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# Perturbative triple excitation corrections to coupled cluster singles and doubles excitation energies

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The contributions from various excitation levels to excitation energies calculated within a coupled cluster framework are analyzed in terms of order in the fluctuation potential. In particular, the role of triple excitations is considered, focusing on their importance for describing excitations of single and double replacement dominated character. Several noniterative triples corrections to the coupled cluster singles and doubles (CCSD) excitation energies are proposed. In the CCSDR(3) approach, which is a noniterative analog to the recently proposed iterative CC3 model, single replacement dominated excitations are correct through third order in the fluctuation potential, and double replacement dominated excitations are correct through second order. The performance of CCSDR(3) is compared to other noniterative and iterative triples models in benchmark calculations on  $\text{CH}^+$ , Ne, BH, and  $\text{CH}_2$ . © 1996 American Institute of Physics. [S0021-9606(96)02528-7]

## I. INTRODUCTION

Second-order Møller–Plesset theory (MP2), coupled cluster singles and doubles (CCSD), and CCSD with perturbative triples contributions, CCSD(T),<sup>1</sup> constitute a hierarchy of approximations where electron correlation is treated at a still higher level of sophistication. Increasing accuracy can therefore be obtained for ground state properties in single configuration dominated systems going to higher levels in this hierarchy. In iterative coupled cluster models like CCSD, both excitation energies<sup>2</sup> and transition moments<sup>3</sup> can be determined from coupled cluster response theory.<sup>4–8</sup> The frequency dependent polarizability derived from a MP2 quasienergy exhibits a pole structure that is inconsistent with the one of the exact response function,<sup>9,10</sup> and excitation energies and transition moments cannot therefore be obtained in MP2. Similarly, for the two-step approach CCSD(T), where perturbative triple excitation corrections are added to the ground state energy, a response function with one set of poles improved relative to the poles of the CCSD response function does not exist. Excitation energies and transition moments therefore cannot be obtained with increasing accuracy in the MP2, CCSD, and CCSD(T) hierarchy.

In a recent series of papers we have introduced a hierarchy of coupled cluster models:<sup>7,11–13</sup>  $\text{CCS}(N^4)$ ,  $\text{CC2}(N^5)$ ,  $\text{CCSD}(N^6)$ ,  $\text{CC3}(N^7)$ , etc., where excitation energies and transition moments can be obtained at increasing accuracy. The numbers in parenthesis indicate the computational effort given in terms of the scaling of the calculations with the number of orbitals  $N$ . The CC2 and CC3 models are introduced as approximations to CCSD and coupled cluster singles, doubles, and triples (CCSDT), respectively. The strategies used in introducing CC2 and CC3 are similar, and are based on a perturbational analysis of the coupled cluster equations in terms of order in the fluctuation potential, and on the crucial role of single excitations in coupled cluster property calculations. In CC2 we approximate the CCSD doubles equation to lowest nonvanishing order in perturbation theory (first order) and in CC3 the CCSDT triples equa-

tion is approximated to lowest nonvanishing order (second order). The singles amplitudes will respond to external perturbations to zeroth order in the fluctuation potential and we therefore treat the singles as zeroth-order parameters. The CC2 model is similar to MP2 in the sense that the ground state energy is correct to second order in the fluctuation potential, and both scale as  $N^5$ . The CC3 ground state energy contains the same fourth- and fifth-order terms as CCSD(T) and scales as  $N^7$ . For ground state energies (and thus all properties obtained from this as derivatives) the CCS, CC2, CCSD, CC3 hierarchy should thus be considered similar to that of HF, MP2, CCSD, and CCSD(T), but the introduction of CC2 and CC3 extends the hierarchical concept to excitation energies, transition moments, etc., as well as frequency dependent molecular properties will have a proper pole structure.

We have derived the response functions for the coupled cluster models in the hierarchy of coupled cluster models.<sup>7,11</sup> From these we have determined excitation energies and transition moments as poles and residues, respectively. This leads to coupled cluster eigenvalue equations for determining the excitation energies. Since CC2 and CC3 are iterative models we need to solve equations iteratively with  $N^5$  and  $N^7$  operation count, respectively, to find both the reference energy and the excitation energies. However perturbational corrections to CCS and CCSD excitation energies can be defined that, from a perturbational point of view, level CC2 and CC3 in accuracy. It should be emphasized that the excitation energies obtained from such perturbational approaches do not represent poles of a response function, and are not rigorously related to a ground state energy. However, the perturbational corrections are interesting because (1) noniterative approaches are computationally preferable to iterative models and (2) they may be helpful in understanding the importance of individual contributions to the excitation energies. Even though a noniterative approach is justified from perturbation theory there is no guarantee that it will perform similar to iterative models. However this does not necessar-

ily imply that the noniterative approaches are inferior to iterative models on the contrary. For ground state energies it is an empirical observation that the noniterative CCSD(T) approach is as good as iterative triples models like CC3 and CCSDT-1a.<sup>14</sup>

A noniterative CC2 approach defines a doubles correction to the CCS excitation energies and in fact becomes equivalent to the CIS(D) approach of Head-Gordon *et al.*<sup>15</sup> We compare models including the doubles iterative or noniterative in another publication. In this paper we investigate triples corrections to CCSD excitation energies.

In Ref. 16 Watts and Bartlett presented excitation energies in the CCSDT-1a model.<sup>17</sup> In a recent paper<sup>7</sup> we analyzed CC3 and CCSDT-1a excitation energies and found that for single replacement dominated excitations CCSDT-1a are only correct to second order in the fluctuation potential, whereas CC3 is correct through third order. The CCSD model is correct through second order. In recent benchmark calculations<sup>13</sup> we found that CCSDT-1a often fails to improve the CCSD results, while in CC3 all considered excitations are improved. The double replacement dominated excitations are significantly improved in both CC3 and CCSDT-1a and are correct through second order in the fluctuation potential in both approximations. In the case of CCSD these excitations are only determined correct through first order. The different behavior of CC3 and CCSDT-1a for single replacement dominated excitation is due to the fact that CC3 includes the direct coupling of single and triple excitations, whereas CCSDT-1a does not,<sup>7,13</sup> and this coupling enters in third order. In Ref. 16 a noniterative triples method denoted EOM-CCSD(T) was proposed based on CCSDT-1a. From the CCSDT-1a eigenvalue equation a triples correction was introduced in a proposed analogy with the connection between CCSDT-1a and CCSD(T) for ground state energies. Since EOM-CCSD(T) is based on CCSDT-1a it does not include either the direct singles–triples coupling and third-order terms are thus neglected for single replacement dominated excitations. As we shall see later, double replacement dominated excitations in EOM-CCSD(T) have errors in second order in the fluctuation potential. EOM-CCSD(T) improved the quality of double replacement dominated excitations considerably relative to CCSD. While both EOM-CCSD(T) and CCSD(T) in a loose sense may be described as a first iteration of CCSDT-1a in, respectively, the ground excitation energy expressions and the ground state energy, the analogy between CCSD(T) and EOM-CCSD(T) has some important shortcomings: (1) CCSD(T) does not have a response function with a pole structure allowing for the identification of CCSD(T) excitation energies; CCSD(T) excitation energies therefore do not exist! (2) A noniterative correction to excitation energies does not have a rigorous connection to ground state energies. (3) The EOM-CCSD(T) excitation energy correction is based on a proposed analogy between eigenvalue equations and reference energy equations. However in the presentation of the EOM-CCSD(T) approach in Ref. 16 an order analysis in the fluctuation potential is not given, while the order concept is essential in establishing the CCSD(T) correction to the ground state

energy.<sup>1</sup> We shall see that the EOM-CCSD(T) excitation energy in this sense is quite inferior to the fourth-order quality of a CCSD(T) ground state energy, and to other approaches for including triples corrections to CCSD excitation energies. (4) The CCSD(T) approach differs from other earlier perturbative corrections like CCSD+T(CCSD)<sup>18</sup> due to the inclusion of a singlet–triplet coupling term, that actually first enter in fifth order. No direct singlet–triplet coupling is included in the EOM-CCSD(T) excitation energy.

In this paper we will introduce corrections to CCSD excitation energies based on perturbation theory arguments. We identify the most important contributions beyond CCSD based on perturbation theory in the fluctuation potential. This leads us to define a pseudoperturbation to the CCSD eigenvalue problem, including the most important higher order contributions. From an expansion of the eigenvalue equation in this pseudoperturbation, we identify the lowest order contributions beyond CCSD. This is a generalization of the approach used by Head-Gordon *et al.* in the introduction of the CIS(D) doubles correction to CIS excitation energies.<sup>15</sup> We obtain a perturbational corrected excitation energy that is correct through *third order in the fluctuation potential* for single replacement dominated excitations, and through *second order in the fluctuation potential* for double replacement dominated excitations. We denote the excitation energies obtained in this approach as coupled cluster single and double response excitation energies with lowest order triples corrections [CCSDR(T)]. The (T) is used to emphasize that noniterative triples corrections are added to the CCSD result. It does not indicate a direct relationship with CCSD(T). The R indicates that we consider coupled cluster response and it is to the response properties we add triples corrections. From iterative triples models like CC3, CCSDT-1a, and CCSDT-1b<sup>17</sup> we may introduce corresponding noniterative perturbational corrections. We denote these approaches CCSDR(3), CCSDR(1a), and CCSDR(1b). None of these excitation energies has a strict relationship to a ground state energy. Of course the triples corrected excitation energy can be added to various ground state energies to obtain an approximation for the excited state energy, but we should keep in mind that this is an additional approximation. We discuss this topic in a forthcoming publication. In this paper we introduce the perturbational triples corrections to CCSD and compare excitation energies for CH<sup>+</sup>, Ne, BH, and CH<sub>2</sub> with results obtained in recent benchmark calculations.

## II. PERTURBATION THEORY ANALYSIS OF EXCITATION ENERGIES IN COUPLED CLUSTER THEORY

Coupled cluster excitation energies are determined solving the coupled cluster response eigenvalue equation,

$$\mathbf{A}\mathbf{R}_k = \omega_k \mathbf{R}_k, \quad (1)$$

where  $\mathbf{A}$  is the nonsymmetric coupled cluster Jacobian.  $\mathbf{R}_k$  is the right eigenvector corresponding to the eigenvalue  $\omega_k$ . The left eigenvector  $\mathbf{L}_k$  is obtained from

$$\mathbf{L}_k \mathbf{A} = \omega_k \mathbf{L}_k. \quad (2)$$

From biorthogonality it follows (if we choose the normalization to unity) that

$$\mathbf{L}_j \mathbf{R}_k = \delta_{jk}. \quad (3)$$

Using the orthonormality we may write the excitation energy as,

$$\omega_k = \mathbf{L}_k \mathbf{A} \mathbf{R}_k. \quad (4)$$

Consider now the Jacobian of exact coupled cluster theory,

$$A_{\mu_i v_j} = \langle \mu_i | \exp(-T) [H_0, \tau_{v_j}] \exp(T) | HF \rangle, \quad (5)$$

where the  $\mu$  excitations in excitation class  $i=1,2,\dots,n$  are designated  $\mu_i$ . Without truncations in the expansion of  $T$  we can represent the exact solution in terms of a coupled cluster parametrization. Partitioning the Hamiltonian  $H_0$  into the Fock potential  $F$ , and the fluctuation potential  $U$ ,  $H_0 = F + U$ , the Jacobian in Eq. (5) can be expressed in terms of contributions from various excitation levels in different orders in the fluctuation potential.

Recognizing that  $T_2$  enters in first order,  $T_1$  and  $T_3$  in second order, and higher excitation cluster operators to higher order, we may expand the matrix elements of the Jacobian as

$$\begin{aligned} A_{\mu_i v_j} = & \langle \mu_i | [F, \tau_{v_j}] | HF \rangle + \langle \mu_i | [U, \tau_{v_j}] | HF \rangle \\ & + \langle \mu_i | [[U, \tau_{v_j}], T_2] | HF \rangle \\ & + \langle \mu_i | \frac{1}{2} [[[U, \tau_{v_j}], T_2], T_2] + [[U, \tau_{v_j}], T_1 \\ & + T_3] | HF \rangle + o(4), \end{aligned} \quad (6)$$

where the zero-, first-, second-, and third-order matrix elements are given explicit. The structure of the Jacobian containing singles(S), doubles(D), triples(T), quadruples(Q), and quintuples(P) becomes

$$\left\{ \begin{array}{cccccc} & \text{S} & \text{D} & \text{T} & \text{Q} & \text{P} \\ \text{S} & d(0)+o(1) & o(1) & o(1) & 0 & 0 \\ \text{D} & o(1) & d(0)+o(1) & o(1) & o(1) & 0 \\ \text{T} & o(2) & o(1) & d(0)+o(1) & o(1) & o(1) \\ \text{Q} & o(3) & o(2) & o(1) & d(0)+o(1) & o(1) \\ \text{P} & o(4) & o(3) & o(2) & o(1) & d(0)+o(1) \end{array} \right\}, \quad (7)$$

where  $d(0)$  denotes the zero-order diagonal elements consisting of Hartree–Fock orbital differences and  $o(n)$  denotes the lowest nonvanishing order of the Jacobian matrix elements. For example the ST block enters in first order since the second term in Eq. (6) contributes, whereas the TS block enters in second order since the first and second terms in Eq. (6) are zero and the third term contributes. We divide the excitation space into two subsets, I and II, and write Eq. (2) accordingly

$$\begin{pmatrix} \mathbf{A}_{\text{I,I}} & \mathbf{A}_{\text{I,II}} \\ \mathbf{A}_{\text{II,I}} & \mathbf{A}_{\text{II,II}} \end{pmatrix} \begin{pmatrix} \mathbf{R}_{\text{I}} \\ \mathbf{R}_{\text{II}} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{R}_{\text{I}} \\ \mathbf{R}_{\text{II}} \end{pmatrix}. \quad (8)$$

Space I may refer to the singles space exclusively or the singles and doubles space combined. The definitions of  $\mathbf{A}_{\text{I,I}}$ ,  $\mathbf{A}_{\text{I,II}}$ ,  $\mathbf{A}_{\text{II,I}}$ , and  $\mathbf{A}_{\text{II,II}}$  are clear from the context. The effect of higher excitation levels on excitations predominately described within the I space can be analyzed using partitioning techniques. Equation (8) can be written as,

$$(\mathbf{A}_{\text{I,I}} - \omega \mathbf{I}) \mathbf{R}_{\text{I}} = -\mathbf{A}_{\text{I,II}} \mathbf{R}_{\text{II}}, \quad (9)$$

$$(\mathbf{A}_{\text{II,II}} - \omega \mathbf{I}) \mathbf{R}_{\text{II}} = -\mathbf{A}_{\text{II,I}} \mathbf{R}_{\text{I}}. \quad (10)$$

The zero-order problem is described by

$$A_{\mu_i v_j} = \langle \mu_i | [F, \tau_{v_j}] | HF \rangle = \omega_{\mu_i} \delta_{\mu_i v_j}, \quad (11)$$

where  $\omega_{\mu_i}$  consist of sum and differences of orbital energies, assuming a canonical molecular orbital basis. Thus the  $\omega_{\mu_i}$  are the zero-order eigenvalues with eigenvectors represented by unit vectors. For single dominated excitations I denote the single excitation space only and the zero-order solution vector becomes  $\mathbf{R}_{\text{I}}^{(0)}$ . From Eqs. (10) and (6) we obtain a right correction vector to first order in the fluctuation potential as,

$$(\omega_{\mu_2} - \omega^{(0)}) R_{\mu_2}^{(1)} = -\langle \mu_2 | [U, R_{\text{I}}^{(0)}] | HF \rangle. \quad (12)$$

We have absorbed the  $\mathbf{R}_{\text{I}}^{(0)}$  vector into a corresponding operator for which we will use the same notation,  $R_{\text{I}}^{(0)} = \sum_{v_1} R_{v_1}^{(0)} \tau_{v_1}$ . Only double excitations contribute to first order. Higher excitations enter in higher order. In particular we find that to second order triples enter in the form,

$$\begin{aligned} (\omega_{\mu_3} - \omega^{(0)}) R_{\mu_3}^{(2)} = & -\langle \mu_3 | [[U, R_{\text{I}}^{(0)}], T_2] | HF \rangle \\ & -\langle \mu_3 | [U, R_{\text{II}}^{(1)}] | HF \rangle. \end{aligned} \quad (13)$$

For the double replacement dominated excitations we find that both singles and triples enter in the first-order correction vector to the zero-order solution  $\mathbf{R}_{\text{II}}^{(0)}$ ,

$$(\omega_{\mu_i} - \omega^{(0)}) R_{\mu_i}^{(1)} = -\langle \mu_i | [U, R_{\text{II}}^{(0)}] | HF \rangle, \quad i=1,3. \quad (14)$$

TABLE I. The order in the fluctuation potential in which different excitation components enter in the excitation vector.

Excitation vector component		S	D	T	Q
Single replacement dominated	R	0	1	2	3
	L	0	1	1	2
Double replacement dominated	R	1	0	1	2
	L	1	0	1	1

For the left-hand solution vectors we can perform a similar analysis. For the single replacement dominated excitations we find the first-order correction vector to  $\mathbf{L}_1^{(0)}$ ,

$$L_{\nu_j}^{(1)}(\omega_{\nu_j} - \omega^{(0)}) = - \sum_{\mu_1} L_{\mu_1}^{(0)} \langle \mu_1 | [U, \tau_{\nu_j}] | HF \rangle, \quad j=2,3. \quad (15)$$

Note that the non-Hermitian nature of the CC Jacobian makes the right- and left-hand eigenvectors different in the way that the left-hand vector contains triples corrections to first order, whereas the triples correction is second order for the right-hand solution vector. This originates from the fact mentioned above that the TS block enters in second order whereas the ST block enters in first order. For the double replacement dominated excitations we have

$$L_{\nu_j}^{(1)}(\omega_{\nu_j} - \omega) = - \sum_{\mu_2} L_{\mu_2}^{(0)} \langle \mu_2 | [U, \tau_{\nu_j}] | HF \rangle, \quad j=1,3. \quad (16)$$

In Table I we have summarized the results obtained from the analysis above. Using the results in Table I, the excitation energy in the form of Eq. (4), and the structure of the Jacobian in Eq. (7), we may identify the order in which contributions from various blocks and excitations enter. The results are given in Table II.

Coupling between ‘‘neighboring’’ excitation levels enter in second order [from the second term on the right-hand side of Eq. (6)], whereas excitation levels separated by two couples in third order [coupling the second and the third

TABLE II. The order in the fluctuation potential in which contributions from various blocks of the Jacobian, and components of the eigenvectors enters in the excitation energies for single and double replacement dominated excitations.

	Single excitations	Double excitations
$L_S A_{SS} R_S$	0	2
$L_S A_{SD} R_D$	2	2
$L_D A_{DS} R_S$	2	2
$L_D A_{DD} R_D$	2	0
$L_S A_{ST} R_T$	3	3
$L_T A_{TS} R_S$	3	4
$L_D A_{DT} R_T$	4	2
$L_T A_{TD} R_D$	3	2
$L_T A_{TT} R_T$	3	2
Q and higher	$o(5)$	$o(3)$

terms in Eq. (6)]. We thus find in Table II that to zero and first order only contributions from the singles space enter for single replacement dominated excitations. The coupling to doubles enters in second order. Since CCSD contains all singles and doubles terms, CCSD is correct through second order for single replacement dominated excitations, and beyond second order it is necessary to include higher excitations. All terms within the singles and doubles space are determined correct through third order in CCSD since the reference singles and doubles amplitudes are correct through second order. The only additional third-order terms enter from the coupling to triples. For double replacement dominated excitations CCSD is only correct through first order, and the coupling to triples enters in second order. We have previously discussed this for iterative coupled cluster models but the term by term analysis summarized in Table II is convenient in analyzing the behavior of noniterative triples corrections to CCSD.

It is evident from the theory above, that to obtain the single replacement excitations correct through third order in a coupled cluster parametrization it is necessary to include the lowest order contributions to all triples blocks, that is the ST, TS, DT, TD, and TT blocks must be taken into account to lowest order which is first, second, first, first and zeroth order, respectively. For obtaining the double excitations correct through second order it is necessary to include the lowest order contributions from DT, TD, and TT.

### III. PERTURBATIONAL CORRECTIONS TO CCSD EXCITATION ENERGIES

In the previous section we identified the most important triples contributions beyond CCSD. All these terms are included in the iterative CC3 model, while the CCSDT-1a model only partially includes the third-order terms for single replacement dominated excitations. The importance of including all terms through a given order was demonstrated in the numerical examples in Refs. 7 and 13. In this section we introduce perturbational corrections to CCSD that include all lowest order triples terms. All third-order terms are included for single replacement dominated excitations and all second-order terms are included for double replacement dominated excitations. We further introduce noniterative triples models corresponding to the iterative CC3, CCSDT-1a, and CCSDT-1b models. We define a pseudoperurbation theory by partitioning the Jacobian,

$$\mathbf{A} = \mathbf{A}^{(0)} + \mathbf{A}^{(1)} + \mathbf{A}^{(2)}. \quad (17)$$

The zeroth-order Jacobian  $\mathbf{A}^{(0)}$  are defined to be the CCSD Jacobian augmented with all zeroth-order orbital energy differences in the triple and higher excitation part of the Jacobian,

$$\mathbf{A}^{(0)} = \begin{pmatrix} \mathbf{A}^{SD} & 0 \\ 0 & \omega \end{pmatrix}, \quad (18)$$

The pseudoperburbations  $\mathbf{A}^{(1)}$  and  $\mathbf{A}^{(2)}$  need to be defined. To ease the understanding of the structure of all elements that

enter in the various approaches, we start off by introducing  $\mathbf{A}^{(1)}$  and  $\mathbf{A}^{(2)}$  based on the CC3 Jacobian. CC3 is the most complete iterative triples model of CC3, CCSDT-1a, and CCSDT-1b, and the other methods can be obtained by neglecting terms in the CC3 Jacobian. From the CC3 Jacobian of Ref. 13 we define the pseudoperturbations,

$$\mathbf{A}^{(1)} = \begin{Bmatrix} 0 & 0 & \langle \mu_1 | [H_0, \tau_{v_3}] | HF \rangle \\ 0 & 0 & \langle \mu_2 | [\hat{H}_0, \tau_{v_3}] | HF \rangle \\ \langle \mu_3 | [[\hat{H}_0, T_2], \tau_{v_1}] | HF \rangle & \langle \mu_3 | [\hat{H}_0, \tau_{v_2}] | HF \rangle & 0 \end{Bmatrix}, \quad (19)$$

and

$$\mathbf{A}^{(2)} = \begin{Bmatrix} 0 & 0 & 0 \\ \langle \mu_2 | [[\hat{H}_0, T_3], \tau_{v_1}] | HF \rangle & 0 & 0 \\ 0 & 0 & 0 \end{Bmatrix} + \mathbf{A}^{\text{SD,ho}}, \quad (20)$$

where ho (higher order) denotes that we consider higher order terms originating from improving the singles and doubles amplitudes beyond CCSD. In Eqs. (19) and (20) we have used the  $T_1$  transformed Hamiltonian of Ref. 19,

$$\hat{o} = \exp(-T_1) o \exp(T_1). \quad (21)$$

The triples dependent DS block in  $\mathbf{A}^{(2)}$  is taken as second order in the pseudoperturbation since this term is itself third order in the fluctuation potential, and it therefore couples singles with doubles in fourth order. The triples amplitudes in  $\mathbf{A}^{(2)}$  include the lowest order contributions in perturbation theory. The explicit expression for the triples amplitudes is the one from the corresponding iterative model. [That is the CC3 triples equation for CCSDR(3) and the CCSDT-1b triples equation for CCSDR(1b).] For CC3 this is

$$t_{\mu_3} = - \frac{\langle \mu_3 | [\hat{U}, T_2] | HF \rangle}{\omega_{\mu_3}}. \quad (22)$$

For CCSDT-1b the  $T_1$  transformation in Eq. (22) is skipped. Further we need to define how the higher order contributions in the SD block are included in  $\mathbf{A}^{\text{SD,ho}}$ . We therefore define triples corrected single and double amplitudes as

$$t_{\mu_i}^* = t_{\mu_i}^{\text{CCSD}} + \frac{\langle \mu_i | [\hat{H}, T_3] | HF \rangle}{\omega_{\mu_i}}, \quad (23)$$

and may then include the lowest order effects defining  $\mathbf{A}^{\text{SD,ho}}$  from

$$\mathbf{A}^{\text{CCSD}} + \mathbf{A}^{\text{SD,ho}} = \mathbf{A}^{\text{SD}}(t_1^*, t_1^*), \quad (24)$$

where  $\mathbf{A}^{\text{SD}}(t_1^*, t_1^*)$  denotes a CCSD Jacobian built from the triples corrected amplitudes in Eq. (23). The effect of  $\mathbf{A}^{\text{SD,ho}}$  enters in fourth order. It is included since it has proven numerically important and because it can be considered as describing the lowest order effects of relaxing the ground state amplitudes to the effect of triples excitations. Note that in CCSDR(3) we have for convenience chosen to calculate the triples contribution in  $\mathbf{A}^{(2)}$  from the triples corrected amplitudes.

The coupling between various blocks in  $\mathbf{A}^{(1)}$  describes the lowest order triples contributions. The different treatments of the terms in  $\mathbf{A}^{(1)}$  and  $\mathbf{A}^{(2)}$  give a simple relationship to the iterative CC3 model (see later). Including terms through second order in the pseudoperturbation ensure that we have included all terms that are second order in the fluctuation potential from these blocks (since all terms in  $\mathbf{A}^{(1)}$  are at least of first order in the fluctuation potential) and in particular that single replacement dominated excitations are correct through third order in the fluctuation potential (since the TS block giving this coupling is second order in the fluctuation potential). To second order in the pseudoperturbation with the above definitions of  $\mathbf{A}^{(1)}$  and  $\mathbf{A}^{(2)}$  we obtain CCSDR(3) excitation energies. As discussed above the  $\mathbf{A}^{(2)}$  terms will contribute in fourth and higher order, and the  $\mathbf{A}^{(2)}$  terms can thus be neglected without consequences for the order in which we have determined the excitation energies correct through. This gives the CCSDR(T) approach. This model includes the lowest order contributions beyond CCSD, and is the natural choice in a strict order correct approach. (Note that we retain the  $T_1$  transformed Hamiltonian since we always treat the singles as zeroth-order parameters).

Neglecting terms in the iterative CC3 model give the CCSDT-1a and CCSDT-1b models. Noniterative models corresponding to the CCSDT-1a and CCSDT-1b Jacobians may be obtained in the same way that CCSDR(3) was obtained from CC3. We denote these as CCSDR(1a) and CCSDR(1b). We have not included the relaxation of the reference amplitudes in these models. This is convenient since it makes it easier to appreciate the difference between our strategy and the EOM-CCSD(T) approach in Ref. 16. The CCSDR(1b) correction is obtained from CCSDR(3) neglecting the TS block of  $\mathbf{A}^{(1)}$  and the  $T_1$  transformation in the TD block, in addition to not considering  $\mathbf{A}^{\text{SD,ho}}$ . CCSDR(1a) is obtained from CCSDR(1b) by further neglecting the  $T_1$  transformation in the DT block and the  $\mathbf{A}^{(2)}$  contribution. The CCSDR(1a) and CCSDR(1b) approaches may improve the double replacement dominated excitations and will fail to improve the single replacement dominated excitations consistently as is evident from the analysis in the preceding section.

Assume now that we have solved the zeroth-order problems, that is we have determined the CCSD left and right eigenvectors,

TABLE III. Excitation energy corrections in various models and the order in the fluctuation potential through which single(S) and double(D) replacement dominated excitations are formally correct.  $\mathbf{L}^{(0)}$ ,  $\mathbf{L}^{(1)}$ ,  $\mathbf{R}^{(0)}$ , and  $\mathbf{R}^{(1)}$  refer to CCSD vectors and first-order vectors in the pseudoperturbation [see Eqs. (27) and (33)].  $\mathbf{A}^{\text{CCSD}}$  is the CCSD Jacobian build with CCSD amplitudes ( $t_1, t_2$ ) or triples corrected amplitudes.

Model	Expression for the triples corrected excitation energies	S	D
CCSDR(3) <sup>a</sup>	$\mathbf{L}^{(0)}\mathbf{A}^{\text{CCSD}}(t_1^*, t_2^*)\mathbf{R}^{(0)}$ $+ \sum_{\substack{\mu_i \\ i=1,2}} L_{\mu_i}^{(0)} \sum_{\nu_3} \frac{\langle \mu_i   [\hat{U}^*, \tau_{\nu_3}]   HF \rangle \langle \nu_3   [\hat{U}^*, R_2^{(0)}] + [[\hat{U}^*, R_1^{(0)}], T_2^*]   HF \rangle}{\omega_{\nu_3} - \omega^{(0)}}$ $+ \sum_{\mu_2} L_{\mu_2}^{(0)} \langle \mu_2   [[U, R_1^{(0)}], T_3^*]   HF \rangle$	3	2
CCSDR(T)	$\mathbf{L}^{(0)}\mathbf{A}^{\text{CCSD}}(t_1, t_2)\mathbf{R}^{(0)} + \sum_{\substack{\mu_i \\ i=1,2}} L_{\mu_i}^{(0)} \sum_{\nu_3} \frac{\langle \mu_i   [\hat{U}, \tau_{\nu_3}]   HF \rangle \langle \nu_3   [\hat{U}, R_2^{(0)}] + [[\hat{U}, R_1^{(0)}], T_2]   HF \rangle}{\omega_{\nu_3} - \omega^{(0)}}$	2	2
CCSDR(1a)	$\mathbf{L}^{(0)}\mathbf{A}^{\text{CCSD}}(t_1, t_2)\mathbf{R}^{(0)} + \sum_{\substack{\mu_i \\ i=1,2}} L_{\mu_i}^{(0)} \sum_{\nu_3} \frac{\langle \mu_i   [U, \tau_{\nu_3}]   HF \rangle \langle \nu_3   [U, R_2^{(0)}]   HF \rangle}{\omega_{\nu_3} - \omega^{(0)}}$	2	2
CCSDR(1b)	$\mathbf{L}^{(0)}\mathbf{A}^{\text{CCSD}}(t_1, t_2)\mathbf{R}^{(0)} + \sum_{\substack{\mu_i \\ i=1,2}} L_{\mu_i}^{(0)} \sum_{\nu_3} \frac{\langle \mu_i   [U, \tau_{\nu_3}]   HF \rangle \langle \nu_3   [U, R_2^{(0)}]   HF \rangle}{\omega_{\nu_3} - \omega^{(0)}} + \sum_{\mu_2} L_{\mu_2}^{(0)} \langle \mu_2   [[U, R_1^{(0)}], T_3]   HF \rangle$	2	1
EOM-CCSD(T)	$\mathbf{L}^{(0)}\mathbf{A}^{\text{CCSD}}(t_1, t_2)\mathbf{R}^{(0)} + \sum_{\substack{\mu_i \\ i=1,2}} L_{\mu_i}^{(0)} \sum_{\nu_3} \frac{\langle \mu_i   [U, \tau_{\nu_3}]   HF \rangle \langle \nu_3   [U, R_2^{(0)}]   HF \rangle}{\omega_{\nu_3} - \omega^{(0)}} + \omega^{(0)}\mathbf{L}^{(1)}\mathbf{R}^{(1)}$		

<sup>a</sup>The asterisk denotes that the reference state amplitudes are the triples corrected amplitudes in Eq. (23), and correspondingly the triples amplitudes according to Eq. (22), and the  $T_1$  transformed Hamiltonian of Eq. (21) calculated from triples corrected amplitudes.

$$\mathbf{A}^{(0)}\mathbf{R}^{(0)} = \omega^{(0)}\mathbf{R}^{(0)}, \quad (25)$$

$$\mathbf{L}^{(0)}\mathbf{A}^{(0)} = \mathbf{L}^{(0)}\omega^{(0)}. \quad (26)$$

We assume the CCSD eigenvectors are normalized to unity as in Eq. (3). Expanding the coupled cluster eigenvalue equation [Eq. (1)] gives to first and second order in the pseudoperturbation

$$(\mathbf{A}^{(0)} - \omega^{(0)})\mathbf{R}^{(1)} = -(\mathbf{A}^{(1)} - \omega^{(1)})\mathbf{R}^{(0)}. \quad (27)$$

$$(\mathbf{A}^{(0)} - \omega^{(0)})\mathbf{R}^{(2)} = -(\mathbf{A}^{(1)} - \omega^{(1)})\mathbf{R}^{(1)} - (\mathbf{A}^{(2)} - \omega^{(2)})\mathbf{R}^{(0)}. \quad (28)$$

Projecting the first-order equation onto the zeroth-order left-hand solution gives

$$\omega^{(1)} = \mathbf{L}^{(0)}\mathbf{A}^{(1)}\mathbf{R}^{(0)} = 0, \quad (29)$$

where the zero result follows from the structure of  $\mathbf{A}^{(1)}$ , and the fact that  $\mathbf{L}^{(0)}$  and  $\mathbf{R}^{(0)}$  are CCSD solution vectors with zero in the higher excitation part. Projecting the second-order equation we obtain

$$\omega^{(2)} = \mathbf{L}^{(0)}\mathbf{A}^{(1)}\mathbf{R}^{(1)} + \mathbf{L}^{(0)}\mathbf{A}^{(2)}\mathbf{R}^{(0)}. \quad (30)$$

This is the general form for the higher excitation level contributions in the pseudoperturbational approach. Introducing  $\mathbf{R}^{(1)}$  from Eq. (27) we may write the excitation energy correction as

$$\omega^{(2)} = \mathbf{L}^{(0)}(\mathbf{A}^{(2)} - \mathbf{A}^{(1)}(\mathbf{A}^{(0)} - \omega^{(0)}\mathbf{I})^{-1}\mathbf{A}^{(1)})\mathbf{R}^{(0)}. \quad (31)$$

Introducing the various approximations with the corresponding  $\mathbf{A}^{(1)}$  and  $\mathbf{A}^{(2)}$  matrices, we obtain the expressions for the excitation energy correction given in Table III. In Table III we also list the order in the fluctuation potential through which single and double replacement excitations are determined correctly.

It is appropriate to discuss the EOM-CCSD(T) approach in the context of the above development. To better appreciate the differences to the previously described perturbational approaches and EOM-CCSD(T) we recast the EOM-CCSD(T) theory in the notation of this paper. The EOM-CCSD(T) approach was introduced in an equation of motion coupled cluster (EOM-CC) framework.<sup>20</sup> Coupled cluster response theory and EOM-CC give identical excitation energies, but differ for other response properties, e.g., transition moments and polarizabilities. The most important difference is that EOM-CC results do not scale correct with the size of the system for these properties, while coupled cluster response theory does.<sup>3,8</sup> Also if approximations are introduced in the coupled cluster equations as for example in CCSDT-1a, the ground state and the excited state interact in EOM-CC, and the EOM-CC framework cannot be applied in a rigorous way to obtain equations for the excited state. No such problems occur in the pseudoenergy Lagrangian formulation of coupled cluster response theory.<sup>7</sup> The essential formulas in Ref. 16 make it possible to recast the theory in terms of the Jacobian given above. In the EOM-CCSD(T) approach

TABLE IV. CH<sup>+</sup> FCI excitation energies in eV. The error in coupled cluster models (FCI model).<sup>a</sup>

Excitation	FCI <sup>b</sup>	CCSD <sup>c</sup>	CC3 <sup>d</sup>	CCSDR(3)	CCSDR(T)	CCSDT-1a <sup>e</sup>	EOM-CCSD(T) <sup>e</sup>	CCSDR(1a)	CCSDR(1b)	% <i>t</i> <sub>1</sub> (CCSD)
X <sup>1</sup> Σ <sup>+</sup> → <sup>1</sup> Σ <sup>+</sup>	8.549	-0.560	-0.230	-0.206	-0.199	-0.232	-0.234	-0.200	-0.198	1
	13.525	-0.056	-0.016	-0.006	0.011	-0.058	-0.034	-0.032	-0.032	93
	17.217	-0.099	-0.026	-0.020	-0.001	-0.068	-0.052	-0.045	-0.045	84
<sup>1</sup> Π	3.230	-0.031	-0.012	-0.003	0.016	-0.041	-0.016	-0.016	-0.019	97
	14.127	-0.327	-0.219	-0.219	-0.199	-0.272	-0.268	-0.255	-0.259	72
<sup>1</sup> Δ	6.964	-0.924	-0.318	-0.303	-0.279	-0.323	-0.335	-0.281	-0.281	0
	16.833	-0.856	-0.261	-0.249	-0.225	-0.264	-0.344	-0.178	-0.177	24

<sup>a</sup>Basis set and geometry as in Ref. 21. *R*<sub>CH</sub>=2.137 13. Basis is C[1061/531] and H[51/31] from Ref. 21.

<sup>b</sup>FCI numbers from Ref. 21.

<sup>c</sup>CCSD results from Ref. 2.

<sup>d</sup>CC3 results from Ref. 7.

<sup>e</sup>CCSDT-1a and EOM-CCSD(T) results from Ref. 16.

triples correction vectors are introduced into Eq. (4) giving

$$\omega = (\mathbf{L}^{(0)} + \mathbf{L}^{(1)})(\mathbf{A}^{(0)} + \mathbf{A}^{(1)})(\mathbf{R}^{(0)} + \mathbf{R}^{(1)}). \quad (32)$$

The left and right triple correction vectors are obtained as the first iteration of CCSDT-1a. This corresponds to the  $\mathbf{R}^{(1)}$  vector of Eq. (27) with the CCSDT-1a Jacobian as  $\mathbf{A}^{(1)}$  and a similar equation for the left-hand correction,

$$\mathbf{L}^{(1)}(\mathbf{A}^{(0)} - \omega^{(0)}) = -\mathbf{L}^{(0)}\mathbf{A}^{(1)}. \quad (33)$$

Equation (32) is with these assumptions identical to Eq. (11) of Ref. 16. Using Eqs. (27) and (33) we may write the EOM-CCSD(T) excitation energy as

$$\omega = \omega^{(0)} + \mathbf{L}^{(0)}\mathbf{A}^{(1)}\mathbf{R}^{(1)} + \omega^{(0)}\mathbf{L}^{(1)}\mathbf{R}^{(1)}. \quad (34)$$

We now compare the last two terms in Eq. (34) with the triples correction in Eq. (20). The  $\mathbf{A}^{(2)}$  term in Eq. (30) is zero for CCSDT-1a. The last term in Eq. (34), which is second order in the fluctuation potential for double replacement dominated excitations, see Table II, does not show up in Eq. (30). Note that this extra term scale with the size of the CCSD excitation energy. For double replacement dominated excitations Eq. (34) is not correct through second order in the fluctuation potential. Equivalently, it is not correct through second order in the pseudoperturbation, since the terms involving the second-order correction vectors have been left out in Eq. (32). The second-order correction vectors would enter in terms like  $\mathbf{L}^{(2)}\mathbf{A}^{(0)}\mathbf{R}^{(0)} + \mathbf{L}^{(0)}\mathbf{A}^{(0)}\mathbf{R}^{(2)}$ , and these terms together with the last term in Eq. (34) vanish due to the second-order biorthonormality condition

$$\mathbf{L}^{(2)}\mathbf{R}^{(0)} + \mathbf{L}^{(0)}\mathbf{R}^{(2)} + \mathbf{L}^{(1)}\mathbf{R}^{(1)} = 0. \quad (35)$$

The correct second-order result of Eq. (30) is then obtained.

The CCSDR triples corrections can in compact form be written as,

$$\omega^{(2)} = \sum_{\mu_i} L_{\mu_i}^{(0)} \sigma_{\mu_i}(\omega^{(0)}), \quad (36)$$

where the  $\sigma$  vector corresponds to one linear transformation in our partitioned CC3 algorithm or a subset of this transformation. To obtain CCSDR triple corrections we need to calculate the CCSD left and right eigenvectors and then for

each eigenvalue do one transformation according to the expressions given in Table III. The scalar product with the CCSD left solution vector then gives the  $\omega^{(2)}$  excitation energy correction. We do not need to consider the left correction vector, and the final correction is thus somewhat simpler than the EOM-CCSD(T) correction as described in Ref. 16.

#### IV. BENCHMARK CALCULATIONS

The CH<sup>+</sup> FCI calculations of Olsen *et al.*<sup>21</sup> are an often used benchmark for investigating the performance of approximative models. EOM-CCSD(T), CC3, and CCSDT-1a results are available in the literature. In Table IV these results are given together with the results obtained in the perturbative triples models of this paper. All our perturbative triples corrections perform better than the corresponding iterative models. [CCSDR(3) versus CC3 and CCSDR(1a) versus CCSDT-1a]. The perturbative based CCSDR(1a) approach is also closer to FCI than EOM-CCSD(T) for all excitations. Since these approaches are based on the same Jacobian, this may be interpreted according to the theoretical discussion in Sec. III. The differences between CCSDR(1a) and EOM-CCSD(T) are rather small for the states with large single excitation weights as expected since both methods are correct to second order in the fluctuation potential. Both leave out the ST block and no significant improvements are obtained relative to CCSD. The extra term in Eq. (34) is expected to be rather small since in the case the product of the correction vectors is third order. For the double replacement dominated excitations the differences between CCSDR(1a) and EOM-CCSD(T) are larger, and for the largest excitation energy we have the largest deviation of 0.17 eV. This agrees with the fact that the extra term in EOM-CCSD(T),  $\omega^{(0)}\mathbf{L}^{(1)}\mathbf{R}^{(1)}$ , depends on the CCSD excitation energy. For double replacement dominated excitations the EOM-CCSD(T) contains an error in second order that scales with the size of the excitation energy. For the double replacement dominated excitations none of the perturbative models is consistently better than the others and the differences are small compared to the overall error. Again this can be explained from the theoretical discussions, since the *perturba-*

TABLE V. FCI excitation energies and deviation from FCI (FCI model) in m hartree,<sup>a</sup> and % $t_1$  in CCSD.<sup>a</sup>

Molecule	State	% $t_1$ <sup>b</sup>	FCI <sup>b</sup>	CCSD <sup>b</sup>	CC3 <sup>b</sup>	CCSDR(3)	CCSDR(T)	CCSDT-1a <sup>b</sup>	CCSDR(1a)	CCSDR(1b)
Ne	$^1P^0$	97	602.6	8.8	-0.5	0.3	-0.1	-0.4	-0.6	-1.3
	$^1D$	97	669.3	9.2	-0.6	0.2	-0.2	-0.4	-0.6	-1.2
	$^1P$	97	670.9	9.2	-0.7	0.2	-0.2	-0.4	-0.5	-1.2
	$^1S$	97	679.3	8.7	-0.3	0.5	-0.2	-0.3	-0.8	-1.4
	$^1S$	96	1618.9	6.2	-3.8	-1.2	-2.1	-5.2	-1.2	-1.7
BH	$A^1\Pi$	95	108.2	-0.8	-0.3	0.1	0.9	-1.1	-0.1	-0.2
	$B^1\Sigma^+$	97	234.4	-1.5	-0.6	-0.4	0.3	-1.7	-0.7	-0.7
	$D^1\Pi$	94	274.4	-1.3	-0.5	-0.2	0.4	-1.7	-0.7	-0.7
	$G^1\Pi$	93	302.8	-1.4	-0.6	-0.4	0.3	-2.0	-1.0	-0.9
	$C^1\Delta$	6	216.1	-29.2	-11.4	-11.1	-10.2	-11.5	-10.3	-10.3
	$C^1\Sigma^+$	62	257.1	-14.4	-6.6	-8.7	-7.9	-6.9	-8.6	-8.5
	$E^1\Sigma^+$	51	277.8	-7.1	-1.9	0.7	1.5	-3.0	-0.8	-0.8
CH <sub>2</sub>	$3^1A_1$	93	239.4	0.2	0.2	1.8	3.0	-2.3	0.7	0.8
	$4^1A_1$	96	311.6	0.7	0.2	1.0	2.2	-2.3	-0.2	-0.1
	$1^1B_1$	95	283.1	-0.4	-0.6	0.0	1.2	-3.0	-1.1	-1.0
	$1^1B_2$	97	65.9	0.5	0.2	1.0	2.3	-2.1	-0.2	-0.4
	$1^1A_2$	97	215.1	-0.2	-0.2	0.6	1.8	-2.3	-0.3	-0.7
	$2^1A_1$	5	171.1	-53.5	-17.3	-16.9	-15.2	-17.3	-15.3	-15.3
	$2^1B_1$	6	294.6	-58.9	-19.0	-18.7	-17.1	-19.1	-17.4	-17.4
	$2^1B_2$	0	327.3	-66.1	-21.0	-20.3	-18.6	-20.9	-18.5	-18.5
	$3^1B_2$	2	387.8	-67.0	-22.6	-22.3	-20.6	-22.4	-20.5	-20.5
	$2^1A_2$	0	345.8	-88.8	-43.1	-42.5	-40.8	-43.0	-40.7	-40.7

<sup>a</sup>Geometry and basis sets as in Ref. 12. Geometries:  $R_{\text{BH}}=2.3289$ , CH<sub>2</sub> coordinates: C(80,0,0), H( $\pm 1.644403, 0, 1.32213$ ). Basis sets: spherical pVDZ with augmented functions. The augmented functions are, with exponents in parenthesis: Ne:  $1s(0.04)$  and  $1p(0.03)$ , BH:  $2s(0.0315, 0.009244)$ ,  $2p(0.02378, 0.005129)$ , and  $2d(0.0904, 0.02383)$  functions on B and on H  $2s(0.0297, 0.00725)$  and  $2p(0.141, 0.02735)$ . CH<sub>2</sub>:  $1s(0.015)$  on C and  $1s(0.025)$  on H.

<sup>b</sup>FCI, CCSD, CCSDT-1a, and CC3 results from Ref. 12.

*tive* triple correction approaches all includes the same second order terms for double replacement dominated excitations.

For single replacement dominated excitations the CCSDR(T) and CCSDR(3) results are closer to FCI than the CCSDR(1a) and CCSDR(1b) results for all excitations. The CCSDR(T) and CCSDR(3) methods are correct through third order since both include the lowest order singlet-triplet coupling. This coupling is not included in CCSDR(1a) and CCSDR(1b). Finally we note that the difference between CCSDR(1a) and CCSDR(1b) is small, indicating little effect of the  $A^{(2)}$  term depending on the triples reference amplitudes that constitute the major difference between these two approximations.

In a recent paper we compared FCI excitation energies of BH, Ne, and CH<sub>2</sub> with those obtained in the hierarchy of coupled cluster models CCS, CC2, CCSD, and CC3. CCSDT-1a excitation energies were presented as well. In Table V we give the FCI results and the errors relative to FCI for CCSD, the perturbative triples corrections models, and the iterative triples models CC3 and CCSDT-1a. We divide the excitations into single replacement dominated excitations (>90%  $T_1$ ) and the rest that has significant double replacement character. For the latter class we see the same picture as for CH<sup>+</sup>. All perturbative corrections behave similarly and are in most cases more accurate than the iterative triples results. CCSDR(T) and CCSDR(1a) appear to be more accurate than CCSDR(3), but only marginally relative to the remaining error to FCI. For the single replacement dominated excitations we find significantly different behaviors of the

perturbative corrections. For Ne we see significant improvement for all triples models relative to the CCSD result. In this case we thus actually obtain improvements of the CCSD results for single replacements dominated excitations even though the lowest order singlet-triplet coupling is not included. The  $A^{(2)}$  term has some effect in this molecule. The CCSDR(3) result is closer to FCI than CC3. For BH we observe that all perturbative triples models improve the CCSD results. It should be noted that CCSDR(T) and CCSDR(3) give the largest shifts relative to CCSD. CCSDR(3) is closest to FCI, and actually closer than CC3. For CH<sub>2</sub> we have very small errors at the CCSD level, and significant differences between the different perturbative triples approaches are observed. CCSDR(1a) and CCSDR(1b) differ from CCSD by less than 0.9 mhartree and these models are thus still rather close to FCI. CCSDR(T) give larger changes of up to 3 mhartree and in the opposite direction. The CCSDR(3) shifts are smaller, indicating the importance of relaxation of the ground state amplitudes. The errors toward FCI in CCSDR(3) are still larger than in the iterative CC3 model that is very close to FCI. We tried to use CC3 reference amplitudes in the CCSDR(T) excitation energy calculation, and obtained shifts in the CCSDR approaches of  $-2.0 \pm 0.2$  mhartree for all single replacement dominated excitations. In CH<sub>2</sub> we thus apparently have large cancellation effects between contributions of *different* order. The good performance of CCSD, CCSDR(1a), and CCSDR(1b) is thus probably fortuitous.

## V. CONCLUDING REMARKS

The CCSD(T) model does not have a response function with a set of poles improved relative to CCSD. Triples correction to CCSD excitation energies cannot therefore be obtained from CCSD(T). We have presented an approach for including triples corrections to CCSD excitation energies based on a perturbational analysis. Several approximations have been proposed and analyzed in terms of order in the fluctuation potential. Numerical tests have been performed and comparison of the perturbative triple correction approaches with similar iterative approaches have been presented. We have found that for double replacement dominated excitations, the excitation energies from the perturbational corrections to CCSD presented in this paper are more accurate than the ones obtained from the corresponding iterative triples models. For single excitation dominated excitations the situation is less clear. From the numerical results we conclude that to obtain significant contributions beyond CCSD it is *necessary* to include the singlet–triplet coupling appearing in third order. The CCSDR(T) and CCSDR(3) approaches provide excitation energies correct through third order in the fluctuation potential, and have in many cases improved the CCSD excitation energies considerably. They both included fourth-order terms coupling doubles and triples. The noniterative analogue to CC3, CCSDR(3) seems to be the most balanced, and behaves very similar to CC3. Thus relaxation of the ground state amplitudes seems to be a third effect that is necessary to take into consideration to obtain a balanced model. In forthcoming benchmark calculations we present more numerical tests on the performance of the noniterative models, which supports these findings.<sup>22</sup> Furthermore we will in the future address the problem of assigning total molecular energies to the excited states in the perturbational approaches.

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