

Perturbative corrections to coupled-cluster and equation-of-motion coupled-cluster energies: A determinantal analysis

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(Received 16 October 2000; accepted 15 December 2000)

We develop a combined coupled-cluster (CC) or equation-of-motion coupled-cluster (EOM-CC) theory and Rayleigh–Schrödinger perturbation theory on the basis of a perturbation expansion of the similarity-transformed Hamiltonian $\bar{H} = \exp(-T)H\exp(T)$. This theory generates a series of perturbative corrections to any of the complete CC or EOM-CC models and hence a hierarchy of the methods designated by $CC(m)PT(n)$ or $EOM-CC(m)PT(n)$. These methods systematically approach full configuration interaction (FCI) as the perturbation order (n) increases and/or as the cluster and linear excitation operators become closer to complete (m increases), while maintaining the orbital-invariance property and size extensivity of CC at any perturbation order, but not the size intensivity of EOM-CC. We implement the entire hierarchy of $CC(m)PT(n)$ and $EOM-CC(m)PT(n)$ into a determinantal program capable of computing their energies and wave functions for any given pair of m and n . With this program, we perform $CC(m)PT(n)$ and $EOM-CC(m)PT(n)$ calculations of the ground-state energies and vertical excitation energies of selected small molecules for all possible values of m and $0 \leq n \leq 5$. When the Hartree–Fock determinant is dominant in the FCI wave function, the second-order correction to CCSD [$CC(2)PT(2)$] reduces the differences in the ground-state energy between CCSD and FCI by more than a factor of 10, and thereby significantly outperforms CCSD(T) or even CCSDT. The third-order correction to CCSD [$CC(2)PT(3)$] further diminishes the energy difference between $CC(2)PT(2)$ and FCI and its performance parallels that of some CCSD(TQ) models. $CC(m)PT(n)$ for the ground state with some multideterminantal character and $EOM-CC(m)PT(n)$ for the excitation energies, however, appear to be rather slowly convergent with respect to n . © 2001 American Institute of Physics. [DOI: 10.1063/1.1346578]

I. INTRODUCTION

The coupled-cluster (CC) method,^{1–8} which includes connected single and double excitations ($T_1 + T_2$), known as CCSD,⁹ usually provides rather accurate results for many properties of molecules in the vicinity of their equilibrium geometries. This may be ascribed to the effective inclusion of the principal part of quadruple excitations ($\frac{1}{2}T_2^2$) and some contributions from disconnected triples (T_1T_2), etc., and also to the size extensivity of the method. When the reference wave function is too poor an approximation to the particular electronic state of interest, however, CCSD will still fail and it becomes necessary to account for the effect of connected triple (T_3) or even higher excitations at least approximately. The efforts to include such higher excitations rigorously lead to a hierarchy of complete CC methods (CCSD, CCSDT,^{10–12} CCSDTQ,^{13,14} . . .), which provides a systematically more accurate treatment of correlation, but at rapidly increasing computational cost. CCSDT, which in-

cludes $T_1 + T_2 + T_3$, is nominally an n^8 procedure (n being the number of orbitals), and CCSDTQ, which includes $T_1 + T_2 + T_3 + T_4$, is n^{10} . Because of this fast growing rank of the computational procedure of the CC methods, it is advantageous to have somewhat simpler methods for the approximate inclusion of T_3 and higher excitations. The development of such approximate CC methods was initiated by Bartlett *et al.*,^{15–17} and there has been intensive research to find the best-performing approximation.^{18–30} These methods are broadly categorized into two groups—iterative and non-iterative. The former includes the first approximate method to incorporate T_3 , CCSDT-1a,¹⁵ and its variants such as CCSDT-1b,¹⁶ CCSDT-2,¹⁶ and CCSDT-3,¹⁶ while the latter includes $CCSD + T(CCSD)$,¹⁶ $CCSD(T)$,²⁰ and $CCSD(TQ)$.^{26,28} $CCSD(T)$ has turned out to be remarkably accurate while requiring a single n^7 procedure after CCSD, and has been widely used in applications.

In the equation-of-motion coupled-cluster (EOM-CC)^{31–46} treatment for electronic excited states, the necessity of incorporating T_3 and higher excitations is even greater. EOM-CCSD, which includes single and double excitations among the cluster and linear excitation operators,

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generally provides reasonably accurate excitation energies only for dominant single replacement transitions and it can be erratic for dominant double replacement and higher rank transitions, even when the CCSD description of the ground state is appropriate. An attempt to estimate the triples contributions to the EOM-CCSD excitation energies has been undertaken by Watts and Bartlett, and has led to several models such as EOM-CCSDT-1,⁴⁷ EOM-CCSDT-3,⁴⁸ EOM-CCSD(T),⁴⁹ and EOM-CCSD(\bar{T}),⁴⁹ as approximations to the complete EOM-CCSDT method. Koch, Christiansen, and their co-workers^{50–52} also advocated some models incorporating triple excitations in EOM-CCSD in iterative and non-iterative manners. These approximate models have shown a significant improvement over EOM-CCSD for dominant double replacement transitions, which attests to the fact that they appropriately capture the triples contributions to the excitation energies. Related to these efforts is the CIS(D) method, proposed by Head-Gordon *et al.*,^{53,54} which adds the doubles corrections to the excitation energies obtained from configuration interaction singles (CIS).

A general noniterative (perturbative) approach that can handle both CC and EOM-CC has been proposed by Stanton and Gauss.^{55,56} They attempted to generate a family of perturbative approximations to any given CC or EOM-CC model from a single perturbation theory framework, rather than to consider approximations to a particular CC or EOM-CC model. Having realized that CC and EOM-CC energies and wave functions were the eigenvalues and eigenvectors of a similarity-transformed Hamiltonian $\bar{H} = \exp(-T)H\exp(T)$ within a certain determinantal space, they derived a perturbation series on the basis of a Löwdin-type perturbation expansion⁵⁷ of the similarity-transformed Hamiltonian within the space. The perturbation corrections thus obtained are size extensive at any perturbation order and the sum of these corrections systematically approached the energies of the parent CC or EOM-CC model, though the implementation of the method was limited to second order. The same strategy has been adopted by Crawford and Stanton,⁵⁸ who derived and implemented the second-order perturbation correction to CCSD. Unlike Stanton and Gauss, they considered a perturbation expansion of the similarity-transformed Hamiltonian in the full Hilbert space, and thereby obtained the perturbation corrections to any CC model that summed to the full configuration interaction (FCI) energy at convergence. We consider that these and related^{59–63} approaches are significant, in that they can potentially lead to a formalism having the following desirable features. (1) It can be applied in a single framework to any of the complete CC or EOM-CC models. In other words, a single formalism applies to CCS, CCSD, CCSDT, etc., and to EOM-CCS=CIS, EOM-CCSD, EOM-CCSDT, etc. (2) It can provide in a single framework a series of perturbation corrections that sums to the exact (FCI) results, rather than to the results of the parent CC or EOM-CC model. (3) At any order of perturbation, the orbital-invariance property and size extensivity of CC and the size intensivity of the excitation energies⁴² of EOM-CC are maintained. (4) It should be accurate and efficient. (5) Preferably, the zeroth-order energy

and wave function are those of the parent CC or EOM-CC model.

In this study, we attempt to develop a combined CC or EOM-CC and Rayleigh–Schrödinger perturbation theory that possesses many of the above-mentioned desirable features by employing the strategy of Stanton, Gauss, and Crawford. We first split the similarity-transformed Hamiltonian within the full Hilbert space into a zeroth-order part and a perturbation and subsequently apply the standard Rayleigh–Schrödinger perturbation theory with an appropriate constraint to the perturbative wave functions arising from the intermediate normalization. This mathematically transparent and unambiguous procedure leads to an energy expression and a recursion relation for the perturbative wave functions, which resemble the familiar expressions of many-body perturbation theory (MBPT). By choosing the zeroth-order part of the similarity-transformed Hamiltonian appropriately, we can insist the zeroth-order energy and wave function to be those of the parent CC or EOM-CC model and we can also ensure the perturbative corrections to maintain the orbital-invariance property of the parent CC or EOM-CC model. The formalism is general in that it can be applied, without any modification, to any of the complete CC or EOM-CC models. We may, therefore, designate the combined CC or EOM-CC and perturbation theory by CC(m)PT(n) or EOM-CC(m)PT(n), respectively, with parameter m representing the truncation order of the parent CC or EOM-CC model and parameter n the order of perturbation. CC(m)PT(n) and EOM-CC(m)PT(n) converge at FCI as parameter m or n increases, regardless of the parent CC or EOM-CC model upon which the perturbation theory is based. CC(m)PT(n) maintains the size extensivity of CC(m) at any perturbation order, but the excitation energies obtained from EOM-CC(m)PT(n) are not size intensive.

To assess the performance of the entire hierarchy of the CC(m)PT(n) and EOM-CC(m)PT(n) methods, we implement them into a general-order program capable of computing the CC(m)PT(n) and EOM-CC(m)PT(n) energies and wave functions for any given pair of parameters m and n . This is accomplished by combining a determinantal CC or EOM-CC algorithm^{64–67} and a determinantal MBPT algorithm.^{68,69} These determinantal algorithms are a unique and powerful tool for the analysis and assessment of a wave function-based method, because they permit the implementation of the entire hierarchy of the method into one program without a substantial effort, but at the sacrifice of applicability as they inevitably involve a factorial number of computational operations. Thus, we may consider them to be complementary to the integral-based algorithms, which can be optimally efficient for a particular model of a hierarchical method. The determinantal algorithms have early been invoked to study the convergence and other properties of MBPT by Laidig *et al.*,⁶⁸ by Knowles *et al.*,⁶⁹ and by Olsen *et al.*,^{70,71} and of multireference perturbation theory by Zarrabian *et al.*^{72–74} They have recently been extended to the analysis of various CC and EOM-CC models by Hirata *et al.*,^{64,66,75} by Kállay and Surján,⁶⁵ and by Olsen.⁶⁷ In this study, with the aid of the determinantal program, we carry out CC(m)PT(n) and EOM-CC(m)PT(n) calculations for

all possible values of m and $0 \leq n \leq 5$ for selected small molecules and compare the results against those of the complete CC or EOM-CC models (which include FCI equivalents) and of some representative iterative and noniterative approximate CC or EOM-CC treatments. This initial assessment of the performance of CC(m)PT(n) indicates that, when the HF determinant is dominant in the FCI wave function, the second-order correction to CCSD [CC(2)PT(2)] reduces the differences in the ground-state energies of the small molecules between CCSD and FCI by more than a factor of 10, and thereby significantly outperforms CCSD(T) or even CCSDT. The third-order correction to CCSD [CC(2)PT(3)] further diminishes the energy difference between CC(2)PT(2) and FCI and its performance parallels that of some CCSD(TQ) models of Kucharski and Bartlett.^{26,28} Hence, CC(m)PT(n) is a promising alternative to the existing perturbative approximations to CC. CC(m)PT(n) for the ground state with some multideterminantal character and EOM-CC(m)PT(n) for the excitation energies, however, appear to be rather slowly convergent with respect to n .

II. THEORY

EOM-CC can be regarded as a configuration interaction (CI) problem involving a similarity-transformed Hamiltonian \bar{H} defined by

$$\bar{H} = \exp(-T)H \exp(T), \quad (1)$$

with the cluster operator T determined by solving a set of CC equations for a reference state. Diagonalizing the matrix representation of \bar{H} , we obtain the energies of the ground- and excited states as the eigenvalues. For the k th state, we may write this eigenvalue problem as

$$\bar{H}|R_k\rangle = E_k|R_k\rangle, \quad (2a)$$

$$\langle L_k|\bar{H} = E_k\langle L_k|, \quad (2b)$$

where we emphasize the distinction between the right-hand-side $|R_k\rangle$ and left-hand-side $\langle L_k|$ eigenvectors associated with the eigenvalue E_k of the non-Hermitian operator \bar{H} . As the similarity transformation of Eq. (1) does not change the spectrum of the original operator, the energies thus obtained are exact within a given one-particle basis set (i.e., the values that would be obtained by FCI) even when the CC wave function of the reference state is only approximate.

In practice, we divide the space of all N -electron determinants into a primary space (which we call P space according to a convention) and the complementary space (Q space) and diagonalize the matrix representation of \bar{H} within the P space to obtain approximate eigenvalues. By designating the projection operators onto the P and Q spaces as P and Q ($P+Q=1$), respectively, we may write the problem in the reduced dimension as

$$P\bar{H}P|R_k^{(0)}\rangle = E_k^{(0)}P|R_k^{(0)}\rangle, \quad (3a)$$

$$\langle L_k^{(0)}|P\bar{H}P = E_k^{(0)}\langle L_k^{(0)}|P, \quad (3b)$$

where we superscript the eigenvalues and eigenvectors by “(0)” to indicate that they are approximate and will be considered as zeroth order in the perturbative treatment described in the following. As $|R_k^{(0)}\rangle$ and $\langle L_k^{(0)}|$ are not defined in the Q space at this moment, we insist for our convenience that

$$Q|R_k^{(0)}\rangle = \langle L_k^{(0)}|Q = 0. \quad (4)$$

We note that the right- and left-hand-side eigenvectors constitute a biorthonormal set

$$\langle L_k^{(0)}|R_l^{(0)}\rangle = \delta_{kl}, \quad (5)$$

and also a complete set within the P space

$$\sum_k P|R_k^{(0)}\rangle\langle L_k^{(0)}|P = P. \quad (6)$$

It is customary to choose the P space of EOM-CC to include the determinants that are accessible by the action of $(1+T)$ on the reference determinant $|0\rangle$; when the T operator contains all single, double, . . . , n -tuple excitation operators, the P space for the corresponding EOM-CC model consists of all singly, doubly, . . . , n -tuply substituted determinants as well as the reference determinant $|0\rangle$. Although the EOM-CC formalism does not limit itself to this particular choice of the P space, this is practical and is also shown to be the best balanced in terms of overall performance.⁶⁶ It should also be appreciated that with this choice, one of the EOM-CC roots corresponds to the CC solution of the reference state, i.e.,

$$|R_0^{(0)}\rangle = |0\rangle, \quad (7a)$$

$$\langle L_0^{(0)}| = \langle 0|(1+\Lambda), \quad (7b)$$

with the so-called Λ operator of CC gradient theory.⁷⁶ Hence, we can formulate the perturbative corrections to CC energies and to EOM-CC energies within a single framework.

We now invoke Rayleigh–Schrödinger perturbation theory to derive the expressions for the perturbative corrections to EOM-CC (CC) energies. We partition the similarity-transformed Hamiltonian \bar{H} into two parts—a zeroth-order part \bar{H}_0 and a perturbation \bar{V} , i.e.,

$$\bar{H} = \bar{H}_0 + \lambda \bar{V}, \quad (8)$$

where we introduce an ordering parameter λ , which will later be set equal to unity. We choose the zeroth-order part of \bar{H} to be

$$\bar{H}_0 = P\bar{H}P + Q\left(E_0^{(0)} - \sum_i^{\text{occ.}} \epsilon_i + F\right)Q, \quad (9)$$

where $E_0^{(0)} = \langle L_0^{(0)}|\bar{H}|R_0^{(0)}\rangle$ is the CC energy of the reference state and F is a sum of the occupied–occupied and virtual–virtual blocks of the Fock operator

$$F = \sum_{i,j}^{\text{occ.}} f_{ij}i^\dagger j + \sum_{a,b}^{\text{virt.}} f_{ab}a^\dagger b. \quad (10)$$

This choice of the zeroth-order Hamiltonian ensures that the orbital-invariance property of the underlying EOM-CC theory, i.e., invariance of the energy to the rotation among occupied orbitals and to the rotation among virtual orbitals, is maintained at any order of perturbation. This may be accomplished also by taking the full Fock operator as F in Eq. (9) instead of the occupied–occupied and virtual–virtual part of the Fock operator, although the latter choice will facilitate the use of semicanonical orbitals as well as canonical orbitals. It should also be noted that the zeroth-order energy and wave function are the CC energy and wave function of the reference state

$$\bar{H}_0|R_k^{(0)}\rangle = E_k^{(0)}|R_k^{(0)}\rangle, \quad (11)$$

by virtue of Eqs. (3a) and (4). The choice of \bar{H}_0 is not limited to the one given by Eq. (9); one may consider different choices of \bar{H}_0 , which will result in different convergence behavior of the perturbation series.

We expand the exact wave function and energy (for the k th state) in a Taylor series in λ

$$|\Psi_k\rangle = |R_k^{(0)}\rangle + \lambda|R_k^{(1)}\rangle + \lambda^2|R_k^{(2)}\rangle + \dots, \quad (12a)$$

$$E_k = E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \dots, \quad (12b)$$

where the i th-order quantities are superscripted by “ (i) .” Then, we impose the intermediate normalization to the exact wave function, i.e.,

$$\langle L_k^{(0)}|\Psi_k\rangle = \langle L_k^{(0)}|R_k^{(0)}\rangle + \lambda\langle L_k^{(0)}|R_k^{(1)}\rangle + \lambda^2\langle L_k^{(0)}|R_k^{(2)}\rangle + \dots = 1, \quad (13)$$

which means

$$\langle L_k^{(0)}|R_k^{(i)}\rangle = 0 \quad (i \geq 1), \quad (14)$$

since Eq. (13) must hold for all values of λ . When the reference state is a degenerate excited state, we require the exact wave function to be biorthogonal against the left-hand-side eigenvectors of all the degenerate roots. Substituting Eq. (8) and Eqs. (12) into Eq. (2a), we obtain

$$\begin{aligned} (\bar{H}_0 + \lambda \bar{V})(|R_k^{(0)}\rangle + \lambda|R_k^{(1)}\rangle + \lambda^2|R_k^{(2)}\rangle + \dots) \\ = (E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \dots) \\ \times (|R_k^{(0)}\rangle + \lambda|R_k^{(1)}\rangle + \lambda^2|R_k^{(2)}\rangle + \dots), \end{aligned} \quad (15)$$

and equating coefficients of λ^i , we find

$$\bar{H}_0|R_k^{(0)}\rangle = E_k^{(0)}|R_k^{(0)}\rangle, \quad (16a)$$

$$\bar{H}_0|R_k^{(1)}\rangle + \bar{V}|R_k^{(0)}\rangle = E_k^{(0)}|R_k^{(1)}\rangle + E_k^{(1)}|R_k^{(0)}\rangle, \quad (16b)$$

$$\bar{H}_0|R_k^{(2)}\rangle + \bar{V}|R_k^{(1)}\rangle = E_k^{(0)}|R_k^{(2)}\rangle + E_k^{(1)}|R_k^{(1)}\rangle + E_k^{(2)}|R_k^{(0)}\rangle, \quad (16c)$$

etc., or generally

$$\bar{H}_0|R_k^{(i)}\rangle + \bar{V}|R_k^{(i-1)}\rangle = \sum_{j=0}^i E_k^{(j)}|R_k^{(i-j)}\rangle \quad (i \geq 1). \quad (17)$$

Note that the expression for the zeroth-order eigenvalue and eigenvector, Eq. (16a), recovers the EOM-CC equation (11).

Multiplying Eq. (17) by $\langle L_0^{(0)}|$ and using the biorthogonality and completeness of the zeroth-order eigenvectors, Eqs. (5) and (6), and the intermediate normalization, Eq. (13), we obtain the following energy expression:

$$E_k^{(i)} = \langle L_k^{(0)}|\bar{V}|R_k^{(i-1)}\rangle \quad (i \geq 1). \quad (18)$$

Rewriting Eq. (17), we obtain a recursion relation for $|R_k^{(i)}\rangle$ as

$$\begin{aligned} (E_k^{(0)} - \bar{H}_0)|R_k^{(i)}\rangle &= \bar{V}|R_k^{(i-1)}\rangle - \sum_{j=1}^i E_k^{(j)}|R_k^{(i-j)}\rangle \\ &\equiv |B_k^{(i)}\rangle \quad (i \geq 1). \end{aligned} \quad (19)$$

The matrix representation of this operator equation amounts to a set of linear equations, where the right-hand-side vector, which we rename as $|B_k^{(i)}\rangle$, is composed of the energies and eigenvectors of lower orders and is known. Since the zeroth-order part of the Hamiltonian \bar{H}_0 as defined by Eq. (9) does not couple vectors in the P space with those in the Q space, the P - and Q -space parts of the linear equations can be handled separately, i.e.,

$$P(E_k^{(0)} - \bar{H}_0)P|R_k^{(i)}\rangle = P|B_k^{(i)}\rangle, \quad (20a)$$

$$Q(E_k^{(0)} - \bar{H}_0)Q|R_k^{(i)}\rangle = Q|B_k^{(i)}\rangle. \quad (20b)$$

When we use the determinants of canonical Hartree–Fock (HF) orbitals as the basis set, the matrix representation of $Q(E_k^{(0)} - \bar{H}_0)Q$ is diagonal and solving the linear equations within the Q space for $Q|R_k^{(i)}\rangle$ is trivial. Solving Eq. (20a) may be more involved as the matrix representation of $P(E_k^{(0)} - \bar{H}_0)P$ is singular and is not invertible. The singularity arises from the fact that the EOM-CC solution of the reference state $P|R_k^{(0)}\rangle$ is an eigenvector of $P(E_k^{(0)} - \bar{H}_0)P$ with the corresponding zero eigenvalue. Consequently, we will not be able to obtain a unique solution vector for $P|R_k^{(i)}\rangle$ from Eq. (20a) alone, but more than one solution vectors. The space of these solution vectors consists of a particular solution vector added to the null-space vector, which in this case is $P|R_k^{(0)}\rangle$, of any length. However, this indeterminacy can be eliminated by the intermediate normalization imposed upon the wave function [Eqs. (13) and (14)], which requires $P|R_k^{(i)}\rangle$ ($i \geq 1$) to be biorthogonal to $\langle L_k^{(0)}|P$. To illustrate this point, we shall derive an explicit expression for the unique solution of $P|R_k^{(i)}\rangle$. Remembering Eq. (6), we may expand $P|B_k^{(i)}\rangle$ as

$$P|B_k^{(i)}\rangle = \sum_l P|R_l^{(0)}\rangle \langle L_l^{(0)}|P|B_k^{(i)}\rangle. \quad (21)$$

We may immediately notice from Eqs. (18) and (19) that

$$\langle L_k^{(0)}|P|B_k^{(i)}\rangle = 0, \quad (22)$$

and hence we can eliminate $l=k$ from the summation in Eq. (21). As $P|R_l^{(0)}\rangle$ is an eigenvector of $P(E_k^{(0)} - \bar{H})_0P$ with the corresponding eigenvalue being $(E_k^{(0)} - E_l^{(0)})$, we can solve Eq. (20a) for $P|R_k^{(i)}\rangle$ as

$$P|R_k^{(i)}\rangle = \sum_{l \neq k} \frac{P|R_l^{(0)}\rangle \langle L_l^{(0)}|P}{E_k^{(0)} - E_l^{(0)}} |B_k^{(i)}\rangle. \quad (23)$$

The argument can be extended straightforwardly for degenerate reference states as we impose the intermediate normalization upon the exact wave function against all the degenerate roots of the reference state.

III. IMPLEMENTATION

A general-order CC(m)PT(n) and EOM-CC(m)PT(n) program has been implemented in the POLYMER program⁷⁷ by employing a determinantal algorithm and a restricted Hartree–Fock (RHF) reference. We first generate all possible determinants for α and β electrons. These α and β determinants may be compactly stored in memory as strings of bits with each bit representing the occupancy of an orbital.⁶⁹ Any determinant can be specified by a pair of α - and β strings, each of which is given an address in a consecutive and lexical order. Thus, any wave function can be represented by an array of α - and β strings, elements of which store the CI coefficients of the corresponding determinants. Likewise, any vector that has the same structure as a wave function, such as right- and left-hand-side eigenvectors of EOM-CC, perturbative corrections to a right-hand-side eigenvector of EOM-CC, and a set of all the t amplitudes, can be conveniently packed into an array of α - and β strings.^{64,66,75}

Having wave functions as explicit linear combinations of determinants, we can operate on these wave functions with any operator which is defined by a finite number of second quantized creation and annihilation operators. We have written some operator subroutines that take any wave function ($|\Psi_A\rangle$) as an input and return as an output the wave function ($|\Psi_B\rangle$) that is obtained by the action of an operator on the input wave function. They perform such basic operations as

$$H|\Psi_A\rangle = |\Psi_B\rangle, \quad (24)$$

$$\exp(\pm T)|\Psi_A\rangle = |\Psi_B\rangle, \quad (25)$$

$$\exp(\pm T^\dagger)|\Psi_A\rangle = |\Psi_B\rangle. \quad (26)$$

The action of the Hamiltonian on any input wave function $|\Psi_A\rangle$, Eq. (24), is a common step in any determinantal FCI program, and efficient algorithms for this procedure have been available in the literature.^{78–80} The action of an exponential operator on $|\Psi_A\rangle$, Eqs. (25) and (26), can be accomplished by operating with $\pm T$ or $\pm T^\dagger$ on $|\Psi_A\rangle$ recursively and by accumulating $(\pm T)^h|\Psi_A\rangle/h!$ or $(\pm T^\dagger)^h|\Psi_A\rangle/h!$. The schematic representation (loop structure) of the algorithm of this procedure can be found in Ref. 64. We note that the Taylor expansion of $\exp(\pm T)$ or $\exp(\pm T^\dagger)$ terminates after a finite number of terms, by virtue of the finite number of electrons and of orbitals, and hence the procedure is computationally well defined. By calling these basic subroutines in an appropriate order, we can also perform the following composite operations:

$$\bar{H}|\Psi_A\rangle = \exp(-T)H\exp(T)|\Psi_A\rangle = |\Psi_B\rangle, \quad (27)$$

$$\bar{H}^\dagger|\Psi_A\rangle = \exp(T^\dagger)H\exp(-T^\dagger)|\Psi_A\rangle = |\Psi_B\rangle. \quad (28)$$

Some modifications of them also allow the operations that are defined by Eqs. (8) and (9), i.e.,

$$(E_k^{(0)} - \bar{H}_0)|\Psi_A\rangle = |\Psi_B\rangle, \quad (29)$$

$$\bar{V}|\Psi_A\rangle = |\Psi_B\rangle. \quad (30)$$

With these subroutines, we first perform a determinantal CC(m) calculation⁶⁴ to determine the t amplitudes. Parameter m indicates that the cluster operator T contains all n -fold excitation operators up to $n=m$. As in the regular CC calculations, the determinantal CC calculations involve an iterative procedure to determine the t amplitudes. With some appropriate initial guess of the t amplitudes, we form an exponential wave function $\exp(T)|\Phi_0\rangle$ by operating with the exponential operator on the reference wave function (in our case, the RHF determinant). Then, we substitute the exponential wave function into the Schrödinger equation and project the equation onto the RHF determinant $|\Phi_0\rangle$ and all singly $\{|\Phi_i^a\rangle\}$, doubly $\{|\Phi_{ij}^{ab}\rangle\}$, ..., m -tuply substituted determinants, i.e.,

$$\langle \Phi_0 | H \exp(T) | \Phi_0 \rangle = E, \quad (31)$$

$$\langle \Phi_i^a | H \exp(T) | \Phi_0 \rangle = E \langle \Phi_i^a | \exp(T) | \Phi_0 \rangle, \quad (32)$$

$$\langle \Phi_{ij}^{ab} | H \exp(T) | \Phi_0 \rangle = E \langle \Phi_{ij}^{ab} | \exp(T) | \Phi_0 \rangle, \quad (33)$$

etc. We upgrade the t amplitudes until all these projection equations are simultaneously satisfied.

Once the converged t amplitudes are obtained from CC(m), we carry out a determinantal EOM-CC(m,m) calculation.⁶⁶ This amounts to obtaining an eigenvalue and the associated right-hand-side eigenvector of the CC(m) similarity-transformed Hamiltonian \bar{H} by diagonalizing its matrix representation within the space of all n -tuply substituted determinants with $0 \leq n \leq m$. In practice, we circumvent the straightforward diagonalization by invoking a non-Hermitian modification⁸¹ of Davidson's iterative subspace method.⁸² In this method, we project $P\bar{H}P$ onto a subspace of greatly reduced dimension spanned by a set of orthonormal trial vectors. Diagonalizing the subspace representation of $P\bar{H}P$, we obtain an approximate eigenvalue and right-hand-side eigenvector. We iteratively increase the subspace size and repeat this process until the approximate eigenvalue and right-hand-side eigenvector satisfy Eq. (3a) within a pre-set tolerance. We perform another determinantal EOM-CC(m,m) calculation to obtain the left-hand-side eigenvector for the same eigenvalue. Realizing that transposed left-hand-side eigenvector $P|L_k^{(0)}\rangle$ satisfies an EOM-CC eigenvalue problem involving $P\bar{H}^\dagger P$,

$$P\bar{H}^\dagger P|L_k^{(0)}\rangle = E_k^{(0)}P|L_k^{(0)}\rangle, \quad (34)$$

we can compute the left-hand-side eigenvector by making some minor modifications to the EOM-CC program for right-hand-side eigenvectors.

At this point, we have the CC energy $E_0^{(0)}$ and the converged t amplitudes for the reference state from the CC(m) calculation and the eigenvalue $E_k^{(0)}$ for an electronic state of interest (k th state) and the corresponding right- and left-

hand-side eigenvectors, $P|R_k^{(0)}\rangle$ and $\langle L_k^{(0)}|P$, of $P\bar{H}P$ from the EOM-CC(m), m) calculations. With these, we compute the CC(m)PT(n) or EOM-CC(m)PT(n) energies and wave functions in a recursive manner by using Eqs. (18) and (19) or (20). The evaluation of $E_k^{(i)}$ and the right-hand-side vector $|B_k^{(i)}\rangle$ of the linear equation can be done straightforwardly in each iteration with the aid of the subroutine (30) that operates with \bar{V} on any given wave function. As we use the RHF reference, the solution of the linear equation in the Q space, Eq. (20b), is trivial; for example, the Φ_{ij}^{ab} element of $Q|R_k^{(i)}\rangle$ array is the Φ_{ij}^{ab} element of $Q|B_k^{(i)}\rangle$ array divided by $(E_k^{(0)} - E_0^{(0)} - \epsilon_a - \epsilon_b + \epsilon_i + \epsilon_j)$. Equation (23) may appear to suggest that we need to have all the left-hand-side eigenvectors $\{\langle L_i^{(0)}|P\}$ and all the right-hand-side eigenvectors $\{|P|R_i^{(0)}\}$ of $P\bar{H}P$ to solve the linear equation (20a). However, we can solve the equation without having either the entire set of left-hand-side eigenvectors or the entire set of right-hand-side eigenvectors. This can be accomplished by expanding the solution vector $P|R_k^{(i)}\rangle$ by a set of trial vectors $\{|P|X_p\rangle\}$ (see Refs. 83 and 84)

$$P|R_k^{(i)}\rangle \approx P(c_1|X_1\rangle + c_2|X_2\rangle + \dots + c_q|X_q\rangle), \quad (35)$$

with each trial vector being biorthogonal to $\langle L_k^{(0)}|P$

$$\langle L_k^{(0)}|P|X_p\rangle = 0 \quad (p = 1, \dots, q). \quad (36)$$

Thus, we can conveniently impose the intermediate normalization to $P|R_k^{(i)}\rangle$ and eliminate the singularity in the linear equations. The coefficients c_1, \dots, c_q may be obtained by requiring that the norm of the residuum

$$P|Y_q\rangle = P(E_k^{(0)} - \bar{H}_0)P(c_1|X_1\rangle + c_2|X_2\rangle + \dots + c_q|X_q\rangle) - P|B_k^{(i)}\rangle, \quad (37)$$

becomes minimal. This requirement reduces to solving a greatly reduced number of linear equations having no singularity. The number of the trial vectors is increased iteratively until the norm of the residuum becomes smaller than a preset tolerance. The new trial vector $P|X_{q+1}\rangle$ may be generated from the residuum vector $P|Y_q\rangle$ as

$$P|X_{q+1}\rangle = P|Y_q\rangle - P|R_k^{(0)}\rangle\langle L_k^{(0)}|P|Y_q\rangle. \quad (38)$$

IV. DEMONSTRATIVE CALCULATIONS

The total energies are calculated by CC(m)PT(n) for the ground states of FH and H₂O at the equilibrium bond length R_e and with bonds stretched to $1.5R_e$ and $2.0R_e$ using the 6-31G basis set. The lowest orbitals are not taken into account in the correlation treatment, and hence CC(8)=FCI. The results of these CC(m)PT(n) calculations ($1 \leq m \leq 8$ and $0 \leq n \leq 5$) are compiled in Table I for FH and in Table II for H₂O. The total energies obtained from MBPT(n) ($0 \leq n \leq 5$) and some iterative and noniterative approximate CC models are also given in these tables. The CC(m)PT(n) and MBPT(n) calculations have been performed with the POLYMER program,⁷⁷ the CCSDT-1a,¹⁵ CCSDT-1b,¹⁶ CCSDT-2,¹⁶ CCSDT-3,¹⁶ CCSD+T(CCSD),¹⁶ and CCSD(T)²⁰ calcula-

TABLE I. Differences (in mE_H) between the FCI energies and the energies obtained from the MBPT(n) and CC(m)PT(n) theory series. The calculations are carried out for the ground state of FH using an RHF reference and the 6-31G basis set within the frozen core approximation at three selected bond lengths: $r_{\text{FH}}=R_e=0.917$ Å; $r_{\text{FH}}=1.5R_e$; $r_{\text{FH}}=2.0R_e$. The FCI energies are $-100.114807E_H$ (R_e), $-100.048130E_H$ ($1.5R_e$), and $-99.979758E_H$ ($2.0R_e$).

Theory	R_e	$1.5R_e$	$2.0R_e$	Annotation ^a
MBPT(1)	131.398	160.173	202.857	MP1=HF
MBPT(2)	3.723	8.782	24.608	MP2
MBPT(3)	4.932	11.733	26.523	MP3
MBPT(4)	0.622	2.445	7.017	MP4
MBPT(5)	0.422	1.845	4.885	MP5
CC(1)	131.398	160.173	202.857	CCS=HF
CC(1)PT(2)	3.723	8.782	24.608	CCS(2)
CC(1)PT(3)	4.932	11.733	26.523	CCS(3)
CC(1)PT(4)	0.543	1.934	5.198	CCS(4)
CC(1)PT(5)	0.416	1.732	3.821	CCS(5)
CC(2)	1.032	2.634	6.007	CCSD
CC(2)PT(2)	0.004	1.537	4.978	CCSD(2)
CC(2)PT(3)	0.034	0.933	4.144	CCSD(3)
CC(2)PT(4)	-0.002	0.577	3.459	CCSD(4)
CC(2)PT(5)	0.002	0.363	2.894	CCSD(5)
CC(3)	0.350	0.626	0.971	CCSDT
CC(3)PT(2)	0.031	0.352	0.791	CCSDT(2)
CC(3)PT(3)	0.008	0.203	0.647	CCSDT(3)
CC(3)PT(4)	0.001	0.118	0.531	CCSDT(4)
CC(3)PT(5)	0.000	0.070	0.436	CCSDT(5)
CC(4)	0.008	0.020	0.038	CCSDTQ
CC(4)PT(2)	0.001	0.010	0.029	CCSDTQ(2)
CC(4)PT(3)	0.000	0.005	0.022	CCSDTQ(3)
CC(4)PT(4)	0.000	0.003	0.017	CCSDTQ(4)
CC(4)PT(5)	0.000	0.001	0.013	CCSDTQ(5)
CC(5)	0.001	0.003	0.005	CCSDTQP
CC(5)PT(2)	0.000	0.002	0.004	CCSDTQP(2)
CC(5)PT(3)	0.000	0.001	0.003	CCSDTQP(3)
CC(5)PT(4)	0.000	0.000	0.002	CCSDTQP(4)
CC(5)PT(5)	0.000	0.000	0.002	CCSDTQP(5)
CC(6)	0.000	0.000	0.000	CCSDTQPH
CC(7)	0.000	0.000	0.000	CCSDTQPHS
CC(8)	0.000	0.000	0.000	CCSDTQPHSO=FCI
CCSDT-1a	0.354	0.622	0.454	
CCSDT-1b	0.350	0.616	0.653	
CCSDT-2	0.403	0.772	1.141	
CCSDT-3	0.409	0.829	1.567	
CCSD+T(CCSD)	0.287	0.282	-1.407	CCSD[T]=CC4SD[T]
CCSD(T)	0.414	0.719	-0.000	
CCSD(TQ) _Λ	0.014	0.114	0.159	
CCSD(TQ _f) _Λ	0.014	0.121	0.161	
CC5SD[TQ] _Λ	0.015	0.081	0.052	

^aCommonly used notations of the theoretical models. The MBPT(1) and CC(1) total energies are the same as the HF energy.

tions with the ACES II program,⁸⁵ and the CCSD(TQ)_Λ,^{26,28} CCSD(TQ_f)_Λ,^{26,28} and CC5SD[TQ]_Λ^{26,28} calculations with a program written by Kucharski and Bartlett.

We first note that the CC(m)PT(n) results systematically approach the corresponding results of FCI as the per-

TABLE II. Differences (in mE_H) between the FCI energies and the energies obtained from the MBPT(n) and CC(m)PT(n) theory series. The calculations are carried out for the ground state of H_2O using an RHF reference and the 6-31G basis set within the frozen core approximation at three selected bond lengths: $r_{OH}=R_e=0.967 \text{ \AA}$ and $a_{HOH}=107.6^\circ$; $r_{OH}=1.5R_e$ and $a_{HOH}=107.6^\circ$; $r_{OH}=2.0R_e$ and $a_{HOH}=107.6^\circ$. The FCI energies are $-76.121\,174E_H$ (R_e), $-75.985\,788E_H$ ($1.5R_e$), and $-75.876\,474E_H$ ($2.0R_e$).

Theory	R_e	$1.5R_e$	$2.0R_e$	Annotation ^a
MBPT(1)	136.671	197.556	295.881	MP1=HF
MBPT(2)	8.215	20.051	48.894	MP2
MBPT(3)	6.577	24.159	66.947	MP3
MBPT(4)	1.300	5.758	15.235	MP4
MBPT(5)	0.583	4.446	14.639	MP5
CC(1)	136.671	197.556	295.881	CCS=HF
CC(1)PT(2)	8.215	20.051	48.894	CCS(2)
CC(1)PT(3)	6.577	24.159	66.947	CCS(3)
CC(1)PT(4)	1.128	4.381	9.213	CCS(4)
CC(1)PT(5)	0.597	4.423	15.172	CCS(5)
CC(2)	1.545	5.710	9.846	CCSD
CC(2)PT(2)	0.102	4.220	8.788	CCSD(2)
CC(2)PT(3)	0.077	3.170	7.838	CCSD(3)
CC(2)PT(4)	0.007	2.402	6.981	CCSD(4)
CC(2)PT(5)	0.007	1.834	6.208	CCSD(5)
CC(3)	0.449	1.199	-1.965	CCSDT
CC(3)PT(2)	0.049	0.891	-2.006	CCSDT(2)
CC(3)PT(3)	0.013	0.667	-2.040	CCSDT(3)
CC(3)PT(4)	0.003	0.502	-2.065	CCSDT(4)
CC(3)PT(5)	0.001	0.379	-2.084	CCSDT(5)
CC(4)	0.012	0.097	0.102	CCSDTQ
CC(4)PT(2)	0.002	0.067	0.089	CCSDTQ(2)
CC(4)PT(3)	0.000	0.047	0.077	CCSDTQ(3)
CC(4)PT(4)	0.000	0.033	0.067	CCSDTQ(4)
CC(4)PT(5)	0.000	0.024	0.059	CCSDTQ(5)
CC(5)	0.003	0.015	0.023	CCSDTQP
CC(5)PT(2)	0.001	0.010	0.020	CCSDTQP(2)
CC(5)PT(3)	0.000	0.007	0.018	CCSDTQP(3)
CC(5)PT(4)	0.000	0.005	0.016	CCSDTQP(4)
CC(5)PT(5)	0.000	0.004	0.015	CCSDTQP(5)
CC(6)	0.000	0.001	0.002	CCSDTQPH
CC(7)	0.000	0.000	0.000	CCSDTQPHS
CC(8)	0.000	0.000	0.000	CCSDTQPHSO=FCI
CCSDT-1a	0.492	1.142	-3.740	
CCSDT-1b	0.493	1.141	-3.491	
CCSDT-2	0.587	1.771	-0.217	
CCSDT-3	0.590	1.803	0.067	
CCSD+T(CCSD)	0.435	0.544	-8.210	CCSD[T]=CC4SD[T]
CCSD(T)	0.534	1.080	-6.308	
CCSD(TQ) _A	0.076	0.255	-1.832	
CCSD(TQ _f) _A	0.075	0.283	-1.763	
CC5SD[TQ] _A	0.036	0.226	-1.226	

^aCommonly used notations of the theoretical models. The MBPT(1) and CC(1) total energies are the same as the HF energy.

turbation order (n) increases, regardless of the reference CC(m) model upon which the perturbation theory is based. Owing to our particular choice of \bar{H}_0 , CC(m)PT(0) simply amounts to CC(m). The first-order correction to the CC en-

ergies is always null, and the first nonvanishing correction to the CC energies occurs in the second order of the perturbation theory. It may be noticed from the tables that CC(1)PT(n) and MBPT(n) are closely related to each other. These two perturbation series are based on the same CC(1)=HF reference state, and hence MBPT(1)=CC(1)PT(0), but they differ in the definition of the primary (P) and complementary (Q) spaces. The P space of MBPT(n) is just the HF determinant, while that of CC(1)PT(n) consists of the HF determinant and all singly substituted determinants thereof. The second- and third-order energies of these two perturbation series are identical to each other, and at the fourth order and onwards the energies of these two series deviate from each other as a consequence of the different definition of the P and Q spaces, but they both converge at FCI with increasing perturbation order. We consider it a pleasant feature for the CC(m)PT(n) hierarchy to comprise a series that closely resembles the most ubiquitous perturbation theory (MBPT) at the lowest end of the hierarchy. The difference between the CC(1)PT(4) and MBPT(4) energies arises from the different ways of including the energy contributions from the singly substituted determinants. The energy differences are marginal, but the CC(1)PT(4) results appear to be systematically closer to FCI than the MBPT(4) results.

At the equilibrium bond lengths, the proposed second-order perturbation theory is remarkably effective. For example, CC(2)PT(2) reduces the errors between CC(2)=CCSD and FCI from 1.032 to 0.004 mE_H and from 1.545 to 0.102 mE_H in the total energies of FH and H_2O at R_e , respectively. The CC(2)PT(2) errors (0.004 mE_H for FH and 0.102 mE_H for H_2O) are significantly smaller than the errors obtained from any of the CCSD models that approximately incorporate T_3 such as CCSDT-1a (0.354 and 0.492 mE_H) and CCSD(T) (0.414 and 0.534 mE_H). They are even smaller than the errors of CC(3)=CCSDT (0.350 and 0.449 mE_H). This may be expected as CC(2)PT(2) incorporates not only T_3 but also all higher-rank cluster operators in an approximate manner. Among the approximate CC models considered here, only the CCSD(TQ) variants of Kucharski and Bartlett, which incorporate T_3 and T_4 in a noniterative manner, outperform CC(2)PT(2). For the same systems, CC(1)PT(2)=MBPT(2) accounts for 94%–97% of the basis-set correlation energies, and CC(3)PT(2) reduces the errors between CC(3)=CCSDT and FCI roughly by a factor of 10. It may be said, therefore, that CC(m)PT(2) is remarkably accurate for the states whose wave functions are predominantly the HF determinant, and is a promising alternative to the existing perturbative approximations to CC. CC(m)PT(n) appears to be particularly effective at even orders of the perturbation theory. The third-order perturbation theory generally provides only modestly improved results or occasionally poorer results than the second-order perturbation theory. Nonetheless, CC(2)PT(3) appears to achieve the comparable accuracy as the CCSD(TQ) models for the ground states of FH and H_2O at R_e .

As bonds are stretched to $1.5R_e$ and $2.0R_e$, the wave function assumes increased multideterminantal character and, accordingly, the convergence of the perturbation theory

TABLE III. Differences between FCI and the EOM-CC(m)PT(n) theory series in the total energy (E) of the ground state and in the vertical excitation energies (ω_1 and ω_2) to the two lowest-lying $^1\Sigma^+$ excited states of CH^+ ($r_{\text{CH}}=1.131 \text{ \AA}$). An RHF reference and the 6-31G** basis set are employed within the frozen core and frozen virtual approximations. The FCI energy for the ground state is $-37.998\,811E_{\text{H}}$ and the FCI vertical excitation energies to the two lowest singlet Σ^+ states are 8.530 and 14.304 eV.

Theory	$\Delta E/mE_{\text{H}}$	$\Delta\omega_1/\text{eV}$	$\Delta\omega_2/\text{eV}$	Annotation ^a
EOM-CC(1)	101.552	...	0.548	EOM-CCS=CIS
EOM-CC(1)PT(2)	31.941	...	0.242	EOM-CCS(2)=CIS-MP2
EOM-CC(1)PT(3)	13.220	...	0.121	EOM-CCS(3)
EOM-CC(1)PT(4)	6.255	...	0.049	EOM-CCS(4)
EOM-CC(1)PT(5)	3.194	...	0.026	EOM-CCS(5)
EOM-CC(2)	1.941	0.544	0.062	EOM-CCSD
EOM-CC(2)PT(2)	1.086	0.370	0.051	EOM-CCSD(2)
EOM-CC(2)PT(3)	0.642	0.255	0.039	EOM-CCSD(3)
EOM-CC(2)PT(4)	0.390	0.179	0.030	EOM-CCSD(4)
EOM-CC(2)PT(5)	0.244	0.127	0.022	EOM-CCSD(5)
EOM-CC(3)	0.097	0.073	0.003	EOM-CCSDT
EOM-CC(3)PT(2)	0.070	0.056	0.002	EOM-CCSDT(2)
EOM-CC(3)PT(3)	0.050	0.044	0.001	EOM-CCSDT(3)
EOM-CC(3)PT(4)	0.036	0.035	0.001	EOM-CCSDT(4)
EOM-CC(3)PT(5)	0.027	0.028	0.001	EOM-CCSDT(5)
EOM-CC(4)	0.000	0.000	0.000	EOM-CCSDTQ=FCI
CCSDT-1a	0.495	
CCSDT-1b	0.499	
CCSDT-2	0.556	
CCSDT-3	0.555	
CCSD+T(CCSD)	0.442	CCSD[T]=CC4SD[T]
CCSD(T)	0.451	
CCSD(TQ) _A	0.481	
CCSD(TQ) _T _A	0.486	
CC5SD[TQ] _A	0.172	
CIS(D)	0.170	
EOM-CCSDT-3	...	0.231	0.022	
EOM-CCSD(\tilde{T})	...	0.202	-0.008	

^aCommonly used notations of the theoretical models. The EOM-CC(1)=EOM-CCS total energies for the ground and excited states are the same as the HF and CIS energies for the ground and excited states, respectively.

becomes significantly slower. The slower convergence is particularly prominent in the results of CC(m)PT(n) with $m \geq 2$. Although CC(1)PT(2)=MBPT(2) accounts for a respectable fraction (83%–95%) of the basis-set correlation energies of FH and H₂O at $1.5R_e$ and $2.0R_e$, CC(2)PT(2) only marginally improves CC(2). This suggests that our choice of \bar{H}_0 within the Q space ($Q\bar{H}_0Q$) renders CC(m)PT(n) remarkably effective for those electronic states that are described well by a HF determinant, but becomes less satisfactory as the states gain some multideterminantal character. It will be of interest to study the optimal choice of $Q\bar{H}_0Q$ that compromises the applicability and accuracy in a well-balanced manner. Such an analysis will be greatly facilitated with a determinantal CC(m)PT(n) program, as one can examine different choices of $Q\bar{H}_0Q$ by a trivial modification of the program.

Table III summarizes the total energies of the ground

state and the vertical excitation energies (ω_1 and ω_2) to the two lowest-lying $^1\Sigma^+$ excited states of CH^+ calculated by EOM-CC(m)PT(n) ($1 \leq m \leq 4$ and $0 \leq n \leq 5$) with the 6-31G** basis set. The lowest and highest orbitals are excluded in the correlation treatment, and hence EOM-CC(4,4)=FCI. The transition to the lowest-lying $^1\Sigma^+$ state (ω_1) is known to be a dominant double replacement from the reference, whereas ω_2 is a dominant single replacement. Thus, EOM-CC(1,1)=CIS and the perturbation theory thereof do not provide ω_1 . The results of some iterative and noniterative approximate CC calculations for the ground states and the results of the CIS(D),⁵³ EOM-CCSDT-3,⁴⁸ and EOM-CCSD(\tilde{T})⁴⁹ calculations for the excitation energies are also listed in the table. The CIS(D) calculation has been performed with the Q-CHEM program⁸⁶ and the EOM-CCSDT-3 and EOM-CCSD(\tilde{T}) calculations with a program written by Watts and Bartlett. In this study, the EOM-CC(m)PT(n) excitation energies are defined as the EOM-CC(m)PT(n) total energies for excited states minus the CC(m)PT(n) total energy for the ground state. With this definition, both the total energies and the excitation energies of EOM-CC(m)PT(n) converge at the corresponding FCI values with increasing perturbation order n , regardless of the parent EOM-CC(m, m) model upon which the perturbation theory is based. This is in contrast to some approximate EOM-CC models, such as EOM-CCSD(\tilde{T}) and CCSDR(3),⁵² in which the total energies of excited states may not be unambiguously defined. Unlike EOM-CCSDT-3, EOM-CCSD(\tilde{T}), or CCSDR(3), however, EOM-CC(m)PT(n) is not size intensive. The lack of the size intensivity of EOM-CC(m)PT(n) may be understood by identifying the EOM-CC(1)PT(2) model as the CIS-MP2 method proposed by Foresman *et al.*,⁸⁷ which also lacks the size intensivity.⁵³

The ground state of CH^+ has substantial multideterminantal character and is a challenging problem for single-reference perturbation theories. The contribution of the RHF determinant in the FCI wave function is only 75%. As may be expected from the results of stretched bond cases, CC(m)PT(n) yields a rather slowly convergent series. For the vertical excitation energy of the dominant single replacement transition (ω_2), the second- and third-order perturbation theories on the basis of EOM-CC(1,1)=CIS reduce the errors in the excitation energies from the FCI result roughly by 50% and 75%, respectively. Consequently, EOM-CC(1)PT(2)=CIS-MP2 performs slightly worse than CIS(D), while EOM-CC(1)PT(3) outperforms CIS(D), the latter reducing the errors from the FCI result by 70%. Going from EOM-CC(1,1)=CIS to EOM-CC(2,2)=EOM-CCSD or a higher EOM-CC model, the perturbation theory tends to become less effective. For ω_2 , EOM-CC(2)PT(2) only marginally improves the EOM-CC(2)=EOM-CCSD result, although the latter is already a remarkably good approximation to the FCI result. For the electronic transition having appreciable double replacement character (ω_1), EOM-CC(m)PT(n) provides a series of rather slowly improving results. This reflects the multideterminantal character of the wave function of the excited state that is the destination of this transition. For this excited state, the second- and third-

order perturbation theories decrease the error in the excitation energy between EOM-CC(2)=EOM-CCSD and FCI roughly by a factor of 1/3 and 1/2, respectively. To arrive at the accuracy of EOM-CCSDT-3 or EOM-CCSD(\tilde{T}), one must resort to EOM-CC(2)PT(3) or EOM-CC(2)PT(4). Considering the lack of size intensivity and the rather slow convergence of the perturbation series, we conclude that EOM-CC(m)PT(n) does not deserve an implementation. This is in striking contrast with CC(m)PT(n) for the ground states, which performs remarkably well at equilibrium geometries, and is promising. It appears to be true that other perturbative corrections to excitation energies such as EOM-CCSD(T), EOM-CCSD(\tilde{T}), CIS(D), and CIS-MP2 also perform less satisfactorily than their ground-state counterparts, i.e., CCSD(T) and MBPT(2). This is perhaps because, for some excited states, neither the EOM-CC or CI method provides an appropriate zeroth-order description on the basis of which a rapidly convergent perturbation series can be generated.

V. CONCLUSION

The efforts to generate a hierarchy of perturbative approximations to CC and EOM-CC from a single general framework and thereby find a better performing series of approximation seem to have converged at a central idea, i.e., the perturbative expansion of the similarity-transformed Hamiltonian.^{55,56,58,62,63} In this study, we have invoked this idea and generated a series of perturbative corrections to the total energies of the ground and excited states of molecules. The resulting combined CC or EOM-CC and Rayleigh–Schrödinger perturbation theory, which we designate by CC(m)PT(n) or EOM-CC(m)PT(n), has the following features: (1) CC(m)PT(n) and EOM-CC(m)PT(n) are based on a single theoretical framework. (2) CC(m)PT(n) and EOM-CC(m)PT(n) systematically approach FCI as the perturbation order (n) increases and/or the cluster operator and the linear excitation operator become closer to complete (m increases), regardless of the parent CC(m) or EOM-CC(m,m) model upon which the perturbation theory is based. (3) At any order of perturbation, the orbital-invariance property and size extensivity of CC are maintained, but the size intensivity of the excitation energies of EOM-CC is violated. (4) The zeroth-order energy and wave function are those of the parent CC or EOM-CC model.

We have developed a program that is capable of computing the CC(m)PT(n) or EOM-CC(m)PT(n) energies and wave functions at any given perturbation order (n) for any of the complete CC or EOM-CC models (m) by combining a determinantal CC or EOM-CC algorithm and a determinantal MBPT algorithm. With this program, we have demonstrated that CC(m)PT(n) performs remarkably well and frequently outperforms CCSD(T) or even CCSDT when the wave function of the system of interest is dominated by the RHF determinant. Therefore, CC(m)PT(n) is a promising alternative to the existing perturbative approximations to CC and the implementation of CC(m)PT(n) into an optimally efficient program is warranted. It is not very meaningful to discuss the accuracy of any quantum chemistry model regardless of the efficiency and applicability. The determinantal

approach employed here allows us to obtain essential information about the accuracy and some information about the applicability of the entire hierarchy of the models with a minimal implementation effort. However, the approach is not capable of providing any piece of information about the efficiency of the models. The integral-based (as opposed to determinant-based) implementation of CC(m)PT(n), which may involve some further approximation (e.g., the factorization approximation²⁶) and is beyond the scope of this study, would provide this important piece of information about the efficiency. For excitation energies, EOM-CC(m)PT(n) has turned out to lack size intensivity and converges rather slowly with respect to n , indicating that one may have to take a different approach for excited states (see, e.g., Ref. 72) than for the ground state to achieve uniformly good results. In other words, the present formalism, which maintains many of the common features of single-reference perturbation theory, is particularly suited for those systems the wave functions of which are predominantly the HF determinant.

ACKNOWLEDGMENTS

The authors would like to thank Professor Leszek Meissner (Nicholas Copernicus University) for illuminating discussions. The authors gratefully acknowledge Professor Stanisław A. Kucharski (Silesian University) for providing a program for CCSD(TQ)_Λ, CCSD(TQ_f)_Λ, and CC5SD[TQ]_Λ and Professor John D. Watts (Jackson State University) for a program for EOM-CCSDT-3 and EOM-CCSD(\tilde{T}). This work was supported by U.S. Air Force Office of Scientific Research under Grant No. F49620-98-0116.

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