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Perturbative treatment of the similarity transformed Hamiltonian in equation-of-motion coupled-cluster approximations

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A series of size-consistent approximations to the equation-of-motion coupled cluster method in the singles and doubles approximation (EOM-CCSD) are developed by subjecting the similarity transformed Hamiltonian $\bar{H} = \exp(-T)H \exp(T)$ to a perturbation expansion. Attention is directed to N and $N-1$ electron final state realizations of the method defined by truncation of \bar{H} at second order. Explicit spin-orbital equations for the energy and its first derivative are documented for both approaches [EOMEE-CCSD(2) and EOMIP-CCSD(2), respectively], and have been implemented in a large-scale quantum chemistry program. Vertical ionization potentials calculated by EOMIP-CCSD(2) are shown to be equivalent to those of an approach presented recently by Nooijen and Snijders [J. Chem. Phys. **102**, 1681 (1995)]. Applications of both EOMIP-CCSD(2) and EOMEE-CCSD(2) provide results for final state properties that compare favorably with those obtained in full EOM-CCSD calculations. Analysis of the computational aspects of the approximate and full EOM-CCSD methods shows that the cost of EOMIP-CCSD(2) energy and gradient calculations scales in proportion to the fifth power of the basis set size, a significant savings over the sixth power dependence of EOMIP-CCSD. This feature is of great practical importance, as it shows that this $N-1$ electron final state approach has a large domain of applicability and is therefore likely to become a valuable tool for application calculations. On the other hand, the same cannot be said for EOMEE-CCSD(2) since its asymptotic computational dependence and storage requirements are the same as the full EOMEE-CCSD method. © 1995 American Institute of Physics.

I. INTRODUCTION

In the past decade, coupled-cluster (CC) theory¹ has proven to be especially useful for molecular applications of quantum chemistry.² A common feature of CC methods is the assumption that correlated wave functions can be generated from a Slater determinant reference state ($|0\rangle$) by the action of an exponential wave operator

$$|\Psi_{\text{CC}}\rangle = \exp(T)|0\rangle. \quad (1)$$

In Eq. (1), T generates determinants in which one or more electrons have been promoted from spin orbitals that are filled in $|0\rangle$ to unoccupied levels, each weighted by a characteristic amplitude, $t_{ijk\cdots}^{abc\cdots}$,³

$$T = \sum_{i=1}^n T_i, \quad (2)$$

$$T_n = \frac{1}{n!^2} \sum_{\substack{ijk\cdots \\ abc\cdots}} t_{ijk\cdots}^{abc\cdots} \mathbf{a}_a^\dagger \mathbf{a}_i \mathbf{a}_b^\dagger \mathbf{a}_j \mathbf{a}_c^\dagger \mathbf{a}_k \cdots. \quad (3)$$

These amplitudes are solutions to a system of coupled nonlinear equations, and are usually obtained by iterative algorithms that employ some kind of preconditioning scheme.^{4,5} If T is not truncated [when n in Eq. (2) is equal to the number of electrons in the system], Eq. (1) represents an exact solution to the electronic Schrödinger equation in the space determined by the one-particle basis set. However, as for all methods that provide exact solutions, the cost of such

a calculation ultimately scales factorially with the size of the system. Hence, simplifications must be made when the theory is applied to chemical problems. Various CC approximations are obtained by limiting T to only certain levels of excitation. For example, the coupled-cluster doubles (CCD) method⁶ is based on the wave function parametrization $T = T_2$, while $T = T_1 + T_2$ defines the singles and doubles approximation known as CCSD.⁷ Both approaches are commonly used in quantum chemistry; the latter has gained more favor because it offers a superior treatment of dynamical electron correlation and orbital relaxation effects⁸ and is only marginally more expensive than CCD. Inclusion of higher excitations in T provides a systematically more accurate treatment of correlation, but at substantial cost. The amount of computer time required for calculations based on the CCSDT (Ref. 9) approximation that includes T_3 is proportional to the eighth power of the basis set dimension \mathcal{N} , while an \mathcal{N}^{10} cost is associated with CCSDTQ (Ref. 10) ($T = T_1 + T_2 + T_3 + T_4$). Because of these severe increases in computational expense (both CCD and CCSD scale with \mathcal{N}^6), various perturbative treatments of higher excitations have been formulated and implemented.¹¹

CC theory can also be used as the basis for deriving the many-body perturbation theory (MBPT) expansion of the wave function and energy.¹² For reference functions obtained in self-consistent field calculations, various orders of MBPT are recovered by suitable low-order iteration of the CC equations, meaning that each common CC approximation may be

viewed as the infinite-order counterpart of a specific level of MBPT. For example, CCD involves an infinite-order summation of all terms included in third-order MBPT [MBPT(3)], while CCSD is related in the same way to a frequently used fourth-order approximation that excludes effects of triple excitations [SDQ-MBPT(4)]. When dynamical correlation effects dominate, the perturbation expansion converges rapidly and the noniterative nature of MBPT makes it attractive for applications.¹³

Central to the success of any calculation that employs truncated CC or finite-order MBPT approximations is a requirement that the exact wave function can be reasonably approximated by a reference determinant, $|0\rangle$. This is generally true for the electronic ground state of closed-shell molecules, particularly organic and main-group inorganic compounds, so relatively inexpensive MBPT and CC treatments allow accurate predictions for a wide variety of systems. However, when the form of the wave function is poorly represented by $|0\rangle$, CC calculations based on low-level truncation of T are no longer adequate (equivalently, the MBPT expansion of the correlation energy converges slowly) and it becomes difficult to determine accurate molecular structures, properties, etc. Two classes of problems that are of substantial interest in chemical physics belong to this category; excited electronic states and quasidegenerate states of open-shell molecules. In both cases, two or more Slater determinants usually make appreciable contributions to the wave function and a balanced treatment is needed for accurate characterization. Traditionally, the best calculations for these systems have been based on zeroth-order multiconfigurational self-consistent field (MCSCF) wave functions,¹⁴ often augmented with a treatment of residual electron correlation via configuration interaction (MRCI) (Refs. 15 and 16) or perturbation theory.¹⁷ Although used with considerable success for small polyatomic molecules, these methods have prohibitive computational scaling properties; maintenance of a consistent level of accuracy involves a factorial dependence on the number of valence orbitals in the system.

In recent years, a group of methods closely related to CC theory has gained popularity for studies of open-shell systems and excited states. These equation-of-motion CC (EOM-CC) approaches^{18–25} provide an even-handed treatment of several Slater determinants while retaining the geometric (as opposed to factorial) computational scaling properties of ground state CC methods. While EOM-CC theory can be formulated in terms of a commutator and is related to Green's function approaches²⁵ (hence the name "equation of motion"²⁶), it is equally valid to view the final states as solutions to a configuration interaction problem involving the similarity transformed Hamiltonian

$$\bar{H} \equiv \exp(-T)H \exp(T). \quad (4)$$

In Eq. (4), T is determined by solving a set of CC equations for a reference state which is usually, but not necessarily, the ground state of an N electron system. The spectrum of \bar{H} includes the correlated reference state as well as approximations to excited states. Diagonalization of \bar{H} in other sectors of Fock space provides solutions that correspond to different ionization states (for example, the diagonal representation of

\bar{H} in the $N-1$ particle space approximates singly ionized states of an N electron system), in which several zeroth-order determinants are again treated equivalently. To date, most implementations of EOM-CC have been based on the CCSD approximation for the ground state,^{20–23} and these "EOM-CCSD" methods have been applied to chemical problems with considerable success.^{27–32} An important advance has been the formulation and implementation of analytic energy derivative methods for EOM-CCSD approaches for excited electronic states³³ (EOMEE-CCSD, \bar{H} is diagonalized in the N electron space spanned by $|0\rangle$ and determinants related to it by promotion of one or two electrons) and singly ionized states³⁴ [EOMIP-CCSD, \bar{H} diagonalized in the $N-1$ electron space spanned by electron detached (Koopmans) determinants and those related to them by promotion of an electron to an orbital that is unoccupied in $|0\rangle$], as these methods can now be routinely used to study potential energy surfaces and properties of polyatomic molecules.

One area ripe for theoretical development and insight is the formulation of methods similar to EOM-CC but which involve additional simplifications. The motivation for such effort is entirely practical, since any approximation to a particular EOM-CC model is necessarily inferior. Nevertheless, substantially less expensive treatments that are comparable in accuracy to full EOM-CC would be valuable for applications. To our knowledge, only two such ideas have been presented in the chemical literature.³⁵ For excited electronic states, Head-Gordon *et al.*³⁶ have developed a perturbation theory that uses the configuration interaction singles (CIS), or Tamm-Dancoff approximation, as the zeroth-order wave function. Analysis of this method, which is known as CIS(D), shows that it represents a second-order approximation to EOMEE-CCSD. Excitation energies evaluated at the CIS(D) level are generally in good agreement with full EOM-CCSD values.³⁶ Furthermore, a recent study of potential energy surfaces indicates that CIS(D) provides an improvement over CIS, provided the zeroth-order function does not fall in a quasidegenerate region of the spectrum.³⁷ A method somewhat similar to EOMIP-CCSD has been suggested by Nooijen and Snijders,³⁸ in which \bar{H} is approximated by replacing the T operator in Eq. (4) with its lowest-order MBPT approximation. Diagonalization of the resulting transformed Hamiltonian in the $N-1$ particle space does not provide size-consistent final state energies like those obtained in full EOMIP-CCSD calculations, a problem which the authors of Ref. 38 circumvent by developing the method in terms of Green's function theory and employing a commutator. Although this complicates the identification of a *total* final state energy, ionization potentials obtained in these calculations agree rather well with EOMIP-CCSD values.³⁸

We adopt an alternative approach for determining approximate solutions to the EOM-CCSD equations which is closer in spirit to the strategy of Nooijen and Snijders³⁸ than that of Head-Gordon *et al.*³⁶ The basis of the proposed method is a perturbation expansion of the similarity transformed Hamiltonian, with specific methods defined by consistent truncation at a given order. A set of energies and wave functions is obtained by diagonalizing the resulting effective operator. In this work, attention will be restricted to methods

for excited and ionized states that are based on second-order truncation of \tilde{H} . It will be argued that this class of approximate methods is best suited for calculations of final state properties. To facilitate such efforts, an efficient formalism for evaluating energy derivatives has been developed and implemented; all relevant equations are presented and their computational scaling properties are briefly discussed in the following section. Finally, both of the approximate methods will be applied to a representative example, and results will be compared to those obtained in calculations based on theoretically more complete EOM-CCSD methods.

II. THEORY

A. Form and diagonal representation of truncated operator

The central idea that forms the basis for the class of approximate EOM-CCSD methods proposed here is that the similarity transformed Hamiltonian defined by Eq. (4) can be expanded in a perturbation series

$$\tilde{H} = \tilde{H}^{[0]} + \tilde{H}^{[1]} + \tilde{H}^{[2]} + \dots, \quad (5)$$

where the bracketed superscript refers to order in the correlation perturbation. Before continuing, it is important to recognize that the operator product $\exp(-T)H\exp(T)$ is equivalent to the truncated commutator expansion

$$\begin{aligned} \tilde{H} = H &+ [H, T] + \frac{1}{2}[[H, T], T] + \frac{1}{6}[[[H, T], T], T] \\ &+ \frac{1}{24}[[[[H, T], T], T], T]. \end{aligned} \quad (6)$$

Equation (6) includes no additional terms because the Hamiltonian contains only one and two-particle operators. Alternatively, \tilde{H} is given by

$$\tilde{H} = [H \exp(T)]_c, \quad (7)$$

where c implies a restriction to terms that have a connected diagrammatic representation. Algebraically, the only nonvanishing contributions are those in which Hamiltonian matrix elements share at least one index with all participating T amplitudes; all others cancel because of the commutators that appear in Eq. (6) since elements of the T operator commute with one another.

After separating H into a zeroth-order part $H^{[0]}$ and the perturbing Hamiltonian $H^{[1]}$ (e.g., Møller–Plesset partitioning), wave function parameters are generated in the usual way

$$T^{[0]} = 0 \quad (8)$$

$$\langle \mathbf{g} | H^{[0]} - E^{[0]} | \mathbf{g} \rangle \langle \mathbf{g} | T^{[1]} | 0 \rangle = - \langle \mathbf{g} | H^{[1]} | 0 \rangle \quad (9)$$

$$\begin{aligned} \langle \mathbf{g} | H^{[0]} - E^{[0]} | \mathbf{g} \rangle \langle \mathbf{g} | T^{[2]} | 0 \rangle &= - \langle \mathbf{g} | H^{[1]} | \mathbf{g} \rangle \langle \mathbf{g} | T^{[1]} | 0 \rangle \\ &\quad + \langle \mathbf{g} | E^{[1]} | \mathbf{g} \rangle \langle \mathbf{g} | T^{[1]} | 0 \rangle \end{aligned} \quad (10)$$

\vdots

In the preceding equations as well as throughout the remainder of this section, the set of all Slater determinants \mathbf{h} is partitioned into a reference function $|0\rangle$ (an eigenfunction of

the zeroth-order Hamiltonian $H^{[0]}$) and those related to it by promotion of one or more electrons. The latter set of determinants will be denoted by the symbol \mathbf{g} [$\mathbf{h} \equiv |0\rangle \cup \mathbf{g}$]. In discussing the proposed EOM-CCSD approximations, it is convenient to decompose \mathbf{g} into $\mathbf{p} \cup \mathbf{q}$, where \mathbf{p} is the set of determinants related to $|0\rangle$ by excitation of one or two electrons and \mathbf{q} contains determinants related to $|0\rangle$ by threefold or higher excitation. Finally, the sets of singly and doubly excited determinants will be denoted by \mathbf{s} and \mathbf{d} , respectively.

Once amplitudes of the $T^{[n]}$ operators are determined, terms contributing to \tilde{H} can be collected according to the overall order of perturbation,

$$\tilde{H}^{[0]} = H^{[0]} \quad (11)$$

$$\tilde{H}^{[1]} = H^{[1]} + (H^{[0]}T^{[1]})_c \quad (12)$$

$$\tilde{H}^{[2]} = (H^{[0]}T^{[2]})_c + (H^{[1]}T^{[1]})_c + \frac{1}{2}(H^{[0]}T^{[1]}T^{[1]})_c \quad (13)$$

$$\begin{aligned} \tilde{H}^{[3]} &= (H^{[0]}T^{[3]})_c + (H^{[1]}T^{[2]})_c + \frac{1}{2}(H^{[1]}T^{[1]}T^{[1]})_c \\ &\quad + (H^{[0]}T^{[1]}T^{[2]})_c \end{aligned} \quad (14)$$

\vdots

It is now possible to identify a set of hierarchical approximations to the full \tilde{H} operator, the elements of which are complete through a given order of perturbation theory

$$\tilde{H}^{(n)} \equiv \tilde{H}^{[0]} + \tilde{H}^{[1]} + \tilde{H}^{[2]} + \dots + \tilde{H}^{[n]}. \quad (15)$$

In Eq. (15), a notational convention is introduced in which superscripts enclosed by parenthesis indicate that the quantity contains all contributions up to and including those that are n th order in correlation. In order to develop a set of methods that converge to the EOM-CCSD result as n becomes large, only the one- and two-particle parts of T are considered. The diagonal representation of the resulting $\tilde{H}^{(n)}$ offers an approximation to the EOM-CCSD final states. We designate the corresponding theoretical method as EOM-CCSD(n). One obvious alternative would be EOM-MBPT(n), but this would be misleading because the proposed method is *not* a proper perturbation theory since matrix diagonalization is involved. This should be contrasted with the CIS(D) method advocated by Head-Gordon *et al.*,³⁶ which is a rigorous second-order approximation for excited electronic states.

In this work, a conventional partitioning scheme is adopted in which the occupied–occupied and virtual–virtual projections of the Fock operator are assigned to the zeroth-order Hamiltonian,

$$H^{[0]} = |\mathbf{i}\rangle\langle\mathbf{i}|F|\mathbf{j}\rangle\langle\mathbf{j}| \oplus |\mathbf{a}\rangle\langle\mathbf{a}|F|\mathbf{b}\rangle\langle\mathbf{b}| \quad (16)$$

$$H^{[1]} = H - H^{[0]}, \quad (17)$$

and it will further be assumed that the reference determinant $|0\rangle$ is formed from a set of molecular orbitals that satisfy the Brillouin condition $\langle \mathbf{s} | H | 0 \rangle = 0$. Because of the latter assumption, only doubly excited determinants contribute to the first-order perturbed wave function, meaning that $\langle \mathbf{g} | T^{[1]} | 0 \rangle = \langle \mathbf{d} | T^{[1]} | 0 \rangle$. Furthermore, the final terms in Eqs. (13) and (14) vanish for this choice of $H^{[0]}$.

The remainder of this section focuses on the EOM-CCSD(2) approximation in which \tilde{H} is expanded through second order in the correlation perturbation. In the determinantal basis, $\tilde{H}^{(2)}$ contains one-, two-, and three-particle contributions as well as the constant term $\langle 0|\tilde{H}^{(2)}|0\rangle$, which is the total MBPT(2) energy of the reference state

$$\begin{aligned}\tilde{H}^{(2)} = & \langle 0|\tilde{H}^{(2)}|0\rangle + \mathcal{F}_q^p \{ \mathbf{a}_p^\dagger \mathbf{a}_q \} + \frac{1}{4} \mathcal{W}_{rs}^{pq} \{ \mathbf{a}_p^\dagger \mathbf{a}_q^\dagger \mathbf{a}_s \mathbf{a}_r \} \\ & + \frac{1}{36} \mathcal{X}_{stu}^{pqrs} \{ \mathbf{a}_p^\dagger \mathbf{a}_q^\dagger \mathbf{a}_r^\dagger \mathbf{a}_s^\dagger \mathbf{a}_u \mathbf{a}_t \},\end{aligned}\quad (18)$$

where the braces enclosing the electron construction operators specify that they are in normal order with respect to $|0\rangle$. Using spin-orbital notation and the Einstein summation convention, matrix elements of $\tilde{H}^{(2)}$ are given by

$$\mathcal{F}_j^i = f_{ij} + \frac{1}{2} t_{jm}^{ef} \langle im || ef \rangle, \quad (19)$$

$$\mathcal{F}_b^a = f_{ab} - \frac{1}{2} t_{mn}^{ea} \langle mn || eb \rangle, \quad (20)$$

$$\mathcal{F}_i^i = 0, \quad (21)$$

$$\mathcal{F}_a^i = 0, \quad (22)$$

$$\mathcal{W}_{kl}^{ij} = \langle ij || kl \rangle + \frac{1}{2} t_{kl}^{ef} \langle ij || ef \rangle, \quad (23)$$

$$\mathcal{W}_{ka}^{ij} = \langle ij || ka \rangle, \quad (24)$$

$$\mathcal{W}_{jk}^{ia} = \langle ia || jk \rangle + \frac{1}{2} t_{jk}^{ef} \langle ia || ef \rangle - P_-(jk) t_{jm}^{ea} \langle im || ek \rangle, \quad (25)$$

$$\mathcal{W}_{ab}^{ij} = \langle ij || ab \rangle, \quad (26)$$

$$\mathcal{W}_{ij}^{ab} = 0, \quad (27)$$

$$\mathcal{W}_{jb}^{ia} = \langle ia || jb \rangle + P_-(ab) P_-(ij) t_{mj}^{ea} \langle im || eb \rangle, \quad (28)$$

$$\mathcal{W}_{ci}^{ub} = \langle ab || ci \rangle - P_-(ab) t_{im}^{ea} \langle bm || ec \rangle + \frac{1}{2} t_{mn}^{ab} \langle mn || ci \rangle, \quad (29)$$

$$\mathcal{W}_{bc}^{ai} = \langle ai || bc \rangle, \quad (30)$$

$$\mathcal{W}_{cd}^{ub} = \langle ab || cd \rangle + \frac{1}{2} t_{mn}^{ab} \langle mn || cd \rangle, \quad (31)$$

$$\mathcal{X}_{icd}^{abj} = t_{im}^{ab} \langle mj || cd \rangle, \quad (32)$$

$$\mathcal{X}_{ijb}^{akl} = -t_{ij}^{ae} \langle kl || eb \rangle, \quad (33)$$

$$\mathcal{X}_{ijc}^{abk} = P_-(ab) t_{ij}^{af} \langle bk || fc \rangle - P_-(ij) t_{im}^{ab} \langle mk || jc \rangle, \quad (34)$$

where the list of three-body terms (the \mathcal{X}_{stu}^{pqrs}) is limited to those that contribute to the EOMIP-CCSD(2) and EOMEE-CCSD(2) eigenvalue problems considered here. In Eqs. (19)–(34), the f_{pq} and $\langle pq || rs \rangle$ are Fock matrix elements and antisymmetrized two-electron integrals, respectively. The permutation operator $P_-(pq)$ is defined by its action on the arbitrary function \mathcal{F} ,

$$\begin{aligned}P_-(rs) \mathcal{F}(pqrs \cdots tuv) = & \mathcal{F}(pqrs \cdots tuv) \\ & - \mathcal{F}(pqsr \cdots tuv).\end{aligned}\quad (35)$$

The t_{ij}^{ab} amplitudes that contribute to $\tilde{H}^{(2)}$ are those that weight doubly excited determinants in the *first-order* perturbed wave function. All contributions involving second-order amplitudes [the first term in Eq. (13)] cancel with cer-

tain first-order contributions. This can be seen when it is realized that $H^{[0]}T^{[2]}$ is a pure excitation operator and therefore contributes only to $\langle \mathbf{g} | \tilde{H}^{(2)} | 0 \rangle$,

$$\langle \mathbf{g} | \tilde{H}^{(2)} | 0 \rangle = \langle \mathbf{g} | (H^{[0]}T^{[2]})_c | 0 \rangle + \langle \mathbf{g} | (H^{[1]}T^{[1]})_c | 0 \rangle \quad (36)$$

$$= -\langle \mathbf{g} | (H^{[1]}T^{[1]})_c | 0 \rangle + \langle \mathbf{g} | (H^{[1]}T^{[1]})_c | 0 \rangle \quad (37)$$

$$= 0, \quad (38)$$

where Eq. (10) is used in the second step. Similarly straightforward analysis reveals that $\langle \mathbf{g} | \tilde{H}^{(n)} | 0 \rangle$ vanishes for all values of n . This condition insures that final state energies obtained by diagonalizing the matrix will be size-consistent, in the sense that energies obtained in monomer calculations will persist in a supermolecule system.^{20,39} It therefore follows that all EOM-CCSD(n) approximations are size-consistent by construction. Furthermore, because of the resulting block structure of the transformed Hamiltonian,

$$\tilde{H}^{(n)} = \begin{pmatrix} \tilde{H}_{00}^{(n)} & \tilde{H}_{0s}^{(n)} & \tilde{H}_{0d}^{(n)} \\ 0 & \tilde{H}_{ss}^{(n)} & \tilde{H}_{sd}^{(n)} \\ 0 & \tilde{H}_{ds}^{(n)} & \tilde{H}_{dd}^{(n)} \end{pmatrix}, \quad (39)$$

the reference state expectation value of $\tilde{H}^{(n)}$ [i.e., the MBPT(2) ground state energy for EOM-CCSD(2); MBPT(3) for EOM-CCSD(3); SDQ-MBPT(4) for EOM-CCSD(4), etc.] is an element of the eigenvalue spectrum, a feature that allows a correlated reference state to be associated with the final states. Finally, it should be mentioned that $\tilde{H}_{0s}^{(n)}$ vanishes for EOM-CCSD(2) since the first contribution to \mathcal{F}_a^i occurs at third order.⁴⁰

The $\tilde{H}^{(2)}$ matrix can be diagonalized with precisely the same strategy and computer code used for the full EOM-CCSD approach, as only the numerical values of the matrix elements differ. In particular, both features that distinguish the EOM-CCSD eigenproblem from a standard configuration interaction calculation in the basis of $|0\rangle$, $|s\rangle$, and $|d\rangle$ —non-Hermiticity of \tilde{H} and the need to consider three-particle operators—are already present at the EOM-CCSD(2) level of approximation. Computational strategies for dealing with both of these features have been presented in the literature,²¹ and will not be discussed here. The diagonal representation of $\tilde{H}^{(2)}$ (like the full \tilde{H}) provides a biorthogonal description of final states parametrized by the left- and right-hand eigenvectors (\mathcal{L} and \mathcal{R} , respectively) as well as the ground state T amplitudes.⁴¹ The exact form of \mathcal{L} and \mathcal{R} is dictated by the set of final states under consideration. For example, in applications to excited electronic states in the CCSD approximation, the transformed Hamiltonian is diagonalized in a truncated N particle space and the eigenvectors have the operator representation

$$\mathcal{L} \equiv \sum_{ai} l_a^i \mathbf{a}_i^\dagger \mathbf{a}_a + \frac{1}{4} \sum_{abij} l_{ab}^{ij} \mathbf{a}_i^\dagger \mathbf{a}_a^\dagger \mathbf{a}_j \mathbf{a}_b, \quad (40)$$

$$\mathcal{R} \equiv r_0 + \sum_{ai} r_i^a \mathbf{a}_a^\dagger \mathbf{a}_i + \frac{1}{4} \sum_{abij} r_{ij}^{ab} \mathbf{a}_a^\dagger \mathbf{a}_i^\dagger \mathbf{a}_b \mathbf{a}_j, \quad (41)$$

while ionized state calculations explore the spectrum of \tilde{H} in the space spanned by a subset of $N-1$ particle determinants and the eigenvectors no longer correspond to particle-conserving operators

$$\mathcal{L} \equiv \sum_i l_i^\dagger \mathbf{a}_i^\dagger + \frac{1}{2} \sum_{ija} l_{ij}^a \mathbf{a}_i^\dagger \mathbf{a}_a \mathbf{a}_j^\dagger, \quad (42)$$

$$\mathcal{R} \equiv \sum_i r_i \mathbf{a}_i + \frac{1}{2} \sum_{ija} r_{ij}^a \mathbf{a}_i^\dagger \mathbf{a}_a \mathbf{a}_j. \quad (43)$$

B. Connection to the method of Nooijen and Snijders

Quite recently, Nooijen and Snijders³⁸ have suggested an approximate EOMIP-CCSD method which superficially appears to differ substantially from that proposed here. In their work, the full CCSD similarity transformed Hamiltonian is approximated by

$$\tilde{H}_{NS} \equiv \exp(-T^{[1]}) H \exp(T^{[1]}) \quad (44)$$

which is complete only through first order in correlation but contains selected contributions to $\tilde{H}^{[n]}$ for $n=2-5$.⁴² A critical difference between \tilde{H}_{NS} and $\tilde{H}^{(n)}$ is that explicit diagonalization of the former does not provide a size-consistent set of final state energies because the condition $\langle \mathbf{p} | \tilde{H}_{NS} | 0 \rangle = 0$ is not satisfied. However, the problematic disconnected products in the right eigenvector problem are eliminated in the Nooijen–Snijders (NS) method by considering not the matrix elements of \tilde{H}_{NS} itself, but rather

$$\mathbf{A}_{\mu\nu} \equiv \langle 0 | \Omega_\mu [\tilde{H}_{NS}, \Omega_\nu^\dagger] | 0 \rangle, \quad (45)$$

where the Ω^\dagger represent elements of the set of construction operator strings that map $|0\rangle$ into the determinants that span the diagonalization space. It is not difficult to show that the matrix elements of \mathbf{A} and $\tilde{H}^{(2)}$ in the space of all Koopmans determinants and those related to them by excitation of a single electron [$\Omega^\dagger = \{\mathbf{a}_i; \mathbf{a}_i^\dagger \mathbf{a}_a^\dagger \mathbf{a}_j\}$] are *identical*, apart from the constant term of the latter [which corresponds to the total reference state MBPT(2) energy]. All terms in \mathbf{A} that are third and higher order in correlation do not contribute to the truncated diagonalization problem and all “missing” second order terms are implicitly accounted for by the commutator in Eq. (45). Thus, energy *differences* (ionization potentials) calculated with the NS method are precisely equal to corresponding EOM-CCSD(2) values!

The fundamental difference between the EOM-CCSD(2) formulation and the NS method is that the former has a clearly defined *total* energy. This is a desirable feature, since it permits an unambiguous definition of final state properties and potential energy surfaces. One could even argue that EOM-CCSD(2) is more appropriate for final state studies than calculations of energy differences (excitation energies and ionization potentials) since there is a marked difference in the treatment of reference and final states at this level of theory. The former are described by the standard MBPT(2) approximation, while the matrix diagonalization confers a degree of infinite-order character to the final states obtained in EOM-CCSD(2) calculations. Thus, the $N-1$ electron ionized states and N electron excited states best represented by the parametrization—those corresponding to “principal”

ionizations and “single” excitations⁴³—are treated in a consistent fashion at this level of theory. The benchmark ionization potential calculations reported in Nooijen and Snijders’ paper³⁸ are illuminating in this regard. They found that vertical ionization potentials predicted with the NS method deviate systematically from the EOMIP-CCSD values, but that the magnitude of the discrepancy varies only slightly over the principal ionization spectrum. Of course, this is consistent with the fact that the final states are all described by a common parametrization, which in turn differs from that describing the reference state. While one might assume that the treatment of final states is superior due to the inclusion of infinite-order summations in their description, it should be remembered that the molecular orbitals are optimized for the reference state. Furthermore, the method is based on a truncated similarity transformation, and the eigenvalues of $\tilde{H}^{(2)}$ and the true electronic Hamiltonian are therefore inequivalent. The apparent suitability of EOM-CCSD(2) for direct studies of final states provides motivation for developing and implementing a strategy for analytic evaluation of energy derivatives. This subject is addressed in the following subsection.

One advantage of the EOM-CCSD(n) strategy is that it defines a natural sequence of approximations that are size-consistent for all n and converge to the full EOM-CCSD result. It is less clear how to develop analogous extensions of the NS approach. Nevertheless, it must be emphasized that Nooijen and Snijders were the first to recognize and capitalize upon the computational advantages associated with ionized state calculations that are based on an approximate \tilde{H} operator (see Sec. II D for a detailed discussion). Indeed, their exploratory work is what first interested us in this area.

C. Analytic evaluation of energy derivatives

The most convenient starting point for deriving an expression for analytic EOM-CCSD(2) derivatives is the functional representation of the energy

$$E = \langle 0 | \mathcal{L} H \mathcal{R} | 0 \rangle + \langle 0 | \mathcal{L} (H^{[0]} T^{[1]})_c \mathcal{R} | 0 \rangle + \langle 0 | \mathcal{L} (H^{[1]} T^{[1]})_c \mathcal{R} | 0 \rangle + \langle 0 | \mathcal{L} (H^{[0]} T^{[2]})_c \mathcal{R} | 0 \rangle, \quad (46)$$

in which the zeroth-order and perturbing Hamiltonian contributions are both included in the leading term. It is possible to dispense with both the second and last terms since $H^{[0]} T^{[1]}$ and $H^{[0]} T^{[2]}$ are excitation operators (and therefore contribute only to vanishing $\langle \mathbf{p} | \tilde{H}^{[n]} | 0 \rangle$ matrix elements). This is accomplished by excluding all contributions to the remaining terms in which the Hamiltonian is not connected to (does not share indices with) the \mathcal{R} operator except for the constant terms $\langle 0 | H | 0 \rangle$ and $\langle 0 | H^{[1]} T^{[1]} | 0 \rangle$ that determine the reference state MBPT(2) energy, i.e.,

$$E = \langle 0 | \mathcal{L} (H \mathcal{R})_c | 0 \rangle + \langle 0 | \mathcal{L} (\tilde{H}^{[1]} T^{[1]} \mathcal{R})_c | 0 \rangle + \langle 0 | H^{[1]} T^{[1]} | 0 \rangle + \langle 0 | H | 0 \rangle. \quad (47)$$

In passing, we note that the r_0 amplitude makes no contribution to the final state energy. Straightforward differentiation of Eq. (47) with respect to the general perturbation χ yields

$$\begin{aligned}
\frac{\partial E}{\partial \chi} = & \langle 0 | \frac{\partial \mathcal{L}}{\partial \chi} (H \mathcal{R})_c | 0 \rangle + \langle 0 | \mathcal{L} \left(H \frac{\partial \mathcal{R}}{\partial \chi} \right)_c | 0 \rangle + \langle 0 | \mathcal{L} \left(\frac{\partial H}{\partial \chi} \mathcal{R} \right)_c | 0 \rangle + \langle 0 | \frac{\partial \mathcal{L}}{\partial \chi} (H^{[1]} T^{[1]} \mathcal{R})_c | 0 \rangle \\
& + \langle 0 | \mathcal{L} \left(H^{[1]} T^{[1]} \frac{\partial \mathcal{R}}{\partial \chi} \right)_c | 0 \rangle + \langle 0 | \mathcal{L} \left(\frac{\partial H^{[1]}}{\partial \chi} T^{[1]} \mathcal{R} \right)_c | 0 \rangle + \langle 0 | \mathcal{L} \left(H^{[1]} \frac{\partial T^{[1]}}{\partial \chi} \mathcal{R} \right)_c | 0 \rangle + \langle 0 | \frac{\partial H^{[1]}}{\partial \chi} T^{[1]} | 0 \rangle \\
& + \langle 0 | H^{[1]} \frac{\partial T^{[1]}}{\partial \chi} | 0 \rangle + \langle 0 | \frac{\partial H}{\partial \chi} | 0 \rangle.
\end{aligned} \quad (48)$$

It is not difficult to show that the four terms which depend on the eigenvector derivatives sum to zero,⁴⁴

$$\begin{aligned}
& \langle 0 | \frac{\partial \mathcal{L}}{\partial \chi} ([H + H^{[1]} T^{[1]}] \mathcal{R})_c | 0 \rangle \\
& + \langle 0 | \mathcal{L} \left([H + H^{[1]} T^{[1]}] \frac{\partial \mathcal{R}}{\partial \chi} \right)_c | 0 \rangle \\
& = [E - E_{\text{reference state}}^{\text{MBPT}(2)}] \frac{\partial}{\partial \chi} \langle 0 | \mathcal{L} \mathcal{R} | 0 \rangle = 0
\end{aligned} \quad (49)$$

since the eigenvector binormalization condition can always be chosen so that $\langle 0 | \mathcal{L} \mathcal{R} | 0 \rangle$ is equal to unity. Thus, the only surviving terms are

$$\begin{aligned}
\frac{\partial E}{\partial \chi} = & \langle 0 | \mathcal{L} \left(\frac{\partial H}{\partial \chi} \mathcal{R} \right)_c | 0 \rangle + \langle 0 | \mathcal{L} \left(\frac{\partial H^{[1]}}{\partial \chi} T^{[1]} \mathcal{R} \right)_c | 0 \rangle \\
& + \langle 0 | \frac{\partial H^{[1]}}{\partial \chi} T^{[1]} | 0 \rangle + \langle 0 | \frac{\partial H}{\partial \chi} | 0 \rangle \\
& + \langle 0 | \mathcal{L} \left(H^{[1]} \frac{\partial T^{[1]}}{\partial \chi} \mathcal{R} \right)_c | 0 \rangle + \langle 0 | H^{[1]} \frac{\partial T^{[1]}}{\partial \chi} | 0 \rangle.
\end{aligned} \quad (50)$$

All but the last two contributions are of the generalized Hellman–Feynman form and are easily handled computationally by constructing an effective density matrix and contracting it with the differentiated electronic Hamiltonian.⁴⁵ Evaluation of the Hamiltonian matrix elements does not involve a rate-limiting computational dependence, so the cost associated with the first four terms is not sensitive to the number of perturbations. The remaining terms, however, involve derivatives of the first-order reference state wave function parameters and it would be inconvenient to evaluate them via a straightforward implementation of Eq. (50). Fortunately, the Dalgarno–Stewart interchange technique⁴⁶ (also known as the Z-vector method⁴⁷) can be used to eliminate explicit contributions of perturbed wave function parameters to the first derivative of the energy. Although the strategy followed in our energy derivative formalism for the full EOM-CCSD method does not exploit the fact that $\langle \mathbf{p} | \tilde{H} | 0 \rangle = 0$, a similar but slightly more complicated application of the in-interchange technique suffices to eliminate $T^{[1]}$ from the gradient expression given by Eq. (50). To begin, the terms involving derivative $T^{[1]}$ amplitudes are written in the equivalent form

$$\langle 0 | \overbrace{\mathcal{L} H^{[1]} \mathcal{R}}^{\text{contraction}} | \mathbf{d} \rangle \langle \mathbf{d} | \frac{\partial T^{[1]}}{\partial \chi} | 0 \rangle + \langle 0 | H^{[1]} | \mathbf{d} \rangle \langle \mathbf{d} | \frac{\partial T^{[1]}}{\partial \chi} | 0 \rangle, \quad (51)$$

where contraction lines in the first term serve to indicate that the Hamiltonian shares indices with both the \mathcal{R} operator and those that label the doubly promoted intermediate state determinants. By differentiating both sides of Eq. (9),

$$\begin{aligned}
& \langle \mathbf{d} | \frac{\partial (H^{[0]} - E^{[0]})}{\partial \chi} | \mathbf{d} \rangle \langle \mathbf{d} | T^{[1]} | 0 \rangle \\
& + \langle \mathbf{d} | (H^{[0]} - E^{[0]}) | \mathbf{d} \rangle \langle \mathbf{d} | \frac{\partial T^{[1]}}{\partial \chi} | 0 \rangle = - \langle \mathbf{d} | \frac{\partial H^{[1]}}{\partial \chi} | 0 \rangle
\end{aligned} \quad (52)$$

and solving for $\langle \mathbf{d} | (\partial T^{[1]} / \partial \chi) | 0 \rangle$, one obtains an equivalent expression for the final two contributions to the derivative

$$\begin{aligned}
\frac{\partial E}{\partial \chi} \leftarrow & - \{ \langle 0 | \overbrace{\mathcal{L} H^{[1]} \mathcal{R}}^{\text{contraction}} | \mathbf{d} \rangle + \langle 0 | H^{[1]} | \mathbf{d} \rangle \} \\
& \times [\langle \mathbf{d} | (H^{[0]} - E^{[0]}) | \mathbf{d} \rangle]^{-1} \left[\langle \mathbf{d} | \frac{\partial H^{[1]}}{\partial \chi} | 0 \rangle \right. \\
& \left. + \langle \mathbf{d} | \frac{\partial (H^{[0]} - E^{[0]})}{\partial \chi} T^{[1]} | 0 \rangle \right].
\end{aligned} \quad (53)$$

By introducing first-order de-excitation operators Ξ and \mathcal{Z} defined by

$$\langle 0 | \Xi | \mathbf{d} \rangle \equiv \langle 0 | \overbrace{\mathcal{L} H^{[1]} \mathcal{R}}^{\text{contraction}} | \mathbf{d} \rangle + \langle 0 | H^{[1]} | \mathbf{d} \rangle \quad (54)$$

and

$$\langle 0 | \mathcal{Z} | \mathbf{d} \rangle \equiv - \langle 0 | \Xi | \mathbf{d} \rangle [\langle \mathbf{d} | (H^{[0]} - E^{[0]}) | \mathbf{d} \rangle]^{-1}, \quad (55)$$

the EOM-CCSD(2) energy derivative takes the form

$$\begin{aligned}
\frac{\partial E}{\partial \chi} = & \langle 0 | \mathcal{L} \left(\frac{\partial H}{\partial \chi} \mathcal{R} \right)_c | 0 \rangle + \langle 0 | \mathcal{L} \left(\frac{\partial H^{[1]}}{\partial \chi} T^{[1]} \mathcal{R} \right)_c | 0 \rangle \\
& + \langle 0 | \frac{\partial H}{\partial \chi} | 0 \rangle + \langle 0 | \mathcal{Z} \frac{\partial H^{[1]}}{\partial \chi} | 0 \rangle \\
& + \langle 0 | \mathcal{Z} \frac{\partial (H^{[0]} - E^{[0]})}{\partial \chi} T^{[1]} | 0 \rangle,
\end{aligned} \quad (56)$$

which depends solely on unperturbed wave function parameters; the ζ_{ab}^{ij} amplitudes that parametrize \mathcal{Z} and account for the first-order response of $T^{[1]}$; and the differentiated elec-

tronic Hamiltonian. In passing, it should be noted that the strategy used to eliminate the derivative amplitudes is nearly identical to that applied in our earlier work on full EOM-CCSD gradients,^{33,34} but there is an important *computational* difference. In the latter case, amplitudes of the \mathcal{L} operator are obtained by solving a system of linear equations with a nondiagonal coefficient matrix. This is most efficiently accomplished with iterative methods,⁴⁸ and necessitates a computational effort that is proportional to the sixth power of the number of basis functions. However, for EOM-CCSD(2), the matrix of coefficients is *diagonal* (provided canonical molecular orbitals are used); solution of Eq. (54) is therefore trivial and involves only an \mathcal{N}^4 computational scaling. Thus, solving the \mathcal{L} equations is not a rate-determining step in EOM-CCSD(2) gradient evaluation.

Because the only differentiated parameters in the gradient expression given by Eq. (56) are those of the electronic Hamiltonian, the equations can be recast in terms of a contraction between one- and two-particle effective density matrices and the matrix elements of $\partial H/\partial \chi$,

$$\frac{\partial E}{\partial \chi} = \rho_q^p \frac{\partial f_{pq}}{\partial \chi} + \frac{1}{4} \rho_{rs}^{pq} \frac{\partial \langle pq || rs \rangle}{\partial \chi}. \quad (57)$$

Again using the Einstein summation convention, explicit spin orbital expressions for the effective density matrix elements (which depend only upon amplitudes of the \mathcal{L} , \mathcal{R} , $T^{[1]}$, and \mathcal{Z} operators) are

$$\rho_j^i = -l_e^i r_j^e - \frac{1}{2} l_{ef}^{im} r_{jm}^{ef} - \frac{1}{2} t_{jm}^{ef} \zeta_{ef}^{im} + \delta_{ij}, \quad (58)$$

$$\rho_b^a = l_b^m r_m^a + \frac{1}{2} l_{eb}^{mn} r_{mn}^{ea} + \frac{1}{2} t_{mn}^{ae} \zeta_{be}^{mn}, \quad (59)$$

$$\rho_a^i = l_{ae}^{im} r_m^e, \quad (60)$$

$$\rho_i^a = -\frac{1}{2} l_{ef}^{mn} r_i^f t_{mn}^{ea} - \frac{1}{2} l_{ef}^{mn} r_n^a t_{im}^{ef} + l_{ef}^{mn} r_m^e t_{in}^{af} + l_e^m r_{im}^{ae}, \quad (61)$$

$$\rho_{kl}^{ij} = \frac{1}{8} l_{ef}^{ij} r_{kl}^{ef} + \frac{1}{4} P_{-}(ij) P_{-}(kl) \delta_{ik} \delta_{jl}, \quad (62)$$

$$2\rho_{ka}^{ij} = -\frac{1}{2} l_{ea}^{ij} r_k^e, \quad (63)$$

$$2\rho_{jk}^{ia} = -\frac{1}{2} l_e^i r_{jk}^{ea} + \frac{1}{2} P_{-}(jk) l_{fe}^{im} r_k^e t_{jm}^{fa} + \frac{1}{4} l_{fe}^{im} r_m^a t_{jk}^{fe} - \frac{1}{4} P_{-}(jk) l_{fe}^{im} r_k^a t_{jm}^{fe}, \quad (64)$$

$$4\rho_{bj}^{ia} = -\frac{1}{4} P_{-}(ij) P_{-}(ab) l_b^i r_j^a - \frac{1}{4} P_{-}(ij) P_{-}(ab) l_{eb}^{im} r_{jm}^{ea}, \quad (65)$$

$$2\rho_{ci}^{ab} = \frac{1}{2} l_c^m r_{im}^{ba} - \frac{1}{2} P_{-}(ab) l_{ec}^{mn} r_m^b t_{in}^{ea} - \frac{1}{4} l_{ec}^{mn} r_i^e t_{mn}^{ba} + \frac{1}{4} P_{-}(ab) l_{ec}^{mn} r_i^b t_{mn}^{ea}, \quad (66)$$

$$2\rho_{bc}^{ai} = \frac{1}{2} l_{bc}^{mi} r_m^a, \quad (67)$$

$$\rho_{cd}^{ab} = \frac{1}{8} l_{cd}^{mn} r_{mn}^{ab}, \quad (68)$$

$$\begin{aligned} \rho_{ab}^{ij} = & \frac{1}{4} t_{ij}^{ab} - \frac{1}{4} P_{-}(ij) l_e^m r_i^e t_{mj}^{ab} - \frac{1}{8} P_{-}(ab) l_{ef}^{mn} r_{mn}^{ea} t_{ij}^{fb} \\ & - \frac{1}{8} P_{-}(ij) l_{ef}^{mn} r_{im}^{fe} t_{nj}^{ab} - \frac{1}{4} P_{-}(ab) l_e^m r_m^a t_{ij}^{eb} \\ & + \frac{1}{16} l_{ef}^{mn} r_{ij}^{ef} t_{mn}^{ab} + \frac{1}{16} l_{ef}^{mn} r_{mn}^{ab} t_{ij}^{ef} + \frac{1}{4} P_{-}(ij) P_{-}(ab) \\ & \times l_e^m r_j^b t_{im}^{ae} + \frac{1}{4} P_{-}(ij) P_{-}(ab) l_{ef}^{mn} r_{im}^{ae} t_{jn}^{bf} - \frac{1}{8} P_{-}(ij) \\ & \times l_{ef}^{mn} r_{in}^{ab} t_{jm}^{fe} - \frac{1}{8} P_{-}(ab) l_{ef}^{mn} r_{ij}^{af} t_{mn}^{eb} + \frac{1}{4} \zeta_{ab}^{ij}, \end{aligned} \quad (69)$$

$$\rho_{ij}^{ab} = 0, \quad (70)$$

for the EOMEE-CCSD(2) approximation, and

$$\rho_j^i = -l_j^i r_m^e - \frac{1}{2} l_{jm}^{ef} \zeta_{ef}^{im} + \delta_{ij}, \quad (71)$$

$$\rho_b^a = \frac{1}{2} l_b^m r_{mn}^a + \frac{1}{2} t_{mn}^{ae} \zeta_{be}^{mn}, \quad (72)$$

$$\rho_i^a = l_m^m r_{im}^a + l_e^{mn} r_n^a t_{im}^{ae} - \frac{1}{2} l_e^{mn} r_i^e t_{mn}^{ea}, \quad (73)$$

$$\rho_a^i = l_a^{im} r_m^e, \quad (74)$$

$$\rho_{kl}^{ij} = \frac{1}{4} l_e^{ij} r_{kl}^e + \frac{1}{4} P_{-}(ij) P_{-}(kl) \delta_{ik} \delta_{jl}, \quad (75)$$

$$2\rho_{ak}^{ij} = -l_{ik}^j r_a^e, \quad (76)$$

$$2\rho_{jk}^{ia} = -\frac{1}{2} l_j^i r_{kj}^a + \frac{1}{2} P_{-}(jk) l_e^{im} r_k^e t_{mj}^{ae}, \quad (77)$$

$$4\rho_{bj}^{ai} = -\frac{1}{4} P_{-}(ij) P_{-}(ab) l_b^i r_{mj}^a, \quad (78)$$

$$\rho_{ci}^{ab} = \frac{1}{4} l_c^{mn} r_n^a t_{mi}^{ab} - \frac{1}{8} l_c^{mn} r_i^e t_{mn}^{ab}, \quad (79)$$

$$\begin{aligned} \rho_{ij}^{ab} = & \frac{1}{4} t_{ij}^{ab} + \frac{1}{4} \zeta_{ab}^{ij} - \frac{1}{4} P_{-}(ij) l_m^m r_j^a t_{im}^{ab} - \frac{1}{8} P_{-}(ab) l_e^{nm} r_{nm}^a t_{ij}^{eb} \\ & - \frac{1}{4} P_{-}(ij) l_e^{nm} r_{im}^e t_{nj}^{ab} + \frac{1}{4} P_{-}(ij) P_{-}(ab) l_e^{nm} r_{im}^a t_{jn}^{be} \\ & - \frac{1}{8} P_{-}(ab) l_e^{nm} r_{ji}^b t_{mn}^{ae} + \frac{1}{8} l_e^{nm} r_{ij}^e t_{nm}^{ab} \end{aligned} \quad (80)$$

for EOMIP-MBPT(2). The only other quantities that need to be evaluated are the matrix elements of the Ξ operator, which are given by

$$\begin{aligned} \xi_{ab}^{ij} = & -P_{-}(ab) l_a^m r_m^e \langle ij || eb \rangle - P_{-}(ij) l_e^m r_m^e \langle mj || ab \rangle + P_{-}(ij) P_{-}(ab) l_a^i r_m^e \langle mj || eb \rangle + P_{-}(ij) P_{-}(ab) l_{ae}^{im} r_{mn}^{ef} \langle jn || bf \rangle \\ & + \frac{1}{4} l_{ab}^{mn} r_{mn}^{ef} \langle ij || ef \rangle + \frac{1}{4} l_{ef}^{ij} r_{mn}^{ef} \langle mn || ab \rangle - \frac{1}{2} P_{-}(ab) l_{ea}^{mn} r_{mn}^{ef} \langle ij || fb \rangle - \frac{1}{2} P_{-}(ij) l_{ef}^{in} r_{mn}^{ef} \langle mj || ab \rangle - \frac{1}{2} P_{-}(ab) l_{fb}^{ij} r_{mn}^{ef} \langle mn || ea \rangle \\ & - \frac{1}{2} P_{-}(ij) l_{ab}^{mj} r_{mn}^{ef} \langle in || ef \rangle - P_{-}(ij) P_{-}(ab) l_{ae}^{in} r_m^e \langle mj || nb \rangle + P_{-}(ij) P_{-}(ab) l_{af}^{im} r_m^e \langle fj || eb \rangle + P_{-}(ab) l_{af}^{ij} r_m^e \langle fm || be \rangle \\ & - P_{-}(ij) l_{ab}^{in} r_m^e \langle jm || ne \rangle - l_{ef}^{ij} r_m^e \langle fm || ba \rangle - l_{ab}^{mn} r_m^e \langle ij || en \rangle + \langle ij || ab \rangle, \end{aligned} \quad (81)$$

for EOMEE-MBPT(2) and

$$\begin{aligned} \xi_{ab}^{ij} = & P_{-}(ij) l_i^i r_m^e \langle mj || ab \rangle - P_{-}(ij) P_{-}(ab) l_a^{im} r_n^e \langle nj || mb \rangle - l_e^{ij} r_m^e \langle em || ab \rangle + P_{-}(ij) P_{-}(ab) l_a^{in} r_{mn}^e \langle mj || eb \rangle \\ & - P_{-}(ij) l_e^{mi} r_{mn}^e \langle nj || ab \rangle + \frac{1}{2} l_e^{ij} r_{mn}^e \langle mn || ab \rangle - \frac{1}{2} P_{-}(ab) l_a^{mn} r_{mn}^e \langle ij || eb \rangle - \frac{1}{2} P_{-}(ab) l_a^{ij} r_{mn}^e \langle mn || eb \rangle + \langle ij || ab \rangle \end{aligned} \quad (82)$$

for EOMIP-MBPT(2). For maximum computational efficiency, Eq. (57) is reformulated in terms of differentiated quantities in the atomic orbital representation, as discussed for example in Ref. 33. Energy and gradient methods for EOMIP-CCSD(2) and EOMEE-CCSD(2) have been implemented in the ACES II program system,⁴⁹ which was used for all calculations reported in Sec. III.

D. Computational considerations

The replacement of the similarity transformed Hamiltonian defined in terms of converged CCSD reference state cluster amplitudes by its second-order approximation in the EOM-CCSD(2) methods outlined here means that these calculations are less expensive than those carried out at the full EOM-CCSD level. However, the merit of these approximate approaches ultimately depends on the extent to which savings are offset by a loss in accuracy due to truncation of \tilde{H} . The computational requirements of EOMIP-CCSD(2) and EOMEE-CCSD(2) are discussed in this subsection, with special attention paid to the *computational* benefits (as measured by reduction in arithmetic operations and disk storage requirements) relative to corresponding full EOM-CCSD calculations. A definitive conclusion regarding the second issue—the relative accuracy of results obtained with approximate and full EOM-CCSD treatments—cannot be drawn until considerable experience has been gained in application calculations. Nevertheless, the examples presented in the following section provide some general indication of reliability.

Although the replacement of \tilde{H} by $\tilde{H}^{(2)}$ means that the reference state CCSD equations do not have to be solved for either EOMIP-CCSD(2) or EOMEE-CCSD(2), no savings are realized in the diagonalization of $\tilde{H}^{(2)}$ since the dimension of the basis is precisely the same as in the corresponding full EOM-CCSD eigenproblem. In EOMEE, the transformed Hamiltonian is diagonalized using a generalization⁵⁰ of Davidson's iterative method⁵¹ in which the number of arithmetic operations per iteration rises with \mathcal{N}^6 . This scaling dependence is the same as that encountered in solving the CCSD equations, so both of these iterative processes are rate-limiting computational steps. Thus, the simplifying assumption of EOMEE-CCSD(2) does not alter the overall asymptotic scaling properties of the method. Since the CCSD equations are nonlinear in the cluster amplitudes, each iteration requires slightly more operations than the matrix-vector products used to build up the iterative subspace in the diagonalization procedure. The cost of an EOMEE-CCSD(2) energy calculation should therefore be somewhat less than half that needed for EOMEE-CCSD, with the ratio of floating point operations relatively insensitive to the size of the molecule. For all practical purposes, this fixed ratio property limits the scope of applications for EOMEE-CCSD(2) to those that can also be treated with the full EOMEE-CCSD method. While calculations using the former approach will run somewhat more quickly, the disk storage requirements and asymptotic scaling properties of the two methods are exactly the same.

Examination of the computational aspects of EOMIP-CCSD(2) and EOMIP-CCSD reveals an entirely different situation. In both approaches, the dimension of the diagonal-

ization basis is much smaller than in EOMEE-CCSD {the eigenvectors consist one- and three-index operators instead of two- and four-index operators associated with $|s\rangle$ and $|d\rangle$ [see Eqs. (40)–(43)]} and the number of operations required to perform the matrix-vector products increases in proportion to the *fifth* power of the basis set dimension. Diagonalization of \tilde{H} is therefore *not* a rate-limiting step in EOMIP-CCSD calculations; the cost of an energy calculation is instead dominated by solution of the reference state CCSD equations. Since the cluster amplitudes are not evaluated in EOMIP-CCSD(2), no iterative steps with an \mathcal{N}^6 dependence are required. Moreover, matrix elements of the Hamiltonian with four virtual indices (the $\langle ab||cd\rangle$ integrals) contribute only to the CCSD equations and therefore need not be considered in EOMIP-CCSD(2) calculations. As a result, there is an enormous advantage in storage requirements since these quantities can represent a disk space bottleneck in large-scale CCSD calculations. With regard to asymptotic scaling properties, the most demanding steps in EOMIP-CCSD(2) energy calculations superficially appear to be the \mathcal{N}^6 contractions between antisymmetrized two-electron integrals and $T^{[1]}$ amplitudes in Eqs. (23), (25), and (28). However, it is possible to avoid these potentially rate-limiting steps altogether by not forming these $\tilde{H}^{(2)}$ elements explicitly, but rather contracting the trial eigenvector with the integral (or amplitude) in each iteration of the diagonalization procedure. Subsequent contraction with the amplitude (or integral) provides the same result that would be obtained by forming the $\tilde{H}^{(2)}$ elements and combining them with the trial vector.⁵² By following this alternative procedure, \mathcal{N}^6 steps that need be done only once are replaced by an iterative \mathcal{N}^5 procedure. Therefore, with an appropriate computational strategy, the cost of EOM-CCSD(2) calculations scales only with \mathcal{N}^5 . EOMIP-CCSD(2) energy calculations are therefore expected to be vastly more economical than EOMIP-CCSD. Most important, the different asymptotic scaling dependencies of the two methods suggests that the former approach can be applied to a wider range of interesting chemical problems.

Things are much the same for the relative requirements of the corresponding gradient methods. For all methods, gradient evaluation necessitates evaluation of both the \mathcal{L} and \mathcal{R} eigenvectors (only one of these is needed to calculate the energy) and solution of the \mathcal{L} equations. For EOMEE-CCSD, both of these additional steps require iterative algorithms with a rate-limiting (\mathcal{N}^6) dependence, but the \mathcal{L} solution ceases to be rate limiting in EOMEE-CCSD(2) because of the diagonal coefficient matrix discussed in the preceding subsection. Therefore, the ratio of costs is again expected to be approximately 2:1 for EOMEE-CCSD and EOMEE-CCSD(2) since one of two rate-limiting steps is removed by the approximations made in the latter. The \mathcal{L} equations are identical for both EOMIP-CCSD and EOMEE-CCSD apart from the numerical values of the Ξ matrix elements since they account for the response of the cluster amplitudes in both cases. Thus, the diagonal coefficient matrix characteristic of the first-order \mathcal{L} equation is extremely beneficial in EOMIP-CCSD(2) since a potentially rate-limiting \mathcal{N}^6 step is avoided. Therefore, the cost of both energy and

TABLE I. Total electronic energies and excitation energies (relative to the ground state) calculated for selected low-lying levels of CH^+ at the EOMEE-CCSD(2), EOMEE-CCSD and full configuration interaction (FCI) levels of theory. Numbers that label the states do not adhere to any spectroscopic convention but are included to clarify the discussion of Sec. III A.

	Excitation energies (eV)			Total energy (a.u.)		
	EOMEE CCSD(2)	EOMEE CCSD	FCI ^a	EOMEE CCSD(2)	EOMEE CCSD	FCI ^a
Ground electronic state						
1 $^1\Sigma^+$	-37.9868	-38.0177	-38.0196
Excited electronic states						
1 $^1\Pi$	2.663	3.261	3.230	-37.8889	-37.8978	-37.9009
2 $^2\Sigma^+$	8.317	9.109	8.549	-37.6712	-37.6829	-37.7055
3 $^1\Sigma^+$	13.026	13.580	13.525	-37.5081	-37.5186	-37.5226
2 $^1\Pi$	13.909	14.454	14.127	-37.4757	-37.4865	-37.5005
4 $^1\Sigma^+$	16.714	17.315	17.217	-37.3726	-37.3813	-37.3869

^aFrom Ref. 53.

gradient calculations have an \mathcal{N}^5 computational dependence when the EOMIP-CCSD(2) method is used.

III. ILLUSTRATIVE CALCULATIONS

A. Excitation energies of CH^+

As discussed in Sec. II B, the EOM-CCSD(2) method involves a slightly misbalanced representation of the reference and final states. Since the former is approximated by second-order perturbation theory and the latter by a wave function that includes infinite-order contributions, one expects EOM-CCSD(2) energy differences to be shifted from the corresponding EOM-CCSD values. For principal ionization potentials, such a pattern can be seen for most of the results reported by Nooijen and Snijders. The purpose of this subsection is to demonstrate that systematic shifts can also be seen for vertical excitation energies.

The model system chosen for this set of calculations is the diatomic cation CH^+ , which is frequently used as a test case for theoretical methods designed for the prediction of electronic spectra. Provided a modest basis set is used, the system is small enough so that full configuration interaction (FCI) calculations are feasible,⁵³ yet sufficiently complex that an accurate determination of its energy levels is challenging for approximate methods. In particular, CH^+ exhibits relatively strong nondynamical electron correlation in the ground state and moreover has a few low-lying states with appreciable double excitation character. Both features represent potential problems for EOMEE-CCSD and EOMEE-CCSD(n) approximations, since these methods are based on a single determinant ground state reference function and are best suited for studying “singly” excited states.⁴³

Calculations for CH^+ have been carried out at the EOMEE-CCSD and EOMEE-CCSD(2) levels with the basis set and geometry used by Olsen *et al.* in their benchmark FCI study of this system.⁵³ Excitation and total electronic energies for several low-lying states of CH^+ predicted by the two EOMEE methods are listed in Table I, where they are compared to corresponding FCI values. Trends observed in the present set of results qualitatively parallel those seen in the ionization potentials reported by Nooijen and

Snijders³⁸—EOMEE-CCSD(2) excitation energies (relative to the ground state) are systematically lower (about 0.6 eV for CH^+) than the EOMEE-CCSD values, but the relative energies of the various final states are in remarkably good agreement. Thus, the magnitude of the splitting between final states described by EOM-CCSD(2) and EOM-CCSD is similar, but the spectrum calculated by the former method is shifted to longer wavelength.

It is amusing to note that some of the excitation energies predicted by the simpler EOMEE-CCSD(2) method are in better agreement with FCI than the corresponding EOMEE-CCSD results. This improved agreement is clearly spurious, and its underlying cause is easy to understand. In EOM-CCSD, both the reference and final state descriptions involve infinite order contributions; the former state is more accurately represented by the method because it benefits from the full power of the exponential parametrization. As a result (to the extent that energies given by these methods are variational⁵⁴) one often finds that EOMEE-CCSD excitation energies are too high (above the FCI results). In EOMEE-CCSD(2), however, the opposite is true in the present case—final states are treated more accurately than the ground state of CH^+ —and excitation energies are shifted in the “correct” direction.

Qualitative arguments that attribute systematic differences between EOM-CCSD(2) and EOM-CCSD excitation energies and ionization potentials to a misbalanced treatment of reference and final states in CH^+ are supported by total energies calculated for the electronic states. For the excited states dominated by single excitations (3 $^1\Sigma^+$, 4 $^1\Sigma^+$, and 1 $^1\Pi$), EOMEE-CCSD(2) and EOMEE-CCSD energies differ by no more than 10 millihartrees (mE_h), with the latter values no more than 5 mE_h above the full CI values. For the 1 $^1\Sigma^+$ ground state, however, a significant discrepancy is noted. The MBPT(2) energy is in error by 33 mE_h and is 31 mE_h above that predicted by CCSD, which fares considerably better with an overall error of only 2 mE_h . Consequently, EOMEE-CCSD(2) excitation energies undershoot the EOMEE-CCSD values by an amount that is roughly equal to the difference in MBPT(2) and CCSD ground state correlation energies (0.8 eV). Although it does appear that

“singly” excited final states are described more accurately by EOM-CCSD(2) than the reference state, the same cannot be claimed for those with appreciable double excitation character ($2^1\Pi$ and especially $2^1\Sigma^+$) since the parametrization of the method does not allow much flexibility in describing these states. Indeed, one finds that the difference between EOMEE-CCSD(2) and FCI energies for these states is more than twice that for the other states. The rather good agreement of the corresponding excitation energies certainly does not reflect a superiority of EOM-CCSD(2) relative to EOM-CCSD, but rather indicates that *both* the reference and these final states are treated poorly by the simpler model. On the other hand, EOM-CCSD describes the reference state rather well and therefore severely overestimates the excitation energies.

B. Predissociation of \tilde{A} state ammonia

One of the better understood excited state potential energy surfaces is that for the predissociative \tilde{A} state of ammonia. This system plays a prominent role in photodissociation of NH_3 and has been heavily studied by both high-resolution spectroscopy⁵⁵ and theoretical calculations.^{32,56,57} Of principal interest are two stationary points—the planar D_{3h} equilibrium geometry and the predissociative transition state that leads to $\text{NH}_2 + \text{H}$. For some time, a discrepancy persisted between experiment and theory regarding the equilibrium bond length of the \tilde{A} state; *ab initio* calculations^{32,57} consistently predict a significantly shorter N–H distance than those inferred experimentally⁵⁸ or deduced from dynamical simulations⁵⁹ of the absorption and emission spectra. However, a recent spectroscopic analysis of the $\tilde{A} \leftarrow \tilde{X}$ transition by Henck *et al.*⁶⁰ indicates that the equilibrium distance is indeed close to the *ab initio* estimates. Investigation of the equilibrium structure and predissociative transition state of \tilde{A} state NH_3 provides an excellent test of theoretical methods, since experimental information is available and also because this system presents interesting challenges for approximate treatments. In particular, the character of the electronic wavefunction changes markedly as the N–H bond is stretched from its equilibrium position. While the \tilde{A} state has appreciable Rydberg character in the vicinity of the minimum energy structure, the wave function becomes decidedly more valencelike at the transition state.⁶¹ Thus, an accurate calculation of the barrier height requires a balanced description of both correlation and basis set effects.

In Table II, optimized geometrical parameters, total energies, vibrational frequencies, and infrared absorption intensities are listed for the minimum energy and transition state structures. The latter two properties are calculated with the usual simplifying approximation that assumes a quadratic form for the potential energy and a linear dipole moment function. All values were obtained with the basis set designated A in Ref. 56 which contains 65 contracted Gaussian functions. The stationary point geometries were located with EOMEE-CCSD(2) and EOMEE-CCSD gradient techniques; force constants and intensities were calculated by numerical differentiation of analytic gradients and dipole moments. It is gratifying to note that structures and properties given by the two EOMEE approaches are in excellent agreement for both

TABLE II. Structure, energies, harmonic vibrational frequencies, and infrared absorption intensities for the equilibrium structure and predissociative transition state on the \tilde{A} state potential energy surface of NH_3 . Bond lengths are in angstroms, bond angles in degrees, frequencies in cm^{-1} , and intensities in km/mol . The total energies are given in atomic units, and the barrier height is in cm^{-1} .

	EOMEE-CCSD(2)	EOMEE-CCSD
Equilibrium structure		
r_{NH}	1.0487	1.0512
$\omega_1(a_1')$	3180.8	2993.1
$\omega_2(a_2'')$	769.6	741.2
$\omega_3(e')$	3021.0	2997.5
$\omega_4(e')$	1331.1	1335.2
I_1
I_2	14.7	9.7
I_3	4622.1	4447.1
I_4	293.0	376.0
Energy	−56.234 687	−56.246 539
$\text{NH}_3 \rightarrow \text{NH}_2 + \text{H}$ transition state		
r_{NH^*}	1.3219	1.3421
r_{NH}	1.0423	1.0441
$\theta(\text{H}^*\text{NH})$	124.51	124.27
$\omega_1(a_1)$	3069.0	3051.6
$\omega_2(a_1)$	1478.5	1456.0
$\omega_3(a_1)$	1977.3 <i>i</i>	1897.3 <i>i</i>
$\omega_4(b_1)$	1042.0	1023.1
$\omega_5(b_2)$	3274.9	3255.2
$\omega_6(b_2)$	396.5	419.6
I_1	1081.2	1010.6
I_2	48.9	41.0
I_3	2301.1	1921.3
I_4	43.9	69.9
I_5	58.1	56.5
I_6	158.0	167.5
Dipole moment	2.631	2.727
Energy	−56.223 512	−56.234 405
Barrier height	2452	2663

the minimum and the transition state. Inclusion of higher-order contributions in \tilde{H} does not lead to significant changes, a finding that supports our belief that EOM-CCSD(2) models are suitable for the prediction of final state properties. Even more pleasing is the close agreement of barrier heights, as it indicates that the two methods provide comparably accurate approximations to states that have qualitatively different wave functions.

The barrier heights calculated at the EOM-CCSD(2) and EOM-CCSD levels fall below a value of 3226 cm^{-1} obtained at the MCSCF level by McCarthy *et al.* with the same basis set. While our values are in better agreement with a recent experimental estimate of $\sim 2100 \text{ cm}^{-1}$,⁶² no definitive conclusions can be drawn about the relative accuracy of EOMEE and MCSCF methods since a rather large uncertainty is associated with the finite size of the basis. In order to investigate this issue, EOMEE-CCSD(2) and EOMEE-CCSD energy calculations were performed with very large basis sets. The augmented correlation consistent valence triple-zeta and valence quadruple-zeta basis sets of Kendall *et al.*⁶³ (aug-cc-PVTZ and aug-cc-PVQZ), and the generally contracted atomic natural orbital basis of Widmark, Malmqvist, and Roos (WMR)⁶⁴ were chosen for study; corresponding barrier heights are listed in Table III. In these cal-

TABLE III. Predissociation barrier heights (in cm^{-1}) for the \tilde{A} state of ammonia at the EOMEE-CCSD(2) and EOMEE-CCSD levels. All calculations are based on the stationary point geometries obtained with basis A.

Basis	EOMEE-CCSD(2)	EOMEE-CCSD
aug-cc-PVTZ	2782	3123
WMR	2656	2998
aug-cc-PVQZ	2609	2964

culations, only the pure spherical harmonic components of the d , f , and g polarization functions were retained. The aug-cc-PVTZ, WMR, and aug-cc-PVQZ basis sets—which are substantially larger than basis A—comprise 115, 168, and 218 contracted Gaussian functions, respectively, and include those required to satisfactorily describe the diffuse nature of Rydberg states. A modest increase in the predicted barrier height is found for these large basis sets, presumably because they provide a better description of the more extended wave function at the equilibrium geometry. It is likely that the WMR and aug-cc-PVQZ values are close to the basis set limit for the EOM-CCSD(2) and EOM-CCSD methods, so the remaining discrepancy of 500–1000 cm^{-1} is probably due to high-order correlation effects that are neglected in these methods (i.e., triple excitation contributions⁶⁵). A similar basis set effect for the MCSCF barrier is expected, so it appears that the EOMEE methods provide a better, but still imperfect, estimate of the activation energy for predissociation.

C. Structure and harmonic force field of the formyloxyl radical

In this final example, the EOMIP-CCSD(2) model is applied to calculate the structure and harmonic force field of the formyloxyl radical. This system is one of the better known examples that involves an artifactual symmetry breaking phenomenon frequently encountered in theoretical studies of doublet states.¹⁶ The ground electronic state of HCO_2 has a C_{2v} equilibrium geometry and the electronic wave function belongs to the B_2 irreducible representation. However, there is a relatively low-lying 2A_1 excited state that couples to the ground state (second-order Jahn–Teller interaction) when the nuclei are displaced along the antisymmetric stretching coordinate. An accurate description of the potential energy function that governs this vibrational motion requires a balanced treatment of the two corresponding zeroth-order configurations, and presents a sensitive test for theoretical methods, as discussed in Refs. 16 and 34.

In a previous paper,³⁴ we claimed that EOMIP-CCSD is especially well formulated for problems of this sort due to its balanced treatment of the zeroth-order Koopmans determinants. This contention is supported by a number of previous applications by Kaldor⁶⁶ as well as investigations of the X^2B_2 state of HCO_2 and the cyclic radical C_3H ,⁶⁷ in which analytic EOMIP-CCSD gradient techniques were used for the first time. For formyloxyl, the results agree closely with high-level MRCI calculations,¹⁶ even for the problematic b_2 stretching frequency. The ability of EOM-CCSD(2) to treat this delicate problem has been assessed by performing cal-

TABLE IV. Structure and properties of the 2B_2 state of the HCOO radical calculated with the EOMIP-CCSD(2) and EOMIP-CCSD methods. Bond lengths are in angstroms, bond angles in degrees, harmonic frequencies (ω_n) in cm^{-1} and infrared intensities (I_n) in km/mol . The dipole moments are expressed in debye. Also included are the MRCI results of Ref. 20.

	EMIP-CCSD(2)	EOMIP-CCSD	MRCI
$r_e(\text{CO})$	1.261	1.258	1.268
$r_e(\text{CH})$	1.099	1.100	1.099
$\theta(\text{HCO})$	124.1	123.6	123.7
$\omega_1(a_1)$	3184.7	3170.0	3197
$\omega_2(a_1)$	1494.2	1512.5	1477
$\omega_3(a_1)$	640.8	649.8	646
$\omega_4(b_1)$	1016.0	1027.0	a
$\omega_5(b_2)$	1311.0	1317.8	1314
$\omega_6(b_2)$	956.4	1009.6	961
I_1	36.8	39.7	a
I_2	50.2	67.6	a
I_3	20.9	25.6	a
I_4	0.0	0.4	a
I_5	60.3	92.7	a
I_6	355.9	227.0	a
Dipole moment	2.443	2.552	a

^aNot reported.

culations of the equilibrium structure and harmonic force field using the DZP basis set described in Ref. 34; the results are given in Table IV along with the corresponding EOMIP-CCSD and MRCI values. As expected from the performance of the methodologically related EOMEE-CCSD(2) method for the ammonia predissociation problem, agreement between structures and properties calculated at the EOMIP-CCSD(2) and EOMIP-CCSD methods is excellent. An important feature of the results is that high-level contributions to \tilde{H} apparently provide only a small contribution to the description of the asymmetric C–O stretching potential, which is the most difficult feature of the HCO_2 surface to describe accurately. Although a single test case is not sufficient to objectively assess the reliability of EOMIP-CCSD(2), the results are encouraging (especially in view of the favorable computational features of this method!) and offer hope that this approximate treatment will perform similarly well in other challenging situations.

IV. CONCLUSIONS

In the past few years, several applications of EOM-CCSD approaches for excited and quasidegenerate open-shell states of radicals have been reported in the chemical literature. The popularity of this method stems from its black-box nature and consequent ease of application as well as its favorable computational scaling properties. In principle, a requirement that the reference electronic state be adequately treated by the CCSD approximation effectively limits the range of systems that can be accurately represented by these methods to a subset of those described well by large-scale MRCI calculations. However, the enormous difference in computational costs allows EOM-CCSD to be applied to significantly larger molecules. Thus, each of these quite different approaches is best suited to a particular domain of problems. In cases where the reference state has only modest multireference character, EOM-CCSD and MRCI

calculations are expected to provide roughly comparable results, while the latter methods are certainly preferable when nondynamical effects dominate reference state correlation. Practical considerations dictate that EOM-CCSD is the only choice for larger molecules, but some caution should be exercised in its application.

The principal purpose of this paper is to outline a general strategy for obtaining *approximate* solutions to the EOM-CCSD equations and to investigate the extent to which the accuracy of results is compromised by the simplifying assumptions. The EOM-CCSD(n) approach defined by perturbation expansion of the CCSD similarity transformed Hamiltonian provides a well-defined set of approximations that are size-consistent at each order and converge to the full EOM-CCSD result in the limit of large n . Arguments have been presented to suggest that two of the simplest realizations of this strategy—the EOMEE-CCSD(2) and EOMIP-CCSD(2) methods that have been featured in this work—are well suited for predicting final state properties. Results presented for two classic problems—potential energy surfaces governing predissociation of ammonia in the excited \tilde{A} state and antisymmetric C–O stretching in the ground state of the formylxyl radical—provide evidence to support our belief that reliable results can be obtained with both of these methods.

Analysis of the number of required arithmetic operations reveals a striking difference between EOMEE-CCSD(2) and EOMIP-CCSD(2) that has important implications for the use of these methods in chemical applications. Rate-limiting computational steps in EOMEE-CCSD(2) and the full EOMEE-CCSD method have the same asymptotic dependence on the size of the basis set. The only savings achieved in EOMEE-CCSD(2) is that the number of rate-limiting steps is reduced by half (one vs two for energy calculations; two vs four for gradient calculations). In contrast, the truncation of \tilde{H} at second-order means that EOMIP-CCSD(2) energy and gradient calculations can be based on algorithms that scale only with the fifth power of the basis set dimension. This represents a significant improvement over full EOMIP-CCSD, which has an \mathcal{N}^6 dependence. Moreover, the $\langle ab||cd \rangle$ integrals are not required in energy calculations, which allows a substantial savings in disk storage requirements. Based on this analysis, we feel that the EOMIP-CCSD(2) method will be widely used for chemical applications. For doublet radicals, it is the only correlated method developed to date with all of the following features: (1) size-consistency; (2) no computational steps involve an \mathcal{N}^6 or more severe computational dependence; (3) final states are rigorously spin-adapted; (4) implementation of an efficient strategy for analytic evaluation of energy gradients. EOMEE-CCSD(2) has fewer practical advantages and is perhaps best viewed as a pedagogically useful approach for studying the dependence of EOMEE final states on the definition of the transformed Hamiltonian.

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