

A simple correction to final state energies of doublet radicals described by equation-of-motion coupled cluster theory in the singles and doubles approximation

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Abstract. A computationally inexpensive energy correction is suggested for radicals described by the equation-of-motion coupled cluster method for ionized states in the singles and doubles approximation (EOMIP-CCSD). The approach is primarily intended for doublet states that are qualitatively described by Koopmans' approximation. Following a strategy similar to those used in multireference coupled cluster theory, the proposed correction accounts for all correlation effects through third order in perturbation theory and also includes selected contributions to higher-order energies. As an initial test of the numerical performance of the method, total energies and energy splittings are calculated for some small prototype radicals.

Key words: Energy correction – Doublet radicals – Singles approximation – Doubles approximation

1 Introduction

Theoretical studies of open-shell molecular systems are often difficult due to the relatively high density of electronic states characteristic of these species. Unlike closed-shell molecules, the ground state is frequently separated from the lowest lying excited states by an electron volt or less in radicals. Small energy differences can lead to relatively strong pseudo-Jahn–Teller interactions [1], which affect the character of both ground- and excited-state potential energy surfaces along directions corresponding to nuclear displacements of appropriate symmetry. A reliable treatment of such systems requires a balanced description of two or more zeroth-order basis functions that correspond to the interacting electronic states [2]. Traditional treatments of electron correlation in which the wavefunction is generated by perturbation expansion with respect to a single Slater determinant are severely challenged, since one of the “important” zeroth-order determinants is necessarily treated differently than the others. Methods based on multideterminant reference functions have long been advocated for and successfully used for systems of this type [3], but are suitable only for accurate study of small molecules due to unfavorable computational scaling characteristics.

For doublet states, one alternative method that offers both a balanced treatment and geometric (as opposed to factorial) computational scaling is the

equation-of-motion coupled cluster method for ionized states in the singles and doubles approximation (EOMIP-CCSD) [4–6]. In this approach, the electronic Hamiltonian is subjected to a similarity transformation based on wavefunction parameters for some n electron reference state, projected onto a particular basis of $n-1$ electron determinants, and diagonalized. For cases involving strong pseudo-Jahn–Teller effects, potential energy surfaces calculated by the EOMIP-CCSD procedure appear to be uniformly superior to those obtained with the coupled-cluster singles and doubles (CCSD) [7] method [5, 8]. The great promise of the method for these challenging problems led to the formulation and implementation of an analytic gradient strategy for both EOMIP-CCSD [5] and a simplified but related theory that uses an approximate form of the transformed Hamiltonian [9].

While EOMIP-CCSD provides results that are often superior to those obtained in CCSD calculations (especially for cases involving quasidegenerate states), a formal argument can be made on behalf of the latter. From the point of view of perturbation theory, CCSD is exact through third order, while EOMIP-CCSD neglects some terms that appear at this level when Koopman's approximation is used to define a zeroth-order basis [10, 11]. Therefore, CCSD is the preferred choice when a single determinant dominates the form of the exact wavefunction and the perturbation series is well-behaved, exhibiting relatively rapid convergence. EOMIP-CCSD is most useful when strong configuration mixing is involved since arguments based on perturbation theory are of questionable validity in these situations, and the balanced nature of the method is clearly more important.

The purpose of the present paper is to present a simple approach for including the “missing” third-order terms in EOMIP-CCSD and to document some preliminary results obtained with the resulting approximation. The modified method can be expected to be accurate for a range of problems that exceeds that adequately treated by CCSD. For “single reference” cases, the proposed corrected EOMIP-CCSD method should be comparable in accuracy to CCSD calculations based on restricted or unrestricted open-shell reference functions; the latter methods are undoubtedly inferior for more difficult cases since the balanced nature of the EOMIP-CCSD approach is not compromised by the additional energy correction.

It should be pointed out that the work presented here is not the first to address the question of higher-order corrections to EOMIP-CCSD. Nooijen has considered these effects in the calculation of ground state properties by means of a sum over right and left-hand wavefunctions for $n-1$ electron intermediate states, and has carried out a formal analysis of how a balanced description of the reference and final states (and hence, reliable ionization potentials) can be obtained when one goes beyond the CCSD approximation [11]. In addition, there have been recommendations for noniterative corrections to ionization potentials calculated by the Fock space multireference coupled cluster theory in the singles and doubles approximation (FSMRCCSD) [12], a method that is equivalent (although formulated in an entirely different way) to EOMIP-CCSD. Both Pal et al. [10] and Haque and Kaldor [13] have presented formulas that are correct through third order in perturbation theory, with the former also suggesting a modification that includes some higher-order effects. These works employ the language of model spaces and the derivations are less straightforward than that presented in the next section, but the effects included are (necessarily) the same as those summed in our approach through third order with only modest differences in higher orders. Our work should therefore be viewed as simply another approach for improving the description of $n-1$ electron final states rather than a pioneering effort in this direction.

The next section details the theoretical and practical considerations that have led to our particular choice of a noniterative correction. This is followed by a presentation and discussion of preliminary results obtained with the proposed approach and some comments on future directions for research in this area.

2 Theory

The framework for our treatment of corrections to EOMIP-CCSD final state energies is the matrix partitioning approach of Löwdin [14]. In this formalism, the set of basis functions \mathbf{h} used in the matrix representation of an operator A is subdivided into an “important” part \mathbf{p} and a “less important” part \mathbf{q} ($\mathbf{h} = \mathbf{p} \cup \mathbf{q}$). Taking A to be a general (not necessarily Hermitian) operator, the eigenvalue conditions can be written as

$$\begin{bmatrix} A_{pp} & A_{pq} \\ A_{qp} & A_{qq} \end{bmatrix} \begin{bmatrix} \mathcal{R}_p \\ \mathcal{R}_q \end{bmatrix} = \lambda \begin{bmatrix} \mathcal{R}_p \\ \mathcal{R}_q \end{bmatrix} \quad (1)$$

and

$$[\mathcal{L}_p \mathcal{L}_q] \begin{bmatrix} A_{pp} & A_{pq} \\ A_{qp} & A_{qq} \end{bmatrix} = [\mathcal{L}_p \mathcal{L}_q] \lambda, \quad (2)$$

respectively, where $\mathcal{R}_p(\mathcal{L}_p)$ and $\mathcal{R}_q(\mathcal{L}_q)$ represent the projections of the right (left) eigenvector onto the \mathbf{p} and \mathbf{q} spaces. From Eq. (1), it is easily shown that

$$\mathcal{R}_q = [\lambda - A_{qq}]^{-1} A_{qp} \mathcal{R}_p, \quad (3)$$

which can be used to express λ as the eigenvalue of an (eigenvalue-dependent) effective operator whose matrix representation has the same dimension as the basis function subset \mathbf{p} , viz.,

$$A_{\text{eff}} \mathcal{R}_p \equiv \{A_{pp} + A_{pq}[\lambda - A_{qq}]^{-1} A_{qp}\} \mathcal{R}_p = \lambda \mathcal{R}_p. \quad (4)$$

Despite the smaller dimension of the effective matrix, the eigenvalue problem remains computationally demanding due to the need to evaluate the matrix inverse as well as the iterative solution necessitated by the form of the equation above. However, if A is separated into a “zeroth-order” part and a perturbation, Eq. (4) can be used to derive the equations of order-by-order Rayleigh–Schrödinger perturbation theory.

In the present research, our interest focuses on corrections to eigenvalues of the CCSD similarity-transformed Hamiltonian, \bar{H} , which is defined by

$$\bar{H} \equiv \exp(-T) H \exp(T). \quad (5)$$

Here, T comprises the standard one- and two-electron cluster operators associated with CCSD [7]. The amplitudes of T serve to parametrize the CCSD wavefunction of some appropriately chosen n electron state in terms of a Slater determinant reference function $|0\rangle$. In EOMIP-CCSD [4, 5], the \bar{H} operator is projected onto a basis of $n-1$ electron Slater determinants consisting of those obtained by removing one electron from $|0\rangle$ (Koopmans, or h determinants), and those generated from them by promotion of one of the remaining electrons to an orbital that is unoccupied in $|0\rangle$ ($2hp$ determinants). Some care must be exercised in developing a perturbation theory involving \bar{H} , as this operator differs fundamentally in character from the untransformed electronic Hamiltonian [15]. Specifically, \bar{H} contains three-electron and higher-rank components and is not Hermitian.

Moreover, when the occupied–occupied and virtual–virtual projections of the Fock operator are assigned to zeroth order, with all other parts of H constituting the perturbation, \bar{H} also contains terms that are second and higher-order in the correlation perturbation [16].

Multiplying both sides of Eq. (4) by \mathcal{L}_p (the projection of the *exact* left eigenvector onto the p basis) and integrating the resulting expression over all space yields

$$\langle \mathcal{L}_p | \bar{H}_{\text{eff}} | \mathcal{R}_p \rangle \equiv \langle \mathcal{L}_p | \{ \bar{H}_{pp} + \bar{H}_{pq} [\lambda - \bar{H}_{qq}]^{-1} \bar{H}_{qp} \} | \mathcal{R}_p \rangle = \lambda \langle \mathcal{L}_p | \mathcal{R}_p \rangle, \quad (6)$$

when the partitioning approach is applied to the case that $A = \bar{H}$. If the exact eigenvalue λ is written as $\lambda_0 + \Delta\lambda$, where λ_0 is some (as yet unspecified) zeroth-order approximation, and \bar{H} is expanded in terms of order in the correlation perturbation as done in Ref. [9],

$$\bar{H} = \bar{H}^{[0]} + \bar{H}^{[1]} + \bar{H}^{[2]} + \bar{H}^{[3]} + \dots, \quad (7)$$

the operator inverse appearing in Eq. (6) can be written as

$$[\lambda - \bar{H}_{qq}]^{-1} = [\lambda_0 + \Delta\lambda - \bar{H}_{qq}^{[0]} - \bar{H}_{qq}^{[1]} - \bar{H}_{qq}^{[2]} - \dots]^{-1} \quad (8)$$

$$= [(\lambda_0 - \bar{H}_{qq}^{[0]}) (\mathbf{1} - [\lambda_0 - \bar{H}_{qq}^{[0]}]^{-1} [\bar{H}_{qq}^{[1]} + \bar{H}_{qq}^{[2]} + \dots - \Delta\lambda])]^{-1} \quad (9)$$

$$\equiv [(\lambda_0 - \bar{H}_{qq}^{[0]}) (\mathbf{1} - [\lambda_0 - \bar{H}_{qq}^{[0]}]^{-1} [V_{qq} - \Delta\lambda])]^{-1}, \quad (10)$$

which has the series representation

$$\begin{aligned} [\lambda - \bar{H}_{qq}]^{-1} &= [\lambda_0 - \bar{H}_{qq}^{[0]}]^{-1} + [\lambda_0 - \bar{H}_{qq}^{[0]}]^{-1} (V_{qq} - \Delta\lambda) [\lambda_0 - \bar{H}_{qq}^{[0]}]^{-1} \\ &\quad + [\lambda_0 - \bar{H}_{qq}^{[0]}]^{-1} (V_{qq} - \Delta\lambda) [\lambda_0 - \bar{H}_{qq}^{[0]}]^{-1} \\ &\quad \times (V_{qq} - \Delta\lambda) (\lambda_0 - \bar{H}_{qq}^{[0]})^{-1} + \dots \end{aligned} \quad (11)$$

When $p = |0\rangle$ and $\bar{H} = H$, the series above can be used as a basis for deriving the standard equations of many-body perturbation theory.

To derive an approximate correction to the EOMIP-CCSD energy, it is natural to define p as $h \cup 2hp$. λ_0 can then be taken as the EOMIP-CCSD energy $\langle \mathcal{L}_p^{(0)} | \bar{H}_{pp} | \mathcal{R}_p^{(0)} \rangle$, where $\mathcal{L}_p^{(0)}$ and $\mathcal{R}_p^{(0)}$ are the vectors that diagonalize the p projection of \bar{H} . It should be noted that $\mathcal{L}_p^{(0)}$ and $\mathcal{R}_p^{(0)}$ are neither necessarily equal nor proportional to the exact \mathcal{L}_p and \mathcal{R}_p vectors. The latter can however be written as

$$\mathcal{R}_p = \mathcal{R}_p^{(0)} + \mathcal{R}_p^{(2)} + \mathcal{R}_p^{(3)} + \dots, \quad (12)$$

$$\mathcal{L}_p = \mathcal{L}_p^{(0)} + \mathcal{L}_p^{(2)} + \mathcal{L}_p^{(3)} + \dots, \quad (13)$$

where the correction terms may be obtained by the usual methods of perturbation theory when the entire \bar{H}_{pp} is taken as zeroth order. Note that “order” as applied to the eigenvectors has a somewhat different meaning than its use in classifying contributions to \bar{H} ; superscripts are accordingly enclosed in parentheses rather than square brackets to emphasize the distinction. Specifically, $\mathcal{R}_p^{(n)}$ and $\mathcal{L}_p^{(n)}$ contain corrections that are n th order and *higher* in the correlation perturbation as defined by a zeroth-order basis predicated on Koopmans’ approximation. Therefore, if the sum of the superscripts of $\bar{H}_{pp}^{[m]}$, $\mathcal{R}_p^{(n)}$ and $\mathcal{L}_p^{(o)}$ is termed the “overall order”, it should be recognized that the corresponding terms include $m + n + o$ and *higher-order* corrections to the zeroth-order description provided by Koopmans’ approximation. By writing the eigenvalue correction $\Delta\lambda$ as an expansion in this

“overall order”

$$\Delta\lambda = \Delta\lambda_1 + \Delta\lambda_2 + \dots, \quad (14)$$

inserting the expansions for \mathcal{L}_p , \mathcal{R}_p and $\Delta\lambda$ into Eqs. (6) and (11), doing some algebra and collecting terms of a given “overall order”, one finds that

$$\Delta\lambda_1 = 0, \quad (15)$$

$$\Delta\lambda_2 = \langle \mathcal{L}_p^{(0)} | \bar{H}_{pq}^{[1]} [\lambda_0 - \bar{H}_{qq}^{[0]}]^{-1} \bar{H}_{qp}^{[1]} | \mathcal{R}_p^{(0)} \rangle, \quad (16)$$

$$\begin{aligned} \Delta\lambda_3 = & \langle \mathcal{L}_p^{(0)} | \bar{H}_{pq}^{[2]} [\lambda_0 - \bar{H}_{qq}^{[0]}]^{-1} \bar{H}_{qp}^{[1]} | \mathcal{R}_p^{(0)} \rangle + \langle \mathcal{L}_p^{(0)} | \bar{H}_{pq}^{[1]} [\lambda_0 - \bar{H}_{qq}^{[0]}]^{-1} \bar{H}_{qp}^{[2]} | \mathcal{R}_p^{(0)} \rangle \\ & + \langle \mathcal{L}_p^{(0)} | \bar{H}_{pq}^{[1]} [\lambda_0 - \bar{H}_{qq}^{[0]}]^{-1} \bar{H}_{qq}^{[1]} [\lambda_0 - \bar{H}_{qq}^{[0]}]^{-1} \bar{H}_{qp}^{[1]} | \mathcal{R}_p^{(0)} \rangle. \end{aligned} \quad (17)$$

The eigenvector correction terms [Eqs. (12) and (13)] contribute only to $\Delta\lambda_4$ and terms of higher “overall order”. Eqs. (15)–(17) include the terms that must be considered if the resulting energy is to contain all third-order corrections to Koopmans’ approximation. Of course, selected higher-order contributions are included as well by virtue of how $\mathcal{R}_p^{(0)}$ and $\mathcal{L}_p^{(0)}$ are defined. If attention is restricted to states that lie mainly in the space spanned by the h determinants, then elements of the eigenvector that link $|0\rangle$ to them contain contributions that are zeroth-order and higher in the correlation perturbation, while those that connect $|0\rangle$ to the $2hp$ determinants are first- and higher-order quantities.

At this point, it is appropriate to dissect each of the terms in Eqs. (15)–(17) and determine the overall order in the *correlation* perturbation at which they first contribute. The task is considerably simplified by a preliminary analysis of the $\bar{H}_{qp}^{[1]} | \mathcal{R}_p^{(0)} \rangle$ product that appears in all but one of the terms. For the zeroth-order part of $\mathcal{R}_p^{(0)}$ (the projection of the eigenvector onto the h determinants), this vanishes since $\bar{H}_{qp}^{[1]}$ necessarily must then produce a pure two-particle excitation. Matrix elements of this type $[(\bar{H}_{ij}^{ab})^{[1]} a^\dagger i b^\dagger j]$ vanish, as demonstrated in Ref. [9]. Therefore, nonzero contributions to this product come solely from the $2hp$ projection of the eigenvector and are therefore second and higher order in correlation. The product $\langle \mathcal{L}_p^{(0)} | \bar{H}_{pq}^{[1]}$ found on the left side of three terms has a somewhat different character. Unlike the pure excitation part of $\bar{H}^{[1]}$, the pure two-particle deexcitation part does not vanish (the relevant matrix elements are simply equal to those of the untransformed electronic Hamiltonian), so that $\langle \mathcal{L}_p^{(0)} | \bar{H}_{pq}^{[1]}$ contains first- and higher-order contributions. Identifying the lowest contributing order in correlation for $\langle \mathcal{L}_p^{(0)} | \bar{H}_{pq}^{[1]}$ and $\bar{H}_{qp}^{[1]} | \mathcal{R}_p^{(0)} \rangle$ allows one to immediately see that $\Delta\lambda_2$ contributes at third and higher orders, while the same is true for the second term of $\Delta\lambda_3$. However, the other terms of Eq. (17) clearly have no third-order component and will be ignored in the following. Therefore, the energy given by

$$E = E_{\text{EOMIP}} + \Delta E \equiv \lambda_0 + \langle \mathcal{L}_p^{(0)} | \bar{H}_{pq}^{[0]} [\lambda_0 - \bar{H}_{qq}^{[0]}]^{-1} [\bar{H}_{qp}^{[1]} + \bar{H}_{qp}^{[2]}] | \mathcal{R}_p^{(0)} \rangle \quad (18)$$

CCSD

contains all contributions through third order in the correlation perturbation, based on a zeroth-order basis defined by Koopmans’ approximation.

All but one of the contributions to the noniterative energy correction ΔE involves intermediate states that belong to the set of $3h2p$ determinants (those obtained from the h determinants by excitation of two electrons). The corresponding spin-orbital formula [17] is

$$\Delta E \Leftarrow \frac{1}{12} \sum_{ijkab} l_{ab}^{ijk} r_{ijk}^{ab} [\lambda_0 + f_{ii} + f_{jj} + f_{kk} - f_{aa} - f_{bb}], \quad (19)$$

where the f_{pp} are diagonal elements of the Fock matrix. The l_{ab}^{ijk} and r_{ijk}^{ab} amplitudes are defined by

$$\begin{aligned}
 l_{ab}^{ijk} &= P(ijk)l^k \langle ab \parallel ij \rangle - P(ijk) \sum_e l_e^{ij} \langle ab \parallel ek \rangle - P(ab) P(ijk) \sum_m l_a^{mk} \langle ij \parallel mb \rangle, \quad (20) \\
 r_{ijk}^{ab} &= -P(ijk) \sum_e r_{ij}^e \langle ab \parallel ek \rangle - P(ab) P(ijk) \sum_m r_{mk}^a \langle ij \parallel mb \rangle \\
 &\quad - P(ab) P(ijk) \sum_{me} r_m t_{ij}^{ae} \langle mb \parallel ke \rangle + P(kji) \sum_{mn} r_m t_{in}^{ab} \langle mn \parallel kj \rangle \\
 &\quad - P(ijk) \sum_m r_{mk}^e \left[P(ij) \sum_{en} t_{nj}^{ab} \langle mn \parallel ei \rangle \right] + P(ijk)P(ab) \\
 &\quad \times \sum_{mef} r_{mk}^e t_{ij}^{fb} \langle ma \parallel ef \rangle. \quad (21)
 \end{aligned}$$

In Eqs. (20) and (21), the $\langle pq \parallel rs \rangle$ are antisymmetrized two-electron integrals; r_i (l^i) and r_{ij}^a (l_a^{ij}) are amplitudes of the EOMIP-CCSD eigenvectors

$$\mathcal{R}_p \equiv \sum_i r_i i + \frac{1}{2} \sum_{iaj} r_{ij}^a a^\dagger ij \quad (22)$$

and

$$\mathcal{L}_p \equiv \sum_i l^i i^\dagger + \frac{1}{2} \sum_{iaj} l_a^{ij} a j^\dagger i^\dagger. \quad (23)$$

The permutation operators $P_-(pq)$ and $P(pqr)$ are defined by their action on arbitrary two- and three-index quantities

$$P(pq)Z(pq) = Z(pq) - Z(qp) \quad (24)$$

and

$$P(pqr)Z(pqr) = Z(pqr) + Z(qrp) + Z(rpq), \quad (25)$$

while the t_{ij}^{ab} amplitudes are understood to be those that serve as the first-order correction to the n electron wavefunction

$$t_{ij}^{ab} = \frac{\langle ab \parallel ij \rangle}{f_{ii} + f_{jj} - f_{aa} - f_{bb}}. \quad (26)$$

The remaining contribution involving $4h3p$ intermediate states corresponds to the spin-orbital expression

$$\Delta E \Leftarrow \frac{1}{144} \sum_{ijklabc} l_{abc}^{ijkl} r_{ijkl}^{abc} [\lambda_0 + f_{ii} + f_{jj} + f_{kk} + f_{ll} - f_{aa} - f_{bb} - f_{cc}], \quad (27)$$

where

$$l_{abc}^{ijkl} = P(ijkl)P(abc)l_a^{ij} \langle kl \parallel bc \rangle, \quad (28)$$

$$\begin{aligned}
 r_{ijkl}^{abc} &= P(kl)P(ijkl)P(bc)P(abc) \sum_{me} r_{im}^c t_{ij}^{ae} \langle mb \parallel ke \rangle \\
 &\quad - P(il)P(ilkj)P(cab) \sum_{mn} r_{im}^c t_{in}^{ab} \langle mn \parallel kj \rangle, \quad (29)
 \end{aligned}$$

and an additional permutation operator defined by

$$P(pqrs)Z(pqrs) = Z(pqrs) + Z(rqsp) + Z(sqpr) + Z(prsq) + Z(psqr) + Z(rspq) \quad (30)$$

has been introduced.

At this point, a number of different strategies could be followed, and none of these can be regarded as rigorously justified by any criteria. The presence of infinite-order contributions in $\mathcal{L}_p^{(0)}$ and $\mathcal{R}_p^{(0)}$ confounds any attempt to isolate terms that contribute only to a given order, and there is no unambiguously “best” choice of a noniterative correction. The strategy that we have adopted is described below, along with practical and theoretical considerations and a discussion of its relationship to corrections previously formulated for FSMRCCSD calculations

1) The term involving $4h3p$ intermediates is omitted. For the states of principal interest here (those dominated by the h determinants), this makes a fifth-order contribution which is expected to be negligible. Moreover, it is computationally undesirable as evaluation of the r_{ijkl}^{abc} amplitudes involves steps that scale with the eighth power of the system size. None of the proposed FSMRCCSD corrections [10, 13] include this term.

2) All terms in Eqs. (19)–(21) are evaluated. Rather than using the first-order T amplitudes, we follow the lead of Refs. [13, 10] by evaluating all contributions with the converged T amplitudes. It should also be noted that noniterative corrections to the ground-state CCSD energy (for which there is a vast literature [18]) are also based on converged rather than first-order amplitudes [19]. To some degree, use of the converged amplitudes tends to offset the misbalanced nature of a correction based on some wavefunction parameters (the $\mathcal{R}_p^{(0)}$ and $\mathcal{L}_p^{(0)}$ amplitudes) that contain infinite-order contributions and others (T) that are truncated at first order.

3) The major distinction between effects treated by the proposed correction and related methods developed for FSMRCCSD theory [10, 13] are the (fourth-order) contributions that arise by including the last two terms of Eq. (20). It should be noted that these can be dropped without compromising the objective of including all corrections through third order (contributions to the r_{ijk}^{ab} are second-order and higher). However, numerical experimentation performed in the course of this research has shown that they make an important contribution to final state energies that is beneficial in essentially all cases. Since evaluation of the second-order contribution to $\mathcal{L}_p^{(0)}\bar{H}_{pq}^{[1]}$ does not significantly increase the cost of the calculation, retention of this term is desirable.

4) In the FSMRCCSD + T*(3) method formulated by Pal et al. [10], integrals and binary products of integrals and T amplitudes in the equations are replaced by the corresponding matrix elements of the full \bar{H} operator. In our approach, equations for specific truncations of \bar{H} are obtained, and then evaluated with the converged T amplitudes. The former strategy does indeed account for more higher-order effects and seems to provide somewhat better final-state energies [20]. Nevertheless, our interest is in properties and potential energy surfaces of $n-1$ electron final states, and it is well-recognized that efficient analytic evaluation of energy derivatives is essential for any method used for studies of this type. This consideration is raised here because use of the \bar{H} matrix elements would complicate (and increase the cost of) gradient evaluation. In our opinion, this objection far outweighs the modest improvement in accuracy achieved.

5) The evaluation of r_{ijk}^{ab} and l_{ab}^{ijk} amplitudes involves computational steps with at most a sixth-power dependence on the basis set size \mathcal{N} . While this scaling behavior is the same as that of rate-limiting steps in the reference state CCSD calculation, two factors suggest that the cost of evaluating the noniterative correction will make only a small contribution to that of the total calculation. First, unlike the \mathcal{N}^6 steps encountered in CCSD calculations (which must be performed in each iteration), the r_{ijk}^{ab} and l_{ab}^{ijk} amplitudes need to be evaluated only once. Moreover, in the usual case that the number of virtual orbitals (N) greatly exceeds the number of occupied orbitals (n), the most expensive noniterative steps will be those that scale with n^3N^3 , while a more expensive n^2N^4 step must be carried out in solving the CCSD equations [21]. Unlike noniterative corrections proposed for both CCSD [18] and EOM-CCSD for excited (n -electron) states [22], the procedure proposed here will not dominate the overall cost of a calculation. This is a significant point, and suggests that it is probably wise to evaluate the contribution even in routine calculations.

3 Application of the method

As a first application of the noniterative correction to EOMIP-CCSD final-state energies proposed in this paper, total energies have been calculated for the two lowest states of some small prototypical radicals as well as the vertical energy separation between them. The purpose of this exploratory study is to assess how well the corrected EOMIP-CCSD method (hereafter referred to as EOMIP-CCSD*) performs with respect to CCSD and CCSD(T) calculations based on unrestricted Hartree-Fock (UHF) reference functions. It should be noted that the systems considered in this section are those for which the latter "standard" CC methods are expected to work well, and the perturbational arguments used to motivate the present formulation are applicable. As the balanced feature of EOMIP-CCSD is preserved in EOMIP-CCSD*, the performance of the latter for more difficult situations (such as those involving pseudo-Jahn-Teller effects) is expected to be at least as good as EOMIP-CCSD. However, problems of this type are beyond the scope of the present work, and will be deferred for future study. Since a detailed comparison with experimental results is not our objective, a relatively small double-zeta plus polarization (DZP) basis set [23] has been used in all calculations. In addition, the geometries chosen for study are based on representative internuclear distances and bond angles rather than structural optimization of the electronic ground states of the radicals.

Results for HOO and CH₃O, as well as cations of HCN, H₂CO, N₂ are presented in Table 1. Total energies for both ground and excited states are documented, along with corresponding vertical excitation energies in eV. Two trends are apparent from the data. First, excitation energies calculated with EOMIP-CCSD* are in uniformly better agreement with the UHF-CCSD and UHF-CCSD(T) values. This is satisfying because the latter methods (which are exact through third and fourth order in the correlation perturbation, respectively) are expected to work well for these systems since no strong configuration effects are present. Moreover, since the present application focuses on vertical energy differences rather than the shape of potential energy surfaces, problems associated with quasidegenerate states of a different symmetry are avoided.

The total energies calculated with EOMIP-CCSD and EOMIP-CCSD* methods merit some discussion. As seen in the table, the EOMIP-CCSD* energy is

Table 1. Total electronic energies at the EOMIP-CCSD, EOMIP-CCSD*, UHF-CCSD and UHF-CCSD(*T*) levels for the two lowest electronic states of selected radicals. All calculations were performed at the geometries given in the tabular footnotes with the DZP basis set of Ref. [23]. Total energies are in hartrees; energy splittings (vertical excitation energies) in electron volts are also given in the rightmost column

HO ₂	X ² A''	A ² A'	Splitting
EOMIP-CCSD	-150.597373	-150.567336	0.817
EOMIP-CCSD*	-150.597711	-150.568634	0.791
UHF-CCSD	-150.589893	-150.563208	0.726
UHF-CCSD(<i>T</i>)	-150.600054	-150.572156	0.759
CH ₃ O ^b	X ² E	A ² A ₁	Splitting
EOMIP-CCSD	-114.777058	-114.622055	4.218
EOMIP-CCSD*	-114.776445	-114.625188	4.116
UHF-CCSD	-114.770867	-114.618591	4.144
UHF-CCSD(<i>T</i>)	-114.777432	-114.625277	4.140
HCN ^{+,c}	X ² Π	A ² Σ	Splitting
EOMIP-CCSD	-92.711025	-92.701210	0.267
EOMIP-CCSD*	-92.730074	-92.707223	0.622
UHF-CCSD	-92.723168	-92.704110	0.519
UHF-CCSD(<i>T</i>)	-92.731592	-92.714557	0.464
CH ₂ O ^{+,d}	X ² B ₂	A ² B ₁	Splitting
EOMIP-CCSD	-113.854249	-113.709737	3.932
EOMIP-CCSD*	-113.855014	-113.716591	3.767
UHF-CCSD	-113.849875	-113.712988	3.725
UHF-CCSD(<i>T</i>)	-113.858179	-113.718319	3.806
N ₂ ^{+,e}	X ² Σ _g	A ² Π _u	Splitting
EOMIP-CCSD	-108.739671	-108.675096	1.757
EOMIP-CCSD*	-108.746977	-108.697436	1.348
UHF-CCSD	-108.738740	-108.689880	1.330
UHF-CCSD(<i>T</i>)	-108.754336	-108.698133	1.529

^a $r(\text{OH}) = 1.0 \text{ \AA}$, $r(\text{OO}) = 1.4 \text{ \AA}$, $\theta(\text{HOO}) = 120^\circ$

^b $r(\text{OH}) = 1.0 \text{ \AA}$, $r(\text{CO}) = 1.45 \text{ \AA}$, $\theta(\text{HCO}) = 110^\circ$

^c $r(\text{CH}) = 1.0 \text{ \AA}$, $r(\text{CN}) = 1.2 \text{ \AA}$

^d $r(\text{CH}) = 1.0 \text{ \AA}$, $r(\text{CO}) = 1.2 \text{ \AA}$, $\theta(\text{HCO}) = 120^\circ$

^e $r(\text{NN}) = 1.097 \text{ \AA}$

systematically below the UHF-CCSD result in all cases. Although the root-mean-square (rms) deviation between UHF-CCSD energies and those obtained at the EOMIP-CCSD and EOMIP-CCSD* levels is similar (2.0 and 2.3 millihartrees, respectively), the former exhibit considerably more erratic behavior, falling as much as 11 millihartrees (mh) *above* (²Π state of HCN) and 7 mh *below* (²E state of the methoxy radical) the UHF-CCSD results. From this relatively small set of test cases, it appears that average differences between vertical ionization potentials calculated from UHF-CCSD energies and those inferred by the two EOMIP methods will be similar. The only distinction is that EOMIP-CCSD* is likely to

underestimate systematically UHF-CCSD values, while EOMIP-CCSD results would tend to scatter about them. Energy splittings amongst the $n-1$ electron final states may be predicted more reliably with the former method, however, due to its apparently more systematic behavior.

Perhaps most interesting is the rather good agreement between EOMIP-CCSD* energies and those calculated at the UHF-CCSD(T) level. The corresponding rms difference (1.2 mh) is about half that found when EOMIP-CCSD* and UHF-CCSD energies are compared; the behavior is again decidedly systematic with UHF-CCSD(T) somewhat below EOMIP-CCSD* for all of the example systems. These numerical results underscore the assertion of Nooijen [11], who showed that some treatment of connected triple excitations in the (n electron) reference state correlation is needed to counterbalance effects introduced by including $3h2p$ determinants in the description of the final states when these methods are used to calculate ionization potentials. The "connected triple excitation effects" included in EOMIP-CCSD* are entirely due to $3h2p$ operators in which none of the hole indices corresponds to the orbital that is depopulated in the appropriate zeroth-order Koopmans determinant ($|K\rangle$) that describes the state qualitatively. These operators generate determinants that are triply excited with respect to $|K\rangle$ with two electrons in orbitals not occupied in $|0\rangle$ and the third in the orbital that is occupied in $|0\rangle$ but empty in $|K\rangle$. However, EOMIP-CCSD* does not provide a comparable treatment of the other triply excited determinants (those with three electrons in orbitals unoccupied in $|0\rangle$), so it is dangerous to assume that UHF-CCSD(T) and EOMIP-CCSD* are complimentary methods. However, such questions are of practical importance only to those who would use EOMIP-CCSD* to calculate vertical ionization potentials since the issue of how to represent the initial state [CCSD vs. CCSD(T)] is then relevant. However, our interest lies not in this area, but rather with properties of the final states and, to a lesser extent, energy differences between them. The behavior of the EOMIP-CCSD* energies [which appear to be intermediate in quality between UHF-CCSD and UHF-CCSD(T)] is decidedly more systematic than that observed for EOMIP-CCSD. The former approach moreover gives doublet \rightarrow doublet excitation energies that are in uniformly better agreement with both UHF-CCSD and UHF-CCSD(T) values.

4 Conclusions

While further numerical experimentation is clearly needed to establish the relative reliabilities of EOMIP-CCSD and EOMIP-CCSD*, the results of the present study suggest that the latter method offers at least a modest improvement in the description of $n-1$ electron states. Due to this encouraging performance, it is enticing to speculate that similar improvements will be found when EOMIP-CCSD* is applied to the study of other properties. To investigate this issue, we are presently extending the theory for analytic energy derivative calculation at the EOMIP-CCSD level [5] to EOMIP-CCSD*. When a program for performing EOMIP-CCSD* analytic gradient calculations is available, the method will be applied to the demanding problem of characterizing potential energy surfaces of radicals and the study of representative chemical reactions involving molecules in doublet electronic states. At that time, a clear picture of the merits and limitations of the method should emerge.

To conclude, it should be emphasized that evaluation of the noniterative energy correction advocated here does not dominate the cost of the calculation. This

feature distinguishes EOMIP-CCSD* from related coupled-cluster approaches [such as CCSD(T)], since evaluation of the noniterative correction is rate-limiting in all other cases. Provided that the performance of EOMIP-CCSD* for the examples studied here is characteristic of what can be expected from the method, there is actually little reason *not* to include the correction in production calculations.

References

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14. See Lowdin PO (1962) *J Math Phys* 3:969 and reference therein
15. Despite the differences between \bar{H} and H , it should be remembered that they differ by a similarity transformation and therefore have identical spectra if the basis of $n-1$ electron determinants is not truncated
16. See, for example, Refs. [9, 10]
17. In the text, orbitals labeled $i, j, k \dots$ are those that are occupied in $|0\rangle$, while those labeled $a, b, c \dots$ are unoccupied
18. See, for example, Bartlett RJ, Watts JD, Kucharski SA, Noga J (1990) *Chem Phys Lett* 165:513
19. It should be pointed out that the approach used here can also be applied to “derive” corrections for the reference state CCSD description. The reference state CCSD energy is one of the roots of the n electron \bar{H} , specifically that for which the right eigenvector is the identity and the left eigenvector is the “lambda” vector of CC gradient theory [see Adamowicz L, Laidig WD, Bartlett RJ (1984) *Int J Quantum Chem (Symposium)* 18:245]. Following a procedure exactly analogous to that used in this work, one obtains the correction $\Delta E = \mathcal{L}_p^{(0)} \bar{H}^{[1]} [\lambda_0 - \bar{H}_{qq}^{[0]}]^{-1} \bar{H}^{[2]} \mathcal{G}_p^{(0)} = A \bar{H}^{[1]} [\lambda_0 - \bar{H}_{qq}^{[0]}]^{-1} \bar{H}^{[2]}$. This is identical to the triples correction used in the CCSD(T) method [see Ref. [18] and Raghavachari K, Trucks GW, Head-Gordon M, Pople JA (1989) *Chem Phys Lett* 157:479], except that the deexcitation amplitudes used in that approach are taken to be those of the T operator rather than those of A
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