

$$\sum_\eta (\mathbf{UZ})_\eta^e\mathbf{A}_\kappa^\eta+\epsilon_e(\mathbf{UZ})_\kappa^e=(\mathbf{UY})_\kappa^e.\qquad(38)$$

By noting that Eq. (38) decouples into a set of linear equations for each e, it becomes straightforward to solve for $(\mathbf{UZ})_\kappa^e$ and then to recover $\mathbf{Z}_\kappa^f$ from $\mathbf{Z}_\kappa^f=\mathbf{U}^{-1}(\mathbf{UZ})_\kappa^e$.

The procedure for calculating Z^- is exactly equivalent to the above procedure for Z^+. To generate the Z^- equations, it is only necessary to replace the appropriate active virtual indices with active occupied indices, to replace S^+ with S^-, and to replace the $|\mathbf{Q}^+\rangle$ determinants with $|\mathbf{Q}^-\rangle$ determinants. The eigenvalues of the $\mathbf{B}$ matrix are now the IP-EOMCC eigenvalues.

Before taking the derivative of the functional with respect to the coefficients in T, it will be useful to remember that

$$\frac{\partial\bar{H}}{\partial t}=\frac{\partial}{\partial t}(e^{-T}He^{T})=e^{-T}He^{T}\Omega_T-\Omega_Te^{-T}He^{T}=[\bar{H},\Omega_T].\qquad(39)$$

The derivative of Eq. (29) with respect to the coefficients in T is then

$$\begin{aligned}\mathbf{0}=\frac{\partial F}{\partial\mathbf{t}}&=\langle 0|L[\bar{H},\Omega_T]\{e^{S_2}\}R|0\rangle\\ &\quad+\sum_e \langle\Phi^e|Z^+([\bar{H},\Omega_T]+([\bar{H},\Omega_T]S^+)_c)|\Phi^e\rangle\\ &\quad-\sum_e \langle\Phi^e|Z^+S^+|\mathbf{P}^+\rangle\langle\mathbf{P}^+|[\bar{H},\Omega_T](1+S^+)|\Phi^e\rangle\\ &\quad+\sum_m \langle\Phi_m|Z^-([\bar{H},\Omega_T]+([\bar{H},\Omega_T]S^-)_c)|\Phi_m\rangle\\ &\quad-\sum_m \langle\Phi_m|Z^-S^-|\mathbf{P}^-\rangle\langle\mathbf{P}^-|[\bar{H},\Omega_T](1+S^-)|\Phi_m\rangle\\ &\quad+\langle 0|\Lambda[\bar{H},\Omega_T]|0\rangle.\end{aligned}\qquad(40)$$

Focusing on the last term,

$$\begin{aligned}\langle 0|\Lambda[\bar{H},\Omega_T]|0\rangle&=\langle 0|\Lambda\bar{H}\Omega_T|0\rangle-\langle 0|\Lambda\Omega_T\bar{H}|0\rangle\\ &=\langle 0|\Lambda\bar{H}|\mathbf{s}+\mathbf{d}\rangle-\langle 0|\Lambda|\mathbf{s}+\mathbf{d}\rangle\langle 0|\bar{H}|0\rangle\\ &=\langle 0|\Lambda|\mathbf{s}+\mathbf{d}\rangle\langle\mathbf{s}+\mathbf{d}|(\bar{H}-\mathbf{1}E_{\rm CC})|\mathbf{s}+\mathbf{d}\rangle,\end{aligned}\qquad(41)$$

where **1** is a unit matrix of the appropriate rank. The first five terms of Eq. (40) are independent of Λ, and the Jacobian in Eq. (41) is the same as that from EOM-CCSD gradients. Therefore, solving the Λ equations here requires the same procedure as that used to solve for Z in EOM-CCSD gradients,[35] with only a different inhomogeneous term.

With these definitions of $Z^{\pm}$ and Λ, the derivative of the functional with respect to all of the terms which appear in it is zero, and the generalized Hellmann–Feynman theorem[43,44] can be applied. Therefore, the derivative of the STEOM-CCSD energy with respect to any perturbation χ is

$$\begin{aligned}\frac{\partial E}{\partial \chi}=\frac{\partial F}{\partial \chi}=&\langle 0|L\overline{H}^{\chi}\{e^{S_2}\}R|0\rangle \\ &+\sum_e \langle \Phi^e|Z^+(\overline{H}^{\chi}+(\overline{H}^{\chi}S^+)_c)|\Phi^e\rangle \\ &-\sum_e \langle \Phi^e|Z^+S^+|\mathbf{P}^+\rangle\langle \mathbf{P}^+|\overline{H}^{\chi}(1+S^+)|\Phi^e\rangle \\ &+\sum_m \langle \Phi_m|Z^-(\overline{H}^{\chi}+(\overline{H}^{\chi}S^-)_c)|\Phi^m\rangle \\ &-\sum_m \langle \Phi_m|Z^-S^-|\mathbf{P}^-\rangle\langle \mathbf{P}^-|\overline{H}^{\chi}(1+S^-)|\Phi_m\rangle \\ &+\langle 0|\Lambda\overline{H}^{\chi}|0\rangle, \end{aligned}\tag{42}$$

with $\overline{H}^{\chi}=e^{-T}(\partial H/\partial \chi)e^{T}$.

The final step is to introduce one- and two-particle reduced density matrices into Eq. (42), where the density matrix elements consist of coefficients from the operators appearing in Eq. (42). These reduced density matrices can then be backtransformed into the atomic orbital (AO) basis, taking account of the orbital response, and contracted with bare AO derivative integrals.

One extra consideration does arise with STEOM-CC gradients. In normal coupled-cluster gradients, the equations for the response of the orbitals to the perturbation are simplified by using the fact that the method is invariant to rotation among the occupied orbitals and among the virtual orbitals.[45] In STEOM-CC, because of the splitting of the orbitals into an active set and an inactive set, this invariance to orbital rotations does not hold. The solution is straightforward, though. The same problem arises for dropped core gradients (see, e.g., Ref. 46), and the same techniques are applicable here.

Some preliminary tests were performed using finite difference techniques.[47] On average, the EE-STEOM-CCSD geometries and vibrational frequencies were about as accurate as EE-EOM-CCSD geometries and vibrational frequencies. The EE-STEOM-CCSD adiabatic excitation energies tended to be a little better then the EE-EOM-CCSD adiabatic excitation energies.

So far, the derivation has been for EE-STEOM-CCSD gradients, but its extension to DIP-STEOM-CCSD or DEA-STEOM-CCSD is straightforward. The only difference in the algebraic equations is that for DIP-STEOM-CC, S^+ does not appear,[30] and therefore Z^+ will not appear in the functional. Likewise, for DEA-STEOM-CC, S^- does not appear,[30] which leads to Z^- not being in the functional.

IV. SUMMARY

In this paper we have presented algebraic operator equations for calculating the gradient of the STEOM-CCSD energy with respect to a general perturbation. Diagrammatic techniques can be used to translate these into orbital equations. The three new terms beyond those which appear in STEOM-CCSD energy and property calculations and which must be solved for are Λ and $Z^{\pm}$.

The computational strategy involves the following steps. The first step is to solve the ground state coupled-cluster equations and calculate T. Next, T is used to perform the first similarity transformation, and then the IP-EOM-CCSD and the EA-EOM-CCSD equations are solved. Those are then used to form $S^{\pm}$, and the second similarity transformation is performed. The resulting matrix, G, is diagonalized to yield R, L, and the excited state energy. To then calculate the gradient, the next step is to calculate $Z^{\pm}$. Finally, one is able to calculate Λ and form the one- and two-particle density matrices. Because of the hierarchical nature of the equations, at every point in the procedure all terms calculated to that point are needed, but the solution of the current term is decoupled from the solution of all other terms.

This brings us back to our original problem, which was the cost and accuracy of the EOM-CCSD method. This paper presents a way to calculate properties for the STEOM-CCSD method as the analytical derivative of the energy. The resulting energies and properties are cheaper and, based on preliminary results, tend to be more accurate than those from EOM-CCSD. The STEOM-CCSD also has several other advantages. With STEOM-CCSD it is quite feasible to calculate a large number of states and then to select which states to optimize. Also, the method also provides a way to study doubly ionized and double electron-attached states. Finally, it should be noted that in STEOM-CC it is possible to introduce approximations such as STEOM-PT2[28] which further reduce the cost.

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