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ABSTRACT

In cluster perturbation (CP) theory, we consider a target excitation space relative to a Hartree-Fock state and partition the target excitation space into a parent excitation space and an auxiliary excitation space. The zeroth-order state is in CP theory a coupled cluster (CC) state in the parent excitation space, and the target state is a CC state in the target excitation space. In this paper, we derive CP series for excitation energies in orders of the CC parent-state similarity-transformed fluctuation potential where the zeroth-order term in the series is an excitation energy for the CC parent state response eigenvalue equation and where the series formally converge to an excitation energy for the CC target state response eigenvalue equation. We give explicit expressions for the lowest-order excitation energy corrections. We also report calculations for CP excitation energy series for various parent and target excitation spaces and examine how well the lower-order corrections can reproduce the total excitation energies. Considering the fast local convergence we have observed for the CP excitation energy series, it becomes computationally attractive to use low-order corrections in CP series to obtain excitation energies of CC target state quality. For the CPS(D-n) series, the first-order correction vanishes, the second-order correction becomes the CIS(D) model, and for the CPS(D-3) model, our calculations suggest that excitation energies of CCSD quality are obtained. The numerical results also suggest that a similar behavior can be seen for the low-order excitation energy corrections for CP series where the parent state contains more than a singles excitation space, e.g., for the CPSD(T) model. We therefore expect the low-order excitation energy corrections in CP series soon to become state-of-the-art models for determining excitation energies of CC target state quality.

I. INTRODUCTION

In Paper I,[1] we introduced a new class of perturbation models—the cluster perturbation (CP) models—where the major drawbacks of Møller-Plesset perturbation theory (MPPT)[2,3] and coupled cluster perturbation theory (CCPT)[4–6] have been overcome. The theoretical foundation for CP theory is given in Paper I.[1] In Paper I,[1] we also discuss the advantages of using CP theory compared to CCPT and MPPT.

In CP theory, we consider a target excitation space relative to a Hartree-Fock (HF) state and partition the target excitation space into a parent excitation space and an auxiliary excitation space. The zeroth-order state is in CP theory a coupled cluster (CC) state in the parent excitation space, and we here assume that the target state is a CC state in the target excitation space. In Paper I,[1] we determined a perturbation series of ground-state energy corrections in orders of the perturbation—the CC parent-state similarity-transformed fluctuation potential—where the zeroth-order term in the series is the energy of the CC parent state and where the perturbation series formally converge to the energy of the CC target state. We also showed in Paper I[1] that CP series similar to the ones for the ground-state energy exist for molecular properties, including excitation energies.

In this paper, we derive CP series for excitation energies in orders of the CC parent-state similarity-transformed fluctuation potential, where the zeroth-order term in the series is an excitation energy for the CC parent state response eigenvalue equation and where the series formally converge to an excitation energy for the CC target state response eigenvalue equation. We give explicit expressions for the lowest order excitation energy corrections for the series, in particular, for the excitation energy corrections where the parent state is a CCSD state and the target state is a CCSDT state. We also report calculations for CP excitation energy series for various parent and target excitation spaces and examine the convergence of these series. For the lower order corrections, we examine how well these corrections can reproduce the total excitation energy. The theoretical foundation for convergent CP excitation energy series is discussed in Paper IV[7] where it is also discussed how the asymptotic convergence of the CP excitation energy series can be modeled using a simple two state model. The asymptotic convergence of the CP excitation energy series determines the convergence rate and the convergence patterns of the higher order terms in the CP series. In a forthcoming paper, the convergence rate and the convergence patterns of the higher-order terms in the calculated CP excitation energy series will be examined using the two-state model that has been thoroughly analyzed in Ref. 8.

In CP theory, we have introduced a new, generalized order concept in order to enable determination of perturbation series for the ground-state energy and for excitation energies on an equal footing. A key feature of this new generalized order concept is that one contribution, which contains the perturbation operator, is treated as a zeroth-order contribution. In CP theory, we thus treat the CC parent state Jacobian, which contains the perturbation operator, as a zeroth-order contribution. In practice, the CC parent-state Jacobian is treated as a zeroth-order contribution by solving sets of linear equations in the parent excitation space, for the cluster and response amplitudes, where the matrix in the linear equations contains the CC parent space Jacobian. By considering the perturbation operator contribution of the CC parent state Jacobian to be a zeroth-order contribution, internal relaxation in the parent excitation space is treated fully at zeroth-order when the CP ground-state energy and excitation energy series are derived.

Extending CC theory to calculation of energies of excited states can be performed using two separate and closely connected formalisms: (i) Response function theory, where the response eigenvalue equation determines excitation energies that added to the ground-state energy give excited-state energies,[9] and (ii) equation-of-motion coupled cluster (EOM-CC) theory,[10,11] where the energies of the excited states are determined directly as eigenvalues of the EOM-CC eigenvalue equation. Both the response and the EOM-CC formalisms give a straightforward and consistent extension of the ground-state energy description to a description of excited states and yield the same excitation energies and excited state energies when the cluster operator is truncated at a given excitation level. In this paper, we determine CP series for both excitation energies and for the energies of the excited states. Molecular properties for the CC ground state and for CC excited states and for transitions between these states can only be determined using response function theory.

CP models are characterized by a CC parent state defined in the parent excitation space and by an auxiliary excitation space. This may be expressed using a notation where the parent excitation space is followed by the auxiliary space in parentheses. For example, CPSD(T) denotes a CP model with a CCSD parent state and a triples auxiliary space. Furthermore, the notation CPSD(T) implies that a CC target state is used. If the auxiliary space is followed by a number, as, for example, in CPSD(T-3), the number denotes that perturbation corrections are determined through that order.

The development of response function theory for a coupled cluster wave function was initiated by Monkhorst.[12] The development of response functions for a coupled cluster wave function and their practical implementation were described by Koch and Jørgensen,[9] who also derived explicit expressions for the response eigenvalue equation for a coupled cluster state. The first CCSD excitation energy calculations were reported by Koch *et al.*[13] For a CCSDT state, three independent implementations were reported in 2001 by Kucharski *et al.*,[14] Kowalski and Piecuch,[15,16] and Hald *et al.*[17] The former two implementations were conventional term-by-term implementations, whereas the latter implementation used direct CC technology[18] for solving the CC response eigenvalue equation. Using direct CC technology, Kállay *et al.*[19,20] extended the calculation of excitation energies to a CCSDTQ state and to CC states of higher excitation levels.

The hierarchy of coupled cluster models CC2,[21] CCSD,[22] CC3,[23–25] CCSDT,[26,27] etc., was introduced for calculation of excitation energies and response molecular properties where an increased accuracy was obtained, but with an increased iterative computational scaling of N^5, N^6, N^7, N^8, . . ., where N denotes the size of the molecular system.

The CC2 model is one out of many N^5 computational scaling singles-and-doubles excitation energy models, including the second-order polarization propagator approximation (SOPPA),[28–30] the adiabatic-diagrammatic construction of second order [ADC(2)],[31–33] and the P-EOM-MBPT2 model.[34,35] In the EOM-CCSD(2) model,[36] the CCSD Jacobian is reduced to contain only terms that are of second order in Møller-Plesset perturbation theory leading to an N^6 scaling model. In the P-EOM-MBPT2 model, the doubles sub-block is approximated to contain only orbital-energy differences. For the above models, single-configuration dominated excitations are described through second order in Møller-Plesset perturbation theory.[17,24] The ADC(3)[33,37–39] model is a singles-and-doubles model with an iterative N^6 computational scaling that is correct through the third order in the single-and-double excitation space.

In Paper III,[40] we consider in more detail the CPS(D) model where a perturbation series in orders of the fluctuation potential is determined where the zeroth-order contribution is a CCS excitation energy and where the series converge to a CCSD excitation energy. We give explicit expressions for the lowest-order corrections in this series through sixth order and show that the first-order correction vanishes and that the second-order correction gives the non-iterative N^5 scaling CIS(D) model of Head-Gordon *et al.*[41] The CPS(D-2) and CPS(D-3) excitation energies have been extensively benchmarked in Paper III,[40] where it is shown that the third order model CPS(D-3) provides excitation energies of CCSD quality in the sense that the difference between the CPS(D-3) and CCSD excitation energies is of the same size or smaller than the effect of adding triples corrections to the CCSD excitation energies. Furthermore, the deviations of the CPS(D-3) and CCSD excitation energies from triples corrected excitation energies are of similar size.[40]

For the CPS(D) series, the perturbation simplifies and becomes the fluctuation potential. For that reason, the derivation of the CP excitation energy series for arbitrary parent and target excitation spaces, which we perform in this paper, can be simplified in the case of CPS(D). In Paper III,[40] we describe this simple derivation of CPS(D-n) excitation energy series where the excitation energy series is determined without any reference to the general perturbation framework of CP theory.

In the CC3 model,[23–25] single-replacement dominated excitation energies are described through third order in Møller-Plesset theory, while double-replacement dominated excitation energies are described through second order.[17,24] The EOM-CCSDT-1 model[42] and the EOM-CCSDT-3 model[43] have similar characteristics as the CC3 model. Non-iterative triples N^7 scaling models have also been proposed. These include the non-iterative EOM-CCSD(T),[42] EOM-CCSD($\widetilde{\mathrm{T}}$),[43] CCSDR(3),[44] CCSDR(T),[44] and CCSD(T)(a)*[45] models.

There are fundamental structural differences between the theoretical foundation for the lowest-order correction in the CPSD(T-*n*) series and for the other non-iterative approximate triples models. For the CPSD(T-*n*) series, the CP perturbation framework is used both for determining ground-state amplitude corrections and Jacobian response eigenvector corrections. Furthermore, the lowest-order excitation-energy corrections are members of a series that converges to the excitation energies for the CCSDT target state. On the contrary, for the other non-iterative approximate triples models, the triples excitation-energy corrections are one-step approximations that are obtained by simplifying the solution to the CCSDT response eigenvalue equation using a perturbation framework that is different for the determination of the ground-state amplitude corrections and for the Jacobian response eigenvector corrections.

The various excitation energy models have been extensively benchmarked. Goings *et al.*[46] have tested the performance of the CIS(D), CC2, EOM-CCSD(2), and P-EOM-MBPT2 models using CCSD excitation energies as reference values and using a test set of 11 small organic molecules and 69 valence and Rydberg states. Thiel and co-workers have developed the Mülheim test set that contains 28 molecules with more than 100 excited valence and Rydberg states and benchmarked the CC2, CCSD, and CCSDR(3) models using CC3 and CASPT2 reference data[47,48] and a TZVP basis set.[49] Later, this study was extended using the aug-cc-pVTZ basis to estimate basis set effects for the CC2, CCSDR(3), and CC3 methods.[50] The CC3 study was only performed for a small subset, and no data were reported for CCSD. The conclusion was that CC2 performs better than CCSD for vertical excitation energies and that the non-iterative CCSDR(3) method is a cost-effective approximation to CC3.

Watson and co-workers,[51] using the TZVP basis and the Mülheim test set, have benchmarked the methods containing triple excitations. Kánnár and Szalay[52] extended this study to test the reliability of using CC3 results as reference data performing CCSDT calculations for a small test set. The conclusion was that CC2 gives results closer to the high level CC3 and CCSDT results than CCSD, but the CCSD results are more systematic than the CC2 results. Recently, Kánnár, Tajti, and Szalay[53] have benchmarked CIS(D), CC2, EOM-CCSD(2), EOM-CCSD(T)(a)*,CCSDT-3, and CC3 methods against CCSDT results for basis sets up to aug-cc-pVTZ. The results revealed a serious deficiency of the CC2 and CIS(D) results for calculating Rydberg states. This deficiency is not present in the EOM-CCSD(2) and CCSD models. The CC3 model proved to be an accurate choice among the iterative triples models and the EOM-CCSD(T)(a)* method turned out to be the best choice among the non-iterative models.

In Sec. II, standard CC theory is summarized for the calculation of excitation energies. In Sec. III, CP theory is developed for excitation energy series, using general CC parent and CC target states, and explicit expressions are given for the lowest-order excitation energy corrections. Explicit expressions are also given for the CPSD(T) excitation energy series through third order. In Sec. IV, we present calculations of CP excitation energies for general CC parent and CC target states and examine how well these excitation energy corrections can reproduce the total excitation energy. Section V contains a short summary and concluding remarks.

II. STANDARD COUPLED CLUSTER THEORY FOR EXCITATION ENERGIES

In this section, we summarize the CC theory background that is needed for describing the development of CP series for excitation energies and for the energies of excited states for a coupled cluster state.

In CC theory,[54,55] the wave function is exponentially parameterized,

$$|\mathrm{CC}\rangle = \mathrm{e}^{T}|\mathrm{HF}\rangle, \tag{1}$$

where the cluster operator,

$$T = \sum_i T_i, \tag{2a}$$

$$T_i = \sum_{\mu_i} t_{\mu_i}\theta_{\mu_i}, \tag{2b}$$

contains the cluster amplitudes t_{μ_i} and the many-body excitation operators θ_{μ_i} that carry out excitations from the Hartree-Fock state $|\mathrm{HF}\rangle$ to its orthogonal complement set of states,

$$|\mu_i\rangle = \theta_{\mu_i}|\mathrm{HF}\rangle. \tag{3}$$

In Eqs. (2) and (3), i denotes an excitation level and μ_i denotes an excitation at this level. The Hartree-Fock state together with its orthogonal complement set of states forms a complete set of states,

$$|\mathcal{B}\rangle = \Big\{|\mathrm{HF}\rangle, |\mu_i\rangle, \qquad i = 1, 2, \ldots\Big\}. \tag{4}$$

The CC Schrödinger equation may be expressed as

$$\mathrm{e}^{-T}H_0\mathrm{e}^{T}|\mathrm{HF}\rangle = E_0|\mathrm{HF}\rangle, \tag{5}$$

where H_0 is the Hamiltonian and E_0 is the ground-state energy. The CC Schrödinger equation is solved by projection, giving the CC energy and amplitude equations,

$$\begin{aligned} E_0 &= \langle\mathrm{HF}|\mathrm{e}^{-T}H_0\mathrm{e}^{T}|\mathrm{HF}\rangle = \langle\mathrm{HF}|H_0|\mathrm{HF}\rangle + \langle\mathrm{HF}|H_0T_2|\mathrm{HF}\rangle \\ &\quad + \frac{1}{2}\langle\mathrm{HF}|H_0T_1^2|\mathrm{HF}\rangle, \end{aligned} \tag{6}$$

$$\langle\mu_i|\mathrm{e}^{-T}H_0\mathrm{e}^{T}|\mathrm{HF}\rangle = 0, \tag{7}$$

where we have used the Brillouin theorem to obtain the energy in Eq. (6).

In CC theory, excitation energies are determined as eigenvalues of the CC response eigenvalue equation,

$$\mathbf{J}\,\mathbf{R}_x = \omega_x\,\mathbf{R}_x, \tag{8a}$$

$$\mathbf{L}_x\,\mathbf{J} = \mathbf{L}_x\,\omega_x, \tag{8b}$$

$$\mathbf{L}_x\mathbf{R}_y = \delta_{xy}, \tag{8c}$$

where $\mathbf{R}_x$ and $\mathbf{L}_x$ are the right and left eigenvectors of an excited state x and ω_x is the excitation energy. The left and right eigenvectors may be chosen to be biorthonormal [Eq. (8c)]. The CC Jacobian matrix elements are given by

$$J_{\mu_i\nu_j} = \langle\mu_i|\left[e^{-T}H_0e^{T},\theta_{\nu_j}\right]|\mathrm{HF}\rangle, \tag{9}$$

where the amplitudes of the cluster operator in Eq. (9) satisfy the cluster amplitude equations in Eq. (7).

In CC theory, total energies of excited states can be obtained solving the EOM-CC eigenvalue equation,[11]

$$\mathbf{H}_0^T\,\mathbf{C} = \mathbf{C}\,\mathbf{E}, \tag{10}$$

where the electronic Schrödinger equation is solved in the biorthonormal basis

$$|\mathcal{B}^T\rangle = \left\{e^T|\mathrm{HF}\rangle, e^T|\mu_i\rangle;\quad i=1,2,\ldots\right\}, \tag{11a}$$

$$\langle\mathcal{B}^T| = \left\{\langle\mathrm{HF}|e^{-T}, \langle\mu_i|e^{-T};\quad i=1,2,\ldots\right\}. \tag{11b}$$

The matrix elements of the Hamiltonian in Eq. (10) are given by

$$\left(\mathbf{H}_0^T\right)_{\mathrm{HF\,HF}} = \langle\mathrm{HF}|e^{-T}H_0e^{T}|\mathrm{HF}\rangle = E_0, \tag{12}$$

$$\left(\mathbf{H}_0^T\right)_{\mu_i\,\mathrm{HF}} = \langle\mu_i|e^{-T}H_0e^{T}|\mathrm{HF}\rangle = 0, \tag{13}$$

$$\left(\mathbf{H}_0^T\right)_{\mathrm{HF}\,\mu_i} = \langle\mathrm{HF}|e^{-T}H_0e^{T}|\mu_i\rangle = \eta_{\mu_i}, \tag{14}$$

$$\left(\mathbf{H}_0^T\right)_{\mu_i\nu_j} = \langle\mu_i|e^{-T}H_0e^{T}|\nu_j\rangle = \left(\mathbf{H}_0^T\right)^{\perp}_{\mu_i\nu_j}. \tag{15}$$

Equation (13) is the cluster amplitude equation in Eq. (7) and vanishes, and Eq. (12) gives the CC ground-state energy in Eq. (6). The matrix $\mathbf{E}$ in Eq. (10) contains the ground-state energy E_0 and the excited-state energies E_n, $n = 1, 2, \ldots$,

$$\mathbf{E} = \begin{pmatrix} E_0 & & & \\ & E_1 & & \\ & & E_2 & \\ & & & \ddots \end{pmatrix}. \tag{16}$$

The Hamiltonian matrix has the structure

$$\mathbf{H}_0^T = \begin{pmatrix} E_0 & \boldsymbol{\eta} \\ \mathbf{0} & \left(\mathbf{H}_0^T\right)^{\perp} \end{pmatrix}. \tag{17}$$

The Jacobian in Eq. (9) can be written as

$$\begin{aligned} J_{\mu_i\nu_j} &= \langle\mu_i|e^{-T}H_0e^{T}|\nu_j\rangle - \delta_{\mu_i\nu_j}\langle\mathrm{HF}|e^{-T}H_0e^{T}|\mathrm{HF}\rangle \\ &= \left(\mathbf{H}_0^T\right)^{\perp}_{\mu_i\nu_j} - \delta_{\mu_i\nu_j}E_0. \end{aligned} \tag{18}$$

Since $\mathbf{H}_0^T$ has the block upper triangular structure of Eq. (17), $\left(\mathbf{H}_0^T\right)^{\perp}$ can be diagonalized with the matrix $\mathbf{R}$ of Eq. (8),

$$\left(\mathbf{H}_0^T\right)^{\perp}\mathbf{R} = \mathbf{R}\,\mathbf{E}^{\perp}, \tag{19}$$

where $\mathbf{E}^{\perp}$ contains the total energies of the excited states as eigenvalues,

$$\mathbf{E}^{\perp} = \begin{pmatrix} E_1 & & \\ & E_2 & \\ & & \ddots \end{pmatrix}. \tag{20}$$

Equations (8), (18), and (19) show that the total energy of excited state x in CC theory can be determined as a sum of the ground state energy and the excitation energy ω_x obtained by solving the Jacobian response eigenvalue equation in Eq. (8),

$$E_x = \omega_x + E_0. \tag{21}$$

In a standard CC excitation energy calculation, a CC target state is determined using a cluster operator that is truncated at an excitation level t and the cluster amplitude equations in Eq. (7) are solved in the target excitation space $1 \le i \le t$. The amplitudes are then used in the CC Jacobian in Eq. (9), and excitation energies are determined solving the response eigenvalue equation in Eq. (8). In this paper, we describe how CP theory may be used to determine the excitation energies of Eq. (8) without the need of solving the cluster amplitude and the response eigenvalue equations explicitly.

III. CLUSTER PERTURBATION THEORY FOR EXCITATION ENERGIES

In CP theory, we consider a target excitation space, $1 \le i \le t$, that is partitioned into a parent excitation space, $1 \le i \le p$, and an auxiliary excitation space $p < i \le t$. The zeroth-order state is in CP theory a CC state in the parent excitation space. As in Paper I,[1] we assume that the target state is a CC state in the target excitation space. In Paper I,[1] we showed that using CP theory a series of excitation energy corrections in orders of the CC parent-state similarity-transformed fluctuation potential exists where the zeroth-order term in the series is an excitation energy of the CC parent state response eigenvalue equation and where the series formally converges to an excitation energy of the CC target state Jacobian eigenvalue equation. We describe in this paper how the series of excitation energy corrections can be determined.

From the derivation in Paper I,[1] we know that the CC target state in CP theory has to be parameterized with the CC parent state as the expansion point. Furthermore, the parent state Jacobian partitioning of the extended parent space Jacobian has to be used to determine the perturbation series of excitation energy corrections and the eigenvalue equation for the zeroth-order Jacobian has to become the eigenvalue equation for the CC parent state. The expansion of the Jacobian of Eq. (9) in orders of the CC parent-state similarity-transformed fluctuation potential may therefore be expressed as

$$\mathbf{J} = \mathbf{J}^{(0)} + \mathbf{J}^{(1)} + \mathbf{J}^{(2)} + \mathbf{J}^{(3)} + \cdots, \tag{22}$$

where the zeroth-order Jacobian satisfies

$$\mathbf{J}^{(0)}\,\mathbf{R}_x^{(0)} = \omega_x^{(0)}\,\mathbf{R}_x^{(0)}, \tag{23a}$$

$$\mathbf{L}_x^{(0)}\,\mathbf{J}^{(0)} = \mathbf{L}_x^{(0)}\,\omega_x^{(0)}, \tag{23b}$$

$$\mathbf{L}_x^{(0)}\mathbf{R}_y^{(0)} = \delta_{xy}, \tag{23c}$$

$$\omega_x^{(0)} = \omega_x^{P}, \tag{23d}$$

where ω_x^P is an eigenvalue of the CC parent state response eigenvalue equation. Furthermore, we know from Paper I[1] that a series of excitation energy corrections can be determined substituting the Jacobian expansion in Eq. (22) into Eq. (8) and solving the response eigenvalue equation in Eq. (8) order by order in the CC parent-state similarity-transformed fluctuation potential where the excitation energy and the right eigenvector have been expanded in orders of the CC parent-state similarity-transformed fluctuation potential,

$$\mathbf{R}_x = \mathbf{R}_x^{(0)} + \mathbf{R}_x^{(1)} + \mathbf{R}_x^{(2)} + \mathbf{R}_x^{(3)} + \cdots, \tag{24}$$

$$\omega_x = \omega_x^{(0)} + \omega_x^{(1)} + \omega_x^{(2)} + \omega_x^{(3)} + \cdots. \tag{25}$$

We describe in Subsection III A how the Jacobian expansion in Eq. (22) can be determined where the zeroth-order Jacobian satisfies the zeroth-order eigenvalue equation in Eq. (23). In Subsection III B, explicit expressions are determined for the lowest-order corrections for the Jacobian and for the cluster amplitudes. In Subsection III C, we determine the excitation energy corrections of Eq. (25), and in Subsection III D, CP series are determined for the energies of CC excited states. In Subsection III E, we give explicit expressions for the excitation energy corrections through third order for a CP model with a general parent and auxiliary excitation space, and in Subsection III F, the excitation energy corrections through third order are given for the CPSD(T) model.

A. Perturbation series for the Jacobian

In CP theory, the zeroth-order state is the CC parent state in the parent excitation space,

$$|\mathrm{CC}^*\rangle = \mathrm{e}^{{}^*T}|\mathrm{HF}\rangle, \tag{26}$$

$${}^*T = {}^*T_1 + \cdots + {}^*T_p, \tag{27}$$

$${}^*T_i = \sum_{\mu_i} {}^*t_{\mu_i}\theta_{\mu_i}, \qquad 1 \le i \le p, \tag{28}$$

where the amplitudes of the CC parent state satisfy the cluster amplitude equations,

$$\langle \mu_i|\mathrm{e}^{-{}^*T}H_0\mathrm{e}^{{}^*T}|\mathrm{HF}\rangle = 0, \qquad 1 \le i \le p, \tag{29}$$

and where the parent-state energy is

$${}^*E_0 = \langle \mathrm{HF}|H_0\mathrm{e}^{{}^*T}|\mathrm{HF}\rangle. \tag{30}$$

The CC target state is in CP theory parameterized with the CC parent state as the expansion point,

$$|\mathrm{CC}\rangle = \mathrm{e}^{T}|\mathrm{HF}\rangle = \mathrm{e}^{\delta T + {}^*T}|\mathrm{HF}\rangle = \mathrm{e}^{\delta T}|\mathrm{CC}^*\rangle, \tag{31}$$

where

$$\delta T = \sum_{i=1}^{t}\sum_{\mu_i}\delta t_{\mu_i}\theta_{\mu_i}. \tag{32}$$

The similarity-transformed Schrödinger equation for the CC target state in Eq. (31) may be written as

$$\mathrm{e}^{-\delta T}\mathrm{e}^{-{}^*T}H_0\mathrm{e}^{{}^*T}\mathrm{e}^{\delta T}|\mathrm{HF}\rangle = E_0|\mathrm{HF}\rangle \tag{33}$$

and solved by projection in the target excitation space giving the cluster energy and amplitude equations,

$$E_0 = \langle \mathrm{HF}|\mathrm{e}^{-\delta T}\mathrm{e}^{-{}^*T}H_0\mathrm{e}^{{}^*T}\mathrm{e}^{\delta T}|\mathrm{HF}\rangle = \langle \mathrm{HF}|\mathrm{e}^{-\delta T}H_0^{{}^*T}\mathrm{e}^{\delta T}|\mathrm{HF}\rangle, \tag{34}$$

$$\begin{gathered}\langle \mu_i|\mathrm{e}^{-\delta T}\mathrm{e}^{-{}^*T}H_0\mathrm{e}^{{}^*T}\mathrm{e}^{\delta T}|\mathrm{HF}\rangle = \langle \mu_i|\mathrm{e}^{-\delta T}H_0^{{}^*T}\mathrm{e}^{\delta T}|\mathrm{HF}\rangle = 0,\\ 1 \le i \le t,\end{gathered} \tag{35}$$

where

$$H_0^{{}^*T} = \mathrm{e}^{-{}^*T}H_0\mathrm{e}^{{}^*T}. \tag{36}$$

The Jacobian of Eq. (9) may similarly be parameterized with the CC parent state as the expansion point,

$$\mathbf{J}_{\mu_i\nu_j} = \langle \mu_i|\big[\mathrm{e}^{-\delta T}H_0^{{}^*T}\mathrm{e}^{\delta T},\theta_{\nu_j}\big]|\mathrm{HF}\rangle, \qquad i,j = 1,2,\ldots,t. \tag{37}$$

Introducing the Møller-Plesset partitioning of the Hamiltonian,

$$H_0 = f + \Phi, \tag{38}$$

where f is the Fock operator and Φ is the fluctuation potential, and carrying out Baker-Campbell-Hausdorff (BCH) expansions, we may write Eqs. (35) and (37) as

$$\begin{aligned}&\langle \mu_i|\Phi^{{}^*T}|\mathrm{HF}\rangle S_{ip} + \sum_{j=1}^{t}\sum_{\nu_j}\langle \mu_i|\big[H_0^{{}^*T},\theta_{\nu_j}\big]|\mathrm{HF}\rangle\delta t_{\nu_j} + \frac{1}{2}\langle \mu_i|\big[\big[\Phi^{{}^*T},\delta T\big],\delta T\big]|\mathrm{HF}\rangle\\ &\quad + \frac{1}{6}\langle \mu_i|\big[\big[\big[\Phi^{{}^*T},\delta T\big],\delta T\big],\delta T\big]|\mathrm{HF}\rangle + \frac{1}{24}\langle \mu_i|\big[\big[\big[\big[\Phi^{{}^*T},\delta T\big],\delta T\big],\delta T\big],\delta T\big]|\mathrm{HF}\rangle\\ &= \langle \mu_i|\Phi^{{}^*T}|\mathrm{HF}\rangle S_{ip} + \sum_{j=1}^{t}\sum_{\nu_j}A_{\mu_i\nu_j}\delta t_{\nu_j} + \frac{1}{2}\langle \mu_i|\big[\big[\Phi^{{}^*T},\delta T\big],\delta T\big]|\mathrm{HF}\rangle\\ &\quad + \frac{1}{6}\langle \mu_i|\big[\big[\big[\Phi^{{}^*T},\delta T\big],\delta T\big],\delta T\big]|\mathrm{HF}\rangle + \frac{1}{24}\langle \mu_i|\big[\big[\big[\big[\Phi^{{}^*T},\delta T\big],\delta T\big],\delta T\big],\delta T\big]|\mathrm{HF}\rangle = 0, \qquad 1 \le i \le t,\end{aligned} \tag{39}$$

$$\begin{aligned}\mathbf{J}_{\mu_i\nu_j} &= \langle \mu_i|\big[H_0^{{}^*T},\theta_{\nu_j}\big]|\mathrm{HF}\rangle + \langle \mu_i|\big[\big[\Phi^{{}^*T},\delta T\big],\theta_{\nu_j}\big]|\mathrm{HF}\rangle\\ &\quad + \frac{1}{2}\langle \mu_i|\big[\big[\big[\Phi^{{}^*T},\delta T\big],\delta T\big],\theta_{\nu_j}\big]|\mathrm{HF}\rangle + \frac{1}{6}\langle \mu_i|\big[\big[\big[\big[\Phi^{{}^*T},\delta T\big],\delta T\big],\delta T\big],\theta_{\nu_j}\big]|\mathrm{HF}\rangle\\ &= A_{\mu_i\nu_j} + \langle \mu_i|\big[\big[\Phi^{{}^*T},\delta T\big],\theta_{\nu_j}\big]|\mathrm{HF}\rangle + \frac{1}{2}\langle \mu_i|\big[\big[\big[\Phi^{{}^*T},\delta T\big],\delta T\big],\theta_{\nu_j}\big]|\mathrm{HF}\rangle\\ &\quad + \frac{1}{6}\langle \mu_i|\big[\big[\big[\big[\Phi^{{}^*T},\delta T\big],\delta T\big],\delta T\big],\theta_{\nu_j}\big]|\mathrm{HF}\rangle, \quad i,j = 1,2,\ldots,t.\end{aligned} \tag{40}$$

To obtain the first term in Eq. (39), we have used Eq. (29) and introduced the integer step function S_{ab},

$$S_{ab} = \begin{cases} 0, & \text{for } a \le b \\ 1, & \text{for } a > b. \end{cases} \tag{41}$$

To obtain the last equality in Eqs. (39) and (40), we have introduced the extended parent-state Jacobian,

$$\begin{aligned} A_{\mu_i\nu_j} &= \frac{\mathrm{d}}{\mathrm{d}\delta t_{\nu_j}} \langle \mu_i | \mathrm{e}^{-\delta T} H_0^{*T} \mathrm{e}^{\delta T} | \mathrm{HF} \rangle \Big|_{\boldsymbol{\delta}\mathbf{t}=\mathbf{0}} \\ &= \langle \mu_i | \big[H_0^{*T}, \theta_{\nu_j} \big] | \mathrm{HF} \rangle, \qquad i,j = 1,2,\ldots,t. \end{aligned} \tag{42}$$

Equations (39) and (40) show that the extended parent-state Jacobian arises both in the amplitude equations in Eq. (39) and in the CC target-state Jacobian in Eq. (40). Furthermore, the CC target-state Jacobian has the extended parent-state Jacobian as its dominant contribution.

To determine the Jacobian expansion and the cluster amplitude equations, we use in CP theory the parent state Jacobian partitioning of the extended parent-state Jacobian in Eq. (42) [cf. Eqs. (29) and (39) of Paper I[1]],

$$A_{\mu_i\nu_j} = A^{(0)}_{\mu_i\nu_j} + A^{(1)}_{\mu_i\nu_j}, \qquad i,j = 1,2,\ldots,t, \tag{43}$$

where

$$\begin{aligned} A^{(0)}_{\mu_i\nu_j} =& \langle \mu_i | \big[H_0^{*T}, \theta_{\nu_j} \big] | \mathrm{HF} \rangle (1 - S_{ip})(1 - S_{jp}) + \varepsilon_{\nu_j} \delta_{\mu_i\nu_j} S_{ip} S_{jp}, \\ & 1 \le i,j \le t, \end{aligned} \tag{44a}$$

$$\begin{aligned} A^{(1)}_{\mu_i\nu_j} =& \langle \mu_i | \big[\Phi^{*T}, \theta_{\nu_j} \big] | \mathrm{HF} \rangle (1 - S_{ip}) S_{jp} \\ &+ \langle \mu_i | \big[\Phi^{*T}, \theta_{\nu_j} \big] | \mathrm{HF} \rangle S_{ip} (1 - S_{jp}) \\ &+ \langle \mu_i | \big[\Phi^{*T}, \theta_{\nu_j} \big] | \mathrm{HF} \rangle S_{ip} S_{jp}, \qquad 1 \le i,j \le t, \end{aligned} \tag{44b}$$

where we have used that in canonical Hartree-Fock basis

$$\langle \mu_i | \big[f^{*T}, \theta_{\nu_j} \big] | \mathrm{HF} \rangle = \varepsilon_{\nu_j} \delta_{\mu_i\nu_j}, \qquad i,j = 1,2,\ldots,t. \tag{45}$$

The parent space sub-block of $\mathbf{A}^{(0)}$ contains in addition to the Fock operator terms also the CC parent-state similarity-transformed fluctuation potential terms and the parent space sub-block of $\mathbf{A}^{(0)}$ therefore becomes the CC parent state Jacobian,

$$J^{P}_{\mu_i\nu_j} = \langle \mu_i | \big[H_0^{*T}, \theta_{\nu_j} \big] | \mathrm{HF} \rangle, \qquad 1 \le i,j \le p. \tag{46}$$

$\mathbf{A}^{(0)}$ is further block-diagonal, and the auxiliary space sub-block contains only the Fock operator contributions. $\mathbf{A}^{(1)}$ has a vanishing parent-space sub-block and contains only terms that are of first order in Φ^{*T}.

Introducing Eq. (43) in Eqs. (39) and (40), we obtain

$$\begin{aligned} &\sum_{j=1}^{t} \sum_{\nu_j} A^{(0)}_{\mu_i\nu_j} \delta t_{\nu_j} + \langle \mu_i | \Phi^{*T} | \mathrm{HF} \rangle S_{ip} + \sum_{j=1}^{t} \sum_{\nu_j} A^{(1)}_{\mu_i\nu_j} \delta t_{\nu_j} \\ &\quad + \frac{1}{2} \langle \mu_i | \big[\big[\Phi^{*T}, \delta T \big], \delta T \big] | \mathrm{HF} \rangle + \frac{1}{6} \langle \mu_i | \big[\big[\big[\Phi^{*T}, \delta T \big], \delta T \big], \delta T \big] | \mathrm{HF} \rangle \\ &\quad + \frac{1}{24} \langle \mu_i | \big[\big[\big[\big[\Phi^{*T}, \delta T \big], \delta T \big], \delta T \big], \delta T \big] | \mathrm{HF} \rangle = 0, \qquad 1 \le i \le t, \end{aligned} \tag{47}$$

$$\begin{aligned} J_{\mu_i\nu_j} =& A^{(0)}_{\mu_i\nu_j} + A^{(1)}_{\mu_i\nu_j} + \langle \mu_i | \big[\big[\Phi^{*T}, \delta T \big], \theta_{\nu_j} \big] | \mathrm{HF} \rangle \\ &+ \frac{1}{2} \langle \mu_i | \big[\big[\big[\Phi^{*T}, \delta T \big], \delta T \big], \theta_{\nu_j} \big] | \mathrm{HF} \rangle \\ &+ \frac{1}{6} \langle \mu_i | \big[\big[\big[\big[\Phi^{*T}, \delta T \big], \delta T \big], \delta T \big], \theta_{\nu_j} \big] | \mathrm{HF} \rangle, \qquad 1 \le i,j \le t. \end{aligned} \tag{48}$$

From Eq. (48), we may identify $\mathbf{J}^{(0)}$ of Eq. (22) as $\mathbf{A}^{(0)}$,

$$\mathbf{J}^{(0)} = \mathbf{A}^{(0)}, \tag{49}$$

where $\mathbf{J}^{(0)}$ in the two-component form may be written as

$$\mathbf{J}^{(0)} = \begin{pmatrix} \mathbf{J}^{P} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\varepsilon}_{A} \end{pmatrix}, \tag{50}$$

where $\mathbf{J}^{P}$ in the CC parent-state Jacobian in Eq. (46) and $\boldsymbol{\varepsilon}_{A}$ is a diagonal matrix referencing the auxiliary space and containing orbital energy differences,

$$(\boldsymbol{\varepsilon}_{A})_{\mu_i\nu_j} = \varepsilon_{\nu_j} \delta_{\mu_i\nu_j}, \qquad p < i,j \le t. \tag{51}$$

Due to the block-diagonal structure of $\mathbf{J}^{(0)}$, the parent space component of $\mathbf{J}^{(0)}$ satisfies the CC parent-state response eigenvalue equation,

$$\begin{pmatrix} \mathbf{J}^{P} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\varepsilon}_{A} \end{pmatrix} \begin{pmatrix} \mathbf{R}^{P}_{x} \\ 0 \end{pmatrix} = \omega^{P}_{x} \begin{pmatrix} \mathbf{R}^{P}_{x} \\ 0 \end{pmatrix}, \tag{52}$$

and we thus have

$$\omega^{(0)}_{x} = \omega^{P}_{x}, \tag{53}$$

$$\mathbf{R}^{(0)}_{x} = \begin{pmatrix} \mathbf{R}^{P}_{x} \\ \mathbf{0} \end{pmatrix}, \tag{54}$$

$$\mathbf{L}^{(0)}_{x} = \begin{pmatrix} \mathbf{L}^{P}_{x} & \mathbf{0} \end{pmatrix}, \tag{55}$$

where

$$\mathbf{L}^{P}_{x} \mathbf{R}^{P}_{x} = 1. \tag{56}$$

The last three terms in Eq. (48) are of at least second order in Φ^{*T}, and $\mathbf{J}^{(1)}$ of Eq. (22) therefore may be identified as

$$\mathbf{J}^{(1)} = \mathbf{A}^{(1)}. \tag{57}$$

To identify $\mathbf{J}^{(0)}$ and $\mathbf{J}^{(1)}$, we have required that the parent state Jacobian in the parent space sub-block of $\mathbf{J}^{(0)}$ becomes a zeroth-order term and that the parent space sub-block of $\mathbf{J}^{(1)}$ vanishes. We have thereby removed internal relaxation in the parent subspace through first-order in the Jacobian of Eq. (22). To identify the second- and higher-order terms in the Jacobian expansion in Eq. (22) from Eq. (48), we will also require that the cluster amplitudes in the δT operator in Eq. (48) are determined from a perturbation series where internal relaxation in the parent subspace is removed. To accomplish this, we determine the cluster amplitudes in Eq. (48) from Eq. (47). Substituting Eqs. (44) and (46) in Eq. (47), we can write the kth-order cluster amplitude equations in the two-component form as

$$\sum_{j=1}^{p}\sum_{\nu_j} J^{P}_{\mu_i\nu_j}\delta t^{(k)}_{\nu_j} = -\sum_{j=p+1}^{t}\sum_{\nu_j}\langle\mu_i|\big[\Phi^{*T},\theta_{\nu_j}\big]|\mathrm{HF}\rangle\delta t^{(k-1)}_{\nu_j} - \bigg\{\frac{1}{2}\langle\mu_i|\big[\big[\Phi^{*T},\delta T\big],\delta T\big]|\mathrm{HF}\rangle + \frac{1}{6}\langle\mu_i|\big[\big[\big[\Phi^{*T},\delta T\big],\delta T\big],\delta T\big]|\mathrm{HF}\rangle + \frac{1}{24}\langle\mu_i|\big[\big[\big[\big[\Phi^{*T},\delta T\big],\delta T\big],\delta T\big],\delta T\big]|\mathrm{HF}\rangle\bigg\}^{\{k\}}, \quad 1 \le i \le p, \tag{58a}$$

$$\varepsilon_{\mu_i}\delta t^{(k)}_{\mu_i} = -\langle\mu_i|\Phi^{*T}|\mathrm{HF}\rangle\delta_{k1} - \sum_{j=1}^{t}\sum_{\nu_j}\langle\mu_i|\big[\Phi^{*T},\theta_{\nu_j}\big]|\mathrm{HF}\rangle\delta t^{(k-1)}_{\nu_j} - \bigg\{\frac{1}{2}\langle\mu_i|\big[\big[\Phi^{*T},\delta T\big],\delta T\big]|\mathrm{HF}\rangle + \frac{1}{6}\langle\mu_i|\big[\big[\big[\Phi^{*T},\delta T\big],\delta T\big],\delta T\big]|\mathrm{HF}\rangle + \frac{1}{24}\langle\mu_i|\big[\big[\big[\big[\Phi^{*T},\delta T\big],\delta T\big],\delta T\big],\delta T\big]|\mathrm{HF}\rangle\bigg\}^{\{k\}}, \quad p < i \le t, \tag{58b}$$

where $\{\,.\,\}^{\{k\}}$ denotes that terms of order k in Φ^{*T} are picked up and gathered from the expression in the parentheses. In Eq. (58a), internal relaxation in the parent excitation space is removed from the perturbation calculation because the first term on the right-hand side of Eq. (58a) only introduces a coupling between the auxiliary excitation space and the parent excitation space and because sets of linear equations containing the zeroth-order CC parent state Jacobian $\mathbf{J}^{P}$ are solved in the parent excitation space.

From Eq. (48), we can identify the series in Eq. (22) for $\mathbf{J}$ where the zeroth-order Jacobian in Eq. (50) satisfies Eqs. (23) and where the cluster amplitudes δt_{μ_i} entering Eq. (48) are determined from the amplitude equation in Eq. (58). For the Jacobian expansion and the cluster amplitude series, we have used the new generalized order concept of CP theory where terms are collected order by order in Φ^{*T} with the exception that $\mathbf{J}^{P}$, and thereby $\mathbf{J}^{(0)}$, is defined to be of zeroth order although it contains a Φ^{*T} contribution projected on to the parent excitation space. As both the Jacobian expansion and the expansion of the cluster amplitudes are determined using the parent state Jacobian partitioning of the extended parent-state Jacobian, direct relaxation in the parent space is removed from both the cluster amplitude expansion and the Jacobian expansion.

It is of interest to briefly discuss alternative and more elaborate choices of the separation of the extended parent-state Jacobian in Eqs. (43). A first choice is to use a zeroth-order Jacobian that includes the full Jacobian in both the parent-parent and auxiliary-auxiliary blocks and neglects the coupling blocks between the parent and auxiliary spaces,

$$\begin{aligned} A^{(0)}_{\mu_i\nu_j} ={}& \langle\mu_i|\big[H_0^{*T},\theta_{\nu_j}\big]|\mathrm{HF}\rangle(1-S_{ip})(1-S_{jp}) \\ &+ \langle\mu_i|\big[H_0^{*T},\theta_{\nu_j}\big]|\mathrm{HF}\rangle S_{ip}S_{jp}, \qquad 1 \le i,j \le t, \end{aligned} \tag{59a}$$

$$\begin{aligned} A^{(1)}_{\mu_i\nu_j} ={}& \langle\mu_i|\big[\Phi^{*T},\theta_{\nu_j}\big]|\mathrm{HF}\rangle(1-S_{ip})S_{jp} \\ &+ \langle\mu_i|\big[\Phi^{*T},\theta_{\nu_j}\big]|\mathrm{HF}\rangle S_{ip}(1-S_{jp}), \qquad 1 \le i,j \le t. \end{aligned} \tag{59b}$$

The use of the partitioning in Eqs. (59) leads to a well-defined perturbation expansion for the ground and excited states, which at zeroth order reproduces the parent state coupled cluster results and converges toward the target state coupled cluster results. Due to the more elaborate zeroth-order Jacobian, this expansion is expected to converge faster toward the target state results than is the case for the CP expansions. However, the use of Φ^{*T} in the auxiliary space block of the zeroth-order Jacobian leads to a formalism, where linear transformations with the zeroth-order Jacobian have the same complexity and computational scaling as if the full target-space Jacobian was used. The iterative solution of the linear equations required to obtain the amplitude corrections of a given order will therefore have a computational scaling that is of the same order as that for a coupled cluster calculation in the target space, so this perturbation expansion does not offer any computational advantages.

Expansions that use the full extended parent-state Jacobian as the zeroth-order expansion,

$$A^{(0)}_{\mu_i\nu_j} = \langle\mu_i|\big[H_0^{*T},\theta_{\nu_j}\big]|\mathrm{HF}\rangle, \qquad 1 \le i,j \le t, \tag{60a}$$

$$A^{(1)}_{\mu_i\nu_j} = 0, \qquad 1 \le i,j \le t, \tag{60b}$$

may also be concocted. With this choice of the zeroth-order Jacobian, the perturbation expansion of the ground-state amplitudes becomes similar to that of standard fixed-Hessian optimization schemes.[56] The error of the first correction is quadratic in the norm $\|{}^{*}\mathbf{t} - {}^{c}\mathbf{t}\|$, where ${}^{c}\mathbf{t}$ denotes the converged CC target state amplitudes, and the error of the nth correction is of order $n + 1$ in the same norm. Such expansions have been extensively tested in connection with MCSCF optimization.[57] In the current context, where the Jacobian is not explicitly constructed, such schemes have limited value; in particular, they would have the same high scaling as the full target-state Jacobian and they do not correspond to a well-defined perturbation expansion from parent- to target-space CC expansions. We conclude that none of these more elaborate zeroth-order Jacobians offers a better combination of computational scaling and accuracy than the separation in CP theory, Eqs. (44).

B. Lowest-order amplitudes and Jacobian corrections

We now determine the lowest-order amplitude corrections from Eqs. (58) and use these amplitude corrections to determine the lowest-order terms in the Jacobian expansion in Eq. (22). The zeroth-order amplitudes vanish,

$$\delta t^{(0)}_{\mu_i} = 0, \qquad 1 \le i \le t. \tag{61}$$

The first-order amplitudes become

$$\delta t^{(1)}_{\mu_i} = 0, \qquad 1 \le i \le p, \tag{62a}$$

$$\varepsilon_{\mu_i}\delta t^{(1)}_{\mu_i} = -\langle\mu_i|\Phi^{*T}|\mathrm{HF}\rangle, \qquad p < i \le t. \tag{62b}$$

The first-order parent space amplitudes vanish because the parent space cluster amplitude equation in Eq. (29) is satisfied. The second-order amplitude corrections become

$$\sum_{j=1}^{p}\sum_{\nu_j} J^{P}_{\mu_i\nu_j}\delta t^{(2)}_{\nu_j} = -\sum_{j=p+1}^{t}\sum_{\nu_j}\langle\mu_i|\big[\Phi^{*T},\theta_{\nu_j}\big]|\mathrm{HF}\rangle\delta t^{(1)}_{\nu_j}, \qquad 1 \le i \le p, \tag{63a}$$

$$\varepsilon_{\mu_i}\delta t^{(2)}_{\mu_i} = -\sum_{j=p+1}^{t}\sum_{\nu_j}\langle\mu_i|\big[\Phi^{*T},\theta_{\nu_j}\big]|\mathrm{HF}\rangle\delta t^{(1)}_{\nu_j}, \qquad p < i \le t, \tag{63b}$$

where to obtain Eq. (63b) we have used Eq. (62a). The third-order amplitudes become

$$\sum_{j=1}^{p}\sum_{\nu_j} J^{P}_{\mu_i\nu_j}\delta t^{(3)}_{\nu_j} = -\sum_{j=p+1}^{t}\sum_{\nu_j}\langle\mu_i|\big[\Phi^{*T},\theta_{\nu_j}\big]|\mathrm{HF}\rangle\delta t^{(2)}_{\nu_j}, \qquad 1 \le i \le p, \tag{64a}$$

$$\begin{aligned}\varepsilon_{\mu_i}\delta t^{(3)}_{\mu_i} &= -\sum_{j=1}^{t}\sum_{\nu_j}\langle\mu_i|\big[\Phi^{*T},\theta_{\nu_j}\big]|\mathrm{HF}\rangle\delta t^{(2)}_{\nu_j}\\ &\quad -\frac{1}{2}\langle\mu_i|\big[\big[\Phi^{*T},\delta T^{(1)}\big],\delta T^{(1)}\big]|\mathrm{HF}\rangle, \qquad p < i \le t.\end{aligned} \tag{64b}$$

The lowest-order terms in the expansion of the Jacobian in Eq. (22) may be determined from Eq. (48) using the amplitude corrections of Eqs. (61)–(64). Below we give explicit expressions through third order for this expansion,

$$\begin{aligned}\mathbf{J}^{(1)}_{\mu_i\nu_j} = A^{(1)}_{\mu_i\nu_j} &= \langle\mu_i|\big[\Phi^{*T},\theta_{\nu_j}\big]|\mathrm{HF}\rangle(1-S_{ip})S_{jp}\\ &\quad + \langle\mu_i|\big[\Phi^{*T},\theta_{\nu_j}\big]|\mathrm{HF}\rangle S_{ip}(1-S_{jp}) + \langle\mu_i|\big[\Phi^{*T},\theta_{\nu_j}\big]|\mathrm{HF}\rangle S_{ip}S_{jp},\\ &\qquad 1 \le i,j \le t \quad ; \quad p < t,\end{aligned} \tag{65}$$

$$\mathbf{J}^{(2)}_{\mu_i\nu_j} = \sum_{q=p+1}^{t}\langle\mu_i|\big[\big[\Phi^{*T},\delta T^{(1)}_q\big],\theta_{\nu_j}\big]|\mathrm{HF}\rangle, \qquad 1 \le i,j \le t, \tag{66}$$

$$\begin{aligned}\mathbf{J}^{(3)}_{\mu_i\nu_j} &= \sum_{q=1}^{t}\langle\mu_i|\big[\big[\Phi^{*T},\delta T^{(2)}_q\big],\theta_{\nu_j}\big]|\mathrm{HF}\rangle + \frac{1}{2}\sum_{q,r=p+1}^{t}\\ &\quad\times\langle\mu_i|\big[\big[\big[\Phi^{*T},\delta T^{(1)}_q\big],\delta T^{(1)}_r\big],\theta_{\nu_j}\big]|\mathrm{HF}\rangle, \qquad 1 \le i,j \le t.\end{aligned} \tag{67}$$

C. Arbitrary-order corrections from right response eigenvalue equation

We now determine the excitation-energy corrections to the CC parent state excitation energy in Eq. (25) that formally converge to an excitation energy of the CC target state. We assume that the right eigenvector $\mathbf{R}_x$ is expanded as in Eq. (24), with $\mathbf{R}_x^{(0)}$ given in Eq. (54), and that $\mathbf{R}_x$ is intermediate normalized against $\mathbf{L}_x^{(0)}$ of Eq. (55),

$$\mathbf{L}_x^{(0)}\mathbf{R}_x = 1, \tag{68}$$

implying [cf. Eq. (23c)]

$$\mathbf{L}_x^{(0)}\mathbf{R}_x^{(k)} = 0, \qquad k > 0. \tag{69}$$

Substituting Eqs. (22)–(25) in Eq. (8a) and collecting terms of order k gives

$$\sum_{p=0}^{k}\mathbf{J}^{(p)}\mathbf{R}_x^{(k-p)} = \sum_{p=0}^{k}\omega_x^{(p)}\mathbf{R}_x^{(k-p)}, \tag{70}$$

which may be rearranged as

$$\big(\mathbf{J}^{(0)} - \omega_x^P\mathbf{I}\big)\mathbf{R}_x^{(k)} = \sum_{p=1}^{k}\omega_x^{(p)}\mathbf{R}_x^{(k-p)} - \sum_{p=1}^{k}\mathbf{J}^{(p)}\mathbf{R}_x^{(k-p)}, \tag{71}$$

where we have used Eq. (23d) and where $\mathbf{I}$ is an identity matrix. Projecting Eq. (71) against the zeroth-order left eigenvector, $\mathbf{L}_x^{(0)}$, we obtain the kth-order correction to the CC parent space excitation energy,

$$\omega_x^{(k)} = \sum_{p=1}^{k}\mathbf{L}_x^{(0)}\mathbf{J}^{(p)}\mathbf{R}_x^{(k-p)}, \tag{72}$$

where we have used Eqs. (23b) and (69). Note that the right-hand side of Eq. (72) depends only on right eigenvectors through order $(k-1)$.

When excitation energy corrections have been determined through order k, they may be substituted in Eq. (71) to determine the kth-order correction to the right eigenvector. The kth-order right eigenvalue equation may in the two-component form be written as (the subscripts P and A denote parent and auxiliary subspace components, respectively)

$$\big(\mathbf{J}^P - \omega_x^P\mathbf{I}\big)\mathbf{R}_{xP}^{(k)} = \sum_{p=2}^{k}\omega_x^{(p)}\mathbf{R}_{xP}^{(k-p)} - \sum_{p=2}^{k}\mathbf{J}_{PP}^{(p)}\mathbf{R}_{xP}^{(k-p)} - \sum_{p=1}^{k-1}\mathbf{J}_{PA}^{(p)}\mathbf{R}_{xA}^{(k-p)}, \tag{73a}$$

$$\begin{aligned}\mathbf{R}_{xA}^{(k)} &= \big(\boldsymbol{\varepsilon}_A - \omega_x^P\mathbf{I}\big)^{-1}\left(\sum_{p=2}^{k-1}\omega_x^{(p)}\mathbf{R}_{xA}^{(k-p)} - \sum_{p=1}^{k}\mathbf{J}_{AP}^{(p)}\mathbf{R}_{xP}^{(k-p)}\right.\\ &\quad\left. - \sum_{p=1}^{k-1}\mathbf{J}_{AA}^{(p)}\mathbf{R}_{xA}^{(k-p)}\right),\end{aligned} \tag{73b}$$

where we have used that the auxiliary space component of the zeroth-order right eigenvector vanishes [cf. Eq. (54)] and that the first-order excitation energy correction, $\omega_x^{(1)}$, also vanishes (*vide infra*). Furthermore, to obtain Eq. (73a), we have used that the first-order Jacobian does not have a *PP* block [see Eq. (65)], and to obtain Eq. (73b), we have used that the matrix $\big(\boldsymbol{\varepsilon}_A - \omega_x^P\mathbf{I}\big)$ is diagonal and non-singular.

The parent space component of the kth-order right eigenvector is obtained solving the linear equation in Eq. (73a). Using iterative algorithms to solve Eq. (73a) requires linear transformations of the parent-state Jacobian $\mathbf{J}^P$ in Eq. (46) on parent space trial vectors $\mathbf{b}^P$

$$\big(\mathbf{J}^P\mathbf{b}^P\big)_{\mu_i} = \langle\mu_i|\big[H_0^{*T},B^P\big]|\mathrm{HF}\rangle, \qquad i = 1,\ldots,p, \tag{74}$$

$$B^P = \sum_{i=1}^{p}\sum_{\mu_i} b^P_{\mu_i}\theta_{\mu_i}. \tag{75}$$

The construction of $\mathbf{J}^P\mathbf{b}^P$ in Eq. (74) has a leading-order computational scaling that is at least two powers in system size smaller than the leading-order computational scaling for constructing the right-hand sides of Eq. (73b), for example, the right-hand side component

$$\left(\mathbf{J}_{AP}^{(1)}\mathbf{R}_{xP}^{(k-1)}\right)_{\mu_i} = \langle\mu_i|\left[H_0^{*T}, R_{xP}^{(k-1)}\right]|\mathrm{HF}\rangle, \qquad i = p+1, \ldots, t, \tag{76}$$

$$R_{xP}^{(k-1)} = \sum_{i=1}^{p}\sum_{\mu_i} R_{\mu_i x}^{(k-1)}\theta_{\mu_i}. \tag{77}$$

Solving the linear equations in Eq. (73a) thus does not affect the leading-order computational scaling for the determination of excitation energy corrections. We also note that when solving Eq. (73a) using iterative algorithms and using a diagonal pre-conditioner, we have to ensure that the initial trial vector is $\mathbf{R}_x^{(0)}$ of Eq. (54) and that new trial vectors satisfy Eq. (69). Note that internal relaxation is removed from the parent excitation subspace when the kth-order response amplitudes are determined because the kth-order response amplitudes $\mathbf{R}_{xP}^{(k)}$ do not depend on $\mathbf{R}_{xP}^{(k-1)}$ but only on $\mathbf{R}_{xA}^{(k-1)}$, and since $\mathbf{R}_{xP}^{(k)}$ is determined solving sets of linear equations containing the zeroth-order parent state Jacobian. For comparison, internal relaxation in the parent subspace is removed for the energy when the cluster amplitudes are determined because the kth-order cluster amplitudes $\boldsymbol{\delta}\mathbf{t}_P^{(k)}$ do not depend on $\boldsymbol{\delta}\mathbf{t}_P^{(k-1)}$ but only on $\boldsymbol{\delta}\mathbf{t}_A^{(k-1)}$ and because $\boldsymbol{\delta}\mathbf{t}_P^{(k)}$ is determined solving set of linear equations containing the parent-state Jacobian $\mathbf{J}^P$ (see Paper I[1]).

D. CP series for excited state energies

We have in Eq. (41) of Paper I[1] determined a CP series for the ground-state energy in Eq. (6),

$$E_0 = E_0^{(0)} + E_0^{(1)} + E_0^{(2)} + \cdots, \tag{78}$$

where $E_0^{(0)}$ is the CC parent-state energy ${}^*E_0$ of Eq. (30). In Eq. (25), we have determined a CP series for the excitation energy ω_x. In accordance with Eq. (21), we can therefore also determine a CP series for the total energy E_x of an excited state x,

$$E_x = \left\{E_x^{(0)}, E_x^{(1)}, E_x^{(2)}, \ldots\right\}, \tag{79}$$

where

$$E_x^{(k)} = \omega_{xk} + E_{0k} \tag{80}$$

and

$$\omega_{xk} = \sum_{q=0}^{k}\omega_x^{(q)}, \tag{81}$$

$$E_{xk} = \sum_{q=0}^{k} E_0^{(q)}. \tag{82}$$

The zeroth-order term in the series in Eq. (79) gives according to Eq. (21) the total energy of excited state x for a CC calculation in the parent excitation space and the series in Eq. (79) formally converges to the CC energy of the excited state x in the target excitation space. To obtain the CP series in Eq. (79), it is necessary that the same perturbation framework is used to establish the perturbation expansion of the Jacobian in Eq. (22), the excitation energy in Eq. (25), and the ground-state energy in Eq. (78), as is performed in CP theory.

The CC parent and target state excitation energies are size-extensive. In addition, the excitation energy corrections that are determined solving the Jacobian eigenvalue equation at each order in Φ^{*T} are size-extensive since the individual contributions in the CC target-state Jacobian are term-wise size-extensive. The excited-state energies that are determined from Eq. (79) are also size-extensive since the ground-state energy corrections and the excitation-energy corrections are size-extensive.

E. Explicit expressions for the lowest-order corrections

In this subsection, we will determine explicit expressions for excitation energy corrections through third order from the arbitrary-order energy corrections in Eq. (72) and the arbitrary-order right eigenvector equations in Eqs. (73).

1. First-order correction

The first-order correction to the excitation energy may be obtained from Eq. (72) as

$$\omega_x^{(1)} = \mathbf{L}_x^{(0)}\mathbf{J}^{(1)}\mathbf{R}_x^{(0)} = \begin{pmatrix}\mathbf{L}_x^p & \mathbf{0}\end{pmatrix}\begin{pmatrix}\mathbf{0} & \mathbf{J}_{PA}^{(1)}\\ \mathbf{J}_{AP}^{(1)} & \mathbf{J}_{AA}^{(1)}\end{pmatrix}\begin{pmatrix}\mathbf{R}_x^P\\ \mathbf{0}\end{pmatrix} = 0, \tag{83}$$

where to obtain the second equality, we have used Eqs. (54), (55), and (65). Equation (83) substantiates that the summation in the $\sum_{p=2}^{k}\omega_x^{(p)}\mathbf{R}_{xP}^{(k-p)}$ term in Eq. (73a) [and in the corresponding term in Eq. (73b)] starts with $p = 2$. The first-order corrections to the right eigenvector are obtained from Eqs. (73),

$$\left(\mathbf{J}^P - \omega_x^P\mathbf{I}\right)\mathbf{R}_{xP}^{(1)} = \mathbf{0}, \tag{84a}$$

$$\mathbf{R}_{xA}^{(1)} = -\left(\boldsymbol{\varepsilon}_A - \omega_x^P\mathbf{I}\right)^{-1}\mathbf{J}_{AP}^{(1)}\mathbf{R}_x^P, \tag{84b}$$

where to obtain Eq. (84b), we have used Eq. (54). Equations (84) show that the first-order correction to the right eigenvector may be written as

$$\mathbf{R}_{x\mu_i}^{(1)} = 0, \qquad 1 \le i \le p, \tag{85a}$$

$$\mathbf{R}_{x\mu_i}^{(1)} = -\left(\varepsilon_{\mu_i} - \omega_x^P\right)^{-1}\langle\mu_i|\left[\Phi^{*T}, R_x^P\right]|\mathrm{HF}\rangle, \qquad p < i \le t, \tag{85b}$$

where we have used Eq. (65) and introduced the cluster operator R_x^P for the cluster parent excited state x,

$$R_x^P = \sum_{i=1}^{p}\sum_{\mu_i}\theta_{\mu_i}R_{x\mu_i}^P. \tag{86}$$

2. Second-order correction

Using Eqs. (72) and (73), we obtain second-order corrections to the excitation energy and eigenvectors as

$$\begin{aligned}\omega_x^{(2)} &= \mathbf{L}_x^{(0)}\mathbf{J}^{(2)}\mathbf{R}_x^{(0)} + \mathbf{L}_x^{(0)}\mathbf{J}^{(1)}\mathbf{R}_x^{(1)}\\ &= \mathbf{L}_x^p\,\mathbf{J}_{PP}^{(2)}\,\mathbf{R}_x^P + \mathbf{L}_x^p\,\mathbf{J}_{PA}^{(1)}\,\mathbf{R}_{xA}^{(1)},\end{aligned} \tag{87}$$

$$\left(\mathbf{J}^\mathbf{P} - \omega_x^P\mathbf{I}\right)\mathbf{R}_{xP}^{(2)} = \omega_x^{(2)}\mathbf{R}_x^P - \mathbf{J}_{PP}^{(2)}\mathbf{R}_x^P - \mathbf{J}_{PA}^{(1)}\mathbf{R}_{xA}^{(1)}, \tag{88a}$$

$$\mathbf{R}_{xA}^{(2)} = -\left(\boldsymbol{\varepsilon}_A - \omega_x^P\mathbf{I}\right)^{-1}\left(\mathbf{J}_{AP}^{(2)}\mathbf{R}_x^P + \mathbf{J}_{AA}^{(1)}\mathbf{R}_{xA}^{(1)}\right), \tag{88b}$$

where to obtain the second equality in Eq. (87) and Eq. (88b), we have used Eq. (85a). The second-order excitation energy in Eq. (87) and the elements of the second-order eigenvectors in Eq. (88) may be written as

$$\begin{aligned}\omega_x^{(2)} = &\sum_{q=p+1}^{t} \langle L_x^P | [[\Phi^{*T}, \delta T_q^{(1)}], R_x^P] | \mathrm{HF}\rangle \\ &+ \langle L_x^P | [\Phi^{*T}, R_{xA}^{(1)}] | \mathrm{HF}\rangle,\end{aligned} \tag{89}$$

$$\begin{aligned}\sum_{j=1}^{p} \sum_{\nu_j} &\left(J_{\mu_i \nu_j}^P - \omega_x^P \, \delta_{\mu_i \nu_j} \right) R_{x\nu_j}^{(2)} \\ &= \omega_x^{(2)} R_{x\mu_i} - \sum_{q=p+1}^{t} \langle \mu_i | [[\Phi^{*T}, \delta T_q^{(1)}], R_x^P] | \mathrm{HF}\rangle \\ &\quad - \langle \mu_i | [\Phi^{*T}, R_{xA}^{(1)}] | \mathrm{HF}\rangle, \qquad 1 \le i \le p,\end{aligned} \tag{90a}$$

$$\begin{aligned}R_{x\mu_i}^{(2)} = -\left(\varepsilon_{\mu_i} - \omega_x^P\right)^{-1} &\left(\sum_{q=p+1}^{t} \langle \mu_i | [[\Phi^{*T}, \delta T_q^{(1)}], R_x^P] | \mathrm{HF}\rangle \right. \\ &\left. + \langle \mu_i | [\Phi^{*T}, R_{xA}^{(1)}] | \mathrm{HF}\rangle \right), \qquad p < i \le t,\end{aligned} \tag{90b}$$

where we have used Eqs. (65), (66), and (86) and introduced the bra state $\langle L_x^P|$ corresponding to a CC parent excited state x,

$$\langle L_x^P | = \sum_{i=1}^{p} \sum_{\mu_i} \mathbf{L}_{x\mu_i}^P \langle \mu_i |, \tag{91}$$

and the first-order auxiliary space cluster operator $R_{xA}^{(1)}$ corresponding to an excited state x,

$$R_{xA}^{(1)} = \sum_{i=p+1}^{t} \sum_{\mu_i} \theta_{\mu_i} R_{x\mu_i}^{(1)}. \tag{92}$$

3. Third-order correction

Following the same route of derivation as for the second-order corrections, we obtain the third-order excitation-energy corrections,

$$\omega_x^{(3)} = \mathbf{L}_x^{(0)} \mathbf{J}^{(3)} \mathbf{R}_x^{(0)} + \mathbf{L}_x^{(0)} \mathbf{J}^{(2)} \mathbf{R}_x^{(1)} + \mathbf{L}_x^{(0)} \mathbf{J}^{(1)} \mathbf{R}_x^{(2)}, \tag{93}$$

$$\begin{aligned}\omega_x^{(3)} = &\langle L_x^P | [[\Phi^{*T}, \delta T^{(2)}], R_x^P] | \mathrm{HF}\rangle \\ &+ \frac{1}{2} \sum_{q,r=p+1}^{t} \langle L_x^P | [[[\Phi^{*T}, \delta T_q^{(1)}], \delta T_r^{(1)}], R_x^P] | \mathrm{HF}\rangle \\ &+ \sum_{q=p+1}^{t} \langle L_x^P | [[\Phi^{*T}, \delta T_q^{(1)}], R_{xA}^{(1)}] | \mathrm{HF}\rangle \\ &+ \langle L_x^P | [\Phi^{*T}, R_{xA}^{(2)}] | \mathrm{HF}\rangle.\end{aligned} \tag{94}$$

F. Explicit expressions for the lowest-order excitation energy corrections for the CPSD(T) model

As a specific example of excitation energy corrections, let us consider the CPSD(T) model where a series of excitation energy corrections to the CCSD excitation energy is determined in orders of the similarity-transformed fluctuation potential, and where the series formally converges to the CCSDT excitation energy. For this model, we have $p = 2$ and $t = 3$. Using Eqs. (53), (83), and (85), the zeroth- and first-order excitation energy and excitation vectors become

$$\omega_x^{(0)} = \omega_x^{\mathrm{CCSD}}, \tag{95}$$

$$\omega_x^{(1)} = 0, \tag{96}$$

$$R_{x\mu_i}^{(1)} = 0, \qquad i = 1, 2, \tag{97a}$$

$$R_{x\mu_3}^{(1)} = -\left(\varepsilon_{\mu_3} - \omega_x^{\mathrm{CCSD}}\right)^{-1} \langle \mu_3 | [\Phi^{*T}, R_x^{\mathrm{CCSD}}] | \mathrm{HF}\rangle. \tag{97b}$$

The second-order corrections are obtained from Eqs. (89) and (90),

$$\omega_x^{(2)} = \langle L_x^{\mathrm{CCSD}} | [[\Phi^{*T}, \delta T_3^{(1)}], R_x^{\mathrm{CCSD}}] | \mathrm{HF}\rangle + \langle L_x^{\mathrm{CCSD}} | [\Phi^{*T}, R_{x3}^{(1)}] | \mathrm{HF}\rangle, \tag{98}$$

$$\begin{aligned}\sum_{j=1}^{2} \sum_{\nu_j} &\left(\mathbf{J}_{\mu_i \nu_j}^{\mathrm{CCSD}} - \omega_x^{\mathrm{CCSD}} \, \delta_{\mu_i \nu_j} \right) R_{x\nu_j}^{(2)} \\ &= \omega_x^{(2)} R_{x\mu_i}^{\mathrm{CCSD}} - \langle \mu_i | [[\Phi^{*T}, \delta T_3^{(1)}], R_x^{\mathrm{CCSD}}] | \mathrm{HF}\rangle \\ &\quad - \langle \mu_i | [\Phi^{*T}, R_{x3}^{(1)}] | \mathrm{HF}\rangle, \qquad i = 1, 2,\end{aligned} \tag{99a}$$

$$\begin{aligned}R_{x\mu_3}^{(2)} = -\left(\varepsilon_{\mu_3} - \omega_x^{\mathrm{CCSD}}\right)^{-1} &\Big(\langle \mu_3 | [[\Phi^{*T}, \delta T_3^{(1)}], R_x^{\mathrm{CCSD}}] | \mathrm{HF}\rangle \\ &+ \langle \mu_3 | [\Phi^{*T}, R_{x3}^{(1)}] | \mathrm{HF}\rangle \Big),\end{aligned} \tag{99b}$$

whereas the third-order excitation energy corrections may be obtained from Eq. (94),

$$\begin{aligned}\omega_x^{(3)} = &\sum_{q=1}^{3} \langle L_x^{\mathrm{CCSD}} | [[\Phi^{*T}, \delta T_q^{(2)}], R_x^{\mathrm{CCSD}}] | \mathrm{HF}\rangle \\ &+ \langle L_x^{\mathrm{CCSD}} | [\Phi^{*T}, R_{x3}^{(2)}] | \mathrm{HF}\rangle.\end{aligned} \tag{100}$$

To obtain Eq. (100), we have used that the second and third terms in Eq. (94) vanish using excitation rank arguments.

IV. NUMERICAL RESULTS

In this section, we report calculations of excitation energies using the CP hierarchies. The CPS(D) and CPSD(T) methods are used to determine excitation energies for the lower excited states of four molecular and atomic systems: hydrogen fluoride at the equilibrium distance (R_e) and a stretched bond length ($1.5R_e$), CH_2, and the fluorine anion. Furthermore, the CPSDT(Q) method is applied to determine excitation energies to states with selected spins and symmetries of the CH_2 molecule. At this point, we note that the first-order excitation energy correction vanishes for CP excitation energy series and that the second-order model CPS(D-2) is identical to the CIS(D)[41] model. The aug-cc-pVDZ basis set is used for all calculations, and the 1s core-orbitals are doubly occupied on all atoms differing from H. The geometries are given in our previous studies of the performance of the CP methods to ground-state energies; see Paper I.[1] These examples have been chosen to study the CP excitation-energy series of electron-rich as well as electron-poor molecular systems with various degrees of multi-configurational character of the ground-state wave functions. The hydrogen fluoride example allows us to study a molecule containing an electron-rich atom. At R_e, the molecule is strongly dominated by the Hartree-Fock configuration, whereas at $1.5R_e$, it has a minor multi-configurational component.

The CP calculations of the excitation energies are performed with the general coupled cluster codes[18] of the LUCIA program,[58] which has been extended to enable the calculation of CP excitation vectors and energies for arbitrary choices of excitation levels for the parent and target states. The codes are rather inefficient, especially for higher orders of the perturbation expansion. The various wave function corrections were determined to an accuracy that ensures that the obtained excitation energies are accurate to 10^{-6} Hartree.

Several topics are of interest when examining the performance of a novel perturbation hierarchy. In this paper, we focus on the performance of the CP methods at lower orders, in particular, the lowest four non-trivial orders. In a forthcoming publication, we will examine the global convergence of the CP excitation energy series and, in particular, the convergence patterns for the higher order terms and how these series patterns can be modeled using a simple two-state model.

The accuracy of the low-order corrections to an excitation energy depends on many factors. One factor that we will consider is whether the state changes position in the energy spectrum when going from the parent to the target state. For example: Is a first excited parent state of a given symmetry and spin also the first excited target state of that symmetry and spin or does it have another position in the target spectrum? If the state changes position, the perturbation expansion is divergent, and this may affect the accuracy of the low-order results. As both parent and target states are explicitly calculated here, we can examine the eigenvectors of the various parent and target states and thereby determine the energy order of the target state for a given parent state. In the present work, the parent and target states are mapped by comparing the dominating excitations of the various parent and target excitation vectors.

To provide a thorough discussion of the accuracy of CP excitation energy series, we report CP series for both the ground-state energy and for excitation energies. In quantum chemistry, ground-state energies are usually reported in Hartree, whereas excitation energies are reported in eV. To compare CP ground-state energy series with CP excitation energies series, the results for both series are reported in Hartree. When we summarize our findings for excitation energy series, results in eV are also reported. We also investigate when CP excitation energy corrections have an accuracy smaller than 0.004 and 0.001 Hartree; these values correspond to 0.109 and 0.027 eV, respectively.

A. CPS(D) calculations

In the CPS(D) series for excitation energies, we determine approximate CCSD excitation energies by adding perturbative corrections to a CCS excitation vector. A prerequisite for obtaining accurate excitation energies from low-order CPS(D) calculations is thus that the targeted CCSD state is well described at the CCS level. We refer to such excitations as single-replacement dominated excitations.

For an excitation to be single-replacement dominated, the zeroth-order CCS state has to be the dominant excitation component in the expansion of $\mathbf{R}_x$ in Eq. (24). Making separate order expansions of the single and double excitation parts of $\mathbf{R}_x$, we may write

$$\mathbf{R}_{xS} = \mathbf{R}_{xS}^{(0)} + \mathbf{R}_{xS}^{(2)} + \cdots, \tag{101}$$

$$\mathbf{R}_{xD} = \mathbf{R}_{xD}^{(1)} + \mathbf{R}_{xD}^{(2)} + \cdots, \tag{102}$$

where we have used that $\mathbf{R}_{xS}^{(1)}$ and $\mathbf{R}_{xD}^{(0)}$ vanish [see Eqs. (85a) and (54)]. The CCS right eigenvector $\mathbf{R}_{xS}^{(0)}$ may be chosen as normalized,

$$|\mathbf{R}_{xS}^{(0)}| = |\mathbf{R}_{xS}^{\mathrm{CCS}}| = 1. \tag{103}$$

For a single-replacement dominated excitation, the norm of the doubles component, $|\mathbf{R}_{xD}|$, truncated at a given order must be small compared to the norm of the singles component. In particular, $|\mathbf{R}_{xD}|$ must be smaller than $|\mathbf{R}_{xS}^{(0)}| = 1$,

$$1 > |\mathbf{R}_{xD}^{(1)}| + |\mathbf{R}_{xD}^{(2)}| + \cdots. \tag{104}$$

In addition, for a single-replacement dominated excitation, we must require that the correction to the CCS state is much smaller than the norm of the CCS state,

$$1 > |\mathbf{R}_{xS}^{(2)}| + |\mathbf{R}_{xS}^{(3)}| + \cdots. \tag{105}$$

When the position of an excited state changes when going from the parent to the target space, the size of $|\mathbf{R}_{xS}^{(2)}|$ may become large and $|\mathbf{R}_{xS}^{(2)}|$ may therefore be used as a diagnostic for judging the quality of the low-order corrections.

1. Calculations on HF at R_e

For the first considered example, hydrogen fluoride at equilibrium geometry, we provide in Table I the results for the considered excited states. All energies in this and the following tables are in Hartree. For each excited state, the table provides the excitation energies at the parent and target level, here corresponding to the results of CCS and CCSD response calculations, respectively, and the energy order of each parent state in the energy spectrum of the target space. With respect to the perturbation expansions, the table gives the errors of the excitation energies for the lowest four non-trivial orders, the order at which the error is less than 0.004 and 0.001 Hartree, and whether the perturbation expansion is convergent or divergent. An error is here defined as the difference between the excitation energy obtained at a given order and the full target space excitation energy. Finally, the table contains the diagnostic $|\mathbf{R}_{xS}^{(2)}|$ for the excited states. The table provides also the similar information about the CPS(D) series for the ground state of hydrogen fluoride.

From Table I, it is first noted that the energy ordering of the parent and target roots is identical for all states. In agreement with this observation, the CPS(D) hierarchy converges for all considered excitations. It is seen from the table that the doubles corrections to the excitation energies all are negative and are in the interval between −0.06 and −0.03 Hartree, except for the lowest $^3\Sigma$ state where the correction is only −0.0066 Hartree. As expected, the corrections to the excitation energies are much smaller than the doubles correlation energy of the ground state, which is about −0.23 Hartree.

TABLE I. Convergence of the CPS(D) ground state and excitation energies for hydrogen fluoride at R_e. Energies, corrections, and errors in a.u. See text for details.

State	$X^1\Sigma$	$1^1\Sigma$	$2^1\Sigma$	$1^3\Sigma$	$2^3\Sigma$	$3^3\Sigma$		
Parent energy	−100.033506	0.5672	0.6558	0.5002	0.5603	0.6684		
Target energy	−100.259434	0.5321	0.5985	0.4936	0.5240	0.6429		
Target root	0	1	2	1	2	3		
$\lvert\mathbf{R}_{xS}^{(2)}\rvert$	...	0.12	0.36	0.18	0.07	0.26		
Correction	−0.225928	−0.0351	−0.0573	−0.0066	−0.0363	−0.0255		
Errors for various orders								
Order 2	0.0037	−0.0194	−0.0299	−0.0052	0.0017	−0.0248		
Order 3	0.0030	0.0035	0.0074	0.0060	−0.0001	0.0020		
Order 4	0.0010	−0.0038	0.0091	−0.0048	−0.0018	−0.0018		
Order 5	0.0006	0.0021	0.0039	0.0017	0.0008	0.0020		
Order with error <0.004(0.001)	4	3(6)	5(8)	5(7)	3(5)	3(6)		
Convergent?	Yes	Yes	Yes	Yes	Yes	Yes		
State	$1^1\Pi$	$2^1\Pi$	$3^1\Pi$	$1^3\Pi$	$2^3\Pi$	$3^3\Pi$	$1^1\Delta$	$1^3\Delta$
Parent exc. energy	0.4326	0.5692	0.6339	0.4072	0.5582	0.6217	0.6018	0.5840
Target exc. energy	0.3788	0.5171	0.5732	0.3639	0.5095	0.5654	0.5525	0.5417
Target root	1	2	3	1	2	3	1	1
$\lvert\mathbf{R}_{xS}^{(2)}\rvert$	0.21	0.29	0.22	0.20	0.34	0.30	0.05	0.04
Correction	−0.0538	−0.0521	−0.0607	−0.0433	−0.0487	−0.0563	−0.0493	−0.0423
Errors for various orders								
Order 2	−0.0002	−0.0312	−0.0327	−0.0175	−0.0292	−0.0332	−0.0240	−0.0206
Order 3	0.0027	0.0015	0.0004	0.0033	0.0017	0.00022	−0.0007	−0.0009
Order 4	−0.0064	−0.0001	0.0026	−0.0066	−0.0030	0.0045	−0.0009	−0.0014
Order 5	0.0027	0.0016	−0.0005	0.0022	0.0026	−0.0013	0.0011	0.0010
Order with error <0.004(0.001)	3(6)	3(4)	3(3)	3(6)	3(6)	3(3)	3(3)	3(3)
Convergent?	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

The first non-vanishing contribution, the CPS(D-2) correction, gives about 98% of the full doubles correction to the ground state correlation energy, whereas the CPS(D-2) correction to the excitation energy overestimates the full doubles correction and gives between 150% and 200% of the full correction. The errors of the CPS(D-2) excitation energies are thus typically in the interval between −0.02 and −0.03 Hartree. The small reduction in the second-order errors should not be considered as a flaw of the CPS(D) method as the size of corrections to the excitation energies is much smaller than the corrections to the total energies of the states, so a minor imbalance in the second-order calculation for the ground and excited state energies can lead to these minor reductions.

The third-order correction is the first correction that includes the full interaction between excitations in the auxiliary space. The inclusion of the third-order correction leads to a reduction in the initial error by a factor that typically is in the range of 4-10 and the size of most of the errors is below 0.004 Hartree. Whereas the second-order excitation energies overestimate the doubles correction to the excitation energies, the third-order corrections typically underestimate the corrections. For a few roots, the CPS(D-3) energies are very accurate. For example, for the $2^3\Sigma$ state, the third-order correction is within 0.3% of the full results. However, there does not seem to be any correlation between the accuracy of the third-order energy and the spin, symmetry, or root number of the excited state.

The addition of the fourth-order corrections leads in general to total corrections that are too large and that are not in better agreement with the full corrections than the third-order results. When the fifth-order corrections also are included, the size of the total corrections is again reduced. By going from third to fifth order, the largest errors in fifth order are thus reduced by about a factor of two. For the excitation energies to a few states, including $3^3\Sigma$ and $2^3\Pi$ states, there is only either a smaller decease or an increase in the deviation when going from order three to five. However, all fifth-order errors are smaller than 0.004 Hartree. To obtain a deviation of less than one milli-Hartree, it is typically required to go to order six and for a few roots to order eight.

The low-order corrections to the ground and to the excited states exhibit a difference: Whereas adding an even order to the ground state energy leads to an improved accuracy, it is the addition of odd order corrections that lead to improvements of the excitation energies.

With respect to the diagnostic $|\mathbf{R}_{xS}^{(2)}|$, its largest value, 0.36, occurs for the slowly convergent $2^1\Sigma$ state, which also has the largest third-order error, 0.007 Hartree. However, for the $3^3\Pi$ state, the diagnostic has a value of 0.30 and the CPS(D) series is well-convergent. For diagnostic values in the range 0.30–0.35, it is therefore not possible to directly link the size of the diagnostic with the accuracy of the low-order results.

2. Calculations on HF at 1.5R_e

We next consider the hydrogen fluoride molecule at the stretched inter-nuclear distance of 1.5R_e, for which the results for the CPS(D) calculations on the ground and excited states are given in Table II. The table uses the same template as Table I. With the exceptions of the excitation energies to the $3^1\Sigma$ and $1^3\Sigma$ states, all corrections to the excitation energies are negative. The sizes of the doubles corrections to the excitation energies are, in general, in the numerical range of 0.01-0.09 Hartree. With respect to the mapping between the parent and target states, the parent states $3^1\Sigma$, $2^3\Sigma$, and $3^3\Sigma$ are not mapped to the target states with the same position in the energy spectrum, and the CPS(D) perturbation expansion will therefore diverge for the excitation energies of these states. It is furthermore seen from the table that the perturbation expansions

TABLE II. Convergence of the CPS(D) ground state and excitation energies for hydrogen fluoride at 1.5R_e. Energies, corrections, and errors in a.u. See text for details.

State	$X^1\Sigma$	$1^1\Sigma$	$2^1\Sigma$	$3^1\Sigma$	$1^3\Sigma$	$2^3\Sigma$	$3^3\Sigma$
Parent energy	−99.922689	0.3713	0.5247	0.6134	0.1514	0.5013	0.5262
Target energy	−100.171773	0.3566	0.5066	0.6301	0.2041	0.4983	0.4714
Target root	0	1	2	5	1	3	2
$\vert\mathbf{R}_{xS}^{(2)}\vert$	...	0.09	0.19	0.54	0.05	0.31	0.36
Correction	−0.249084	−0.0147	−0.0181	0.0167	0.0527	−0.0030	−0.0548
				Errors for various orders			
Order 2	0.0024	−0.0034	−0.0229	−0.0473	0.0017	−0.0290	−0.0300
Order 3	0.0069	0.0048	0.0068	−0.0239	−0.0010	0.0009	−0.0001
Order 4	−0.0022	−0.0022	−0.0054	−0.0496	−0.0007	−0.0086	−0.0029
Order 5	0.0018	0.0024	0.0043	−0.0239	−0.0003	−0.0014	0.0059
Error <0.004(0.001) at order	4(6)	4(6)	7(−)	−(−)	2(3)	0(3)	3(3)
Convergent?	Yes	Yes	No	No	Yes	No	No
State	$1^1\Pi$	$2^1\Pi$	$1^3\Pi$	$2^3\Pi$	$1^1\Delta$	$1^3\Delta$	
Parent exc. Energy	0.2303	0.5077	0.1946	0.5007	0.5661	0.5481	
Target exc. Energy	0.1924	0.4212	0.1767	0.4187	0.4986	0.4881	
Target root	1	2	1	2	1	1	
$\vert\mathbf{R}_{xS}^{(2)}\vert$	...	0.13	0.44	0.12	0.59	0.18	0.16
Correction	−0.0379	−0.0865	−0.0179	−0.0820	−0.0675	−0.0600	
				Errors for various orders			
Order 2	−0.0068	−0.0756	−0.0075	−0.0671	−0.0444	−0.0389	
Order 3	0.0033	0.0044	0.0023	0.0051	−0.0029	−0.0035	
Order 4	−0.0062	−0.0041	−0.0055	−0.0163	−0.0037	−0.0045	
Order 5	0.0027	0.0066	0.0020	0.0114	0.0038	0.0031	
Error <0.004(0.001) at order	3(8)	8(13)	3(8)	10(−)	3(8)	3(7)	
Convergent?	Yes	No	Yes	No	Yes	Yes	

for the second states of $^1\Sigma$, $^3\Sigma$, $^1\Pi$, and $^3\Pi$ symmetry are divergent. The second-order correction overshoots the total correction for all states except the $1^1\Sigma$ state. When the third-order corrections are included, the errors are about 10% for the Π and Δ-states, whereas the errors are larger for a number of Σ states. A noticeably inaccurate result is obtained for the $3^1\Sigma$ state, where the third-order error of −0.0239 Hartree is larger than the zeroth-order error. However, it should be noted that the diagnostic for this state is 0.54, which clearly shows that the zeroth-order excitation vector is not a good approximation to the corresponding excitation vector in the CCSD space. With the exception of the excitation energy to the $3^1\Sigma$ state, the third-order errors at the equilibrium and stretched geometries are comparable. The fourth-order energies overshoot the corrections to the excitation energies also for the stretched geometry. The fifth-order corrections give errors that, in general, are slightly larger than the corresponding corrections at the equilibrium geometry.

With respect to the diagnostic $|\mathbf{R}_{xS}^{(2)}|$, the $3^1\Sigma$ state has the above mentioned value of 0.54, which leads to a very large third-order error of −0.024 Hartree. However, for the $1^1\Delta$ state, the $|\mathbf{R}_{xS}^{(2)}|$ diagnostic is 0.59 and thus of similar size, but the third-order error of −0.0029 Hartree is small. It is thus not possible to link directly the accuracy of the low-order corrections to the value of the diagnostic. However, the trend is clear: for increasing diagnostic values exceeding 0.3, larger errors become more frequent.

3. Calculations on CH_2

For the CH_2 molecule, the lowest closed shell determinant is used as the reference state for the CC and CP calculations, so the excitation energies to the ground state $^1B_1$ will be negative. The CP and CC results are given in Table III. With a few exceptions, the corrections are negative and have typical values in the range of 0.01–0.03 Hartree. Comparing first the energetic order of the parent and target states, it is observed that these disagree for all $^1A_1$ states and

TABLE III. Convergence of the CPS(D) ground state and excitation energies for CH_2. Energies, corrections, and errors in a.u. See text for details.

State	X^1A_1	1^1A_1	2^1A_1	3^1A_1	1^1B_1	2^1B_1	1^1B_2	2^1B_2	1^1A_2	2^1A_2
Parent energy	−38.884374	0.2616	0.3414	0.3883	0.0604	0.3303	0.3049	0.3703	0.2193	0.4979
Target energy	−39.027619	0.2433	0.3277	0.3719	0.0637	0.3130	0.2899	0.3556	0.2105	0.4635
Target root	0	2	3	4	1	2	1	3	1	3
$\|\mathbf{R}_{xS}^{(2)}\|$	…	0.06	0.08	0.05	0.02	0.03	0.07	0.05	0.02	0.13
Correction	−0.143245	−0.0183	−0.0137	−0.0164	0.0033	−0.0173	−0.0150	−0.0147	−0.0088	−0.0344
					Errors for various orders					
Order 2	0.0278	−0.0053	−0.0069	−0.0056	−0.0040	−0.0038	−0.0066	−0.0075	0.0015	0.0142
Order 3	0.0068	−0.0056	−0.0063	−0.0053	−0.0032	−0.0045	−0.0058	−0.0077	−0.0014	0.0103
Order 4	0.0025	−0.0033	−0.0037	−0.0024	−0.0022	−0.0017	−0.0030	−0.0049	−0.0015	0.0072
Order 5	0.0014	−0.0016	−0.0025	−0.0012	−0.0014	−0.0004	−0.0013	−0.0034	−0.0012	0.0050
Error <0.004(0.001) at order	5(6)	4(6)	4(−)	4(6)	2(6)	2(5)	4 (6)	5(−)	2(6)	−(−)
Convergent?	Yes	No	No	No	Yes	Yes	Yes	No	Yes	No
State	1^3A_1	2^3A_1	3^3A_1	1^3B_1	2^3B_1	3^3B_1	1^3B_2	2^3B_2	1^3A_2	2^3A_2
Parent exc. Energy	0.2470	0.2987	0.3757	−0.0181	0.3227	0.4243	0.2911	0.3340	0.1720	0.4881
Target exc. Energy	0.2354	0.3018	0.3638	−0.0015	0.3090	0.4045	0.2822	0.3327	0.1769	0.4704
Target root	1	2	3	1	2	4	1	3	1	4
$\|\mathbf{R}_{xS}^{(2)}\|$	0.12	0.12	0.17	0.02	0.04	0.08	0.25	0.23	0.02	0.13
Correction	−0.0116	0.0031	−0.0119	0.0166	−0.0137	−0.0198	−0.0089	−0.0013	0.0049	−0.0177
					Errors for various orders					
Order 2	−0.0032	−0.0043	−0.0054	−0.0043	−0.0043	0.0194	−0.0020	−0.0053	0.0002	0.0034
Order 3	−0.0040	−0.0040	−0.0045	−0.0018	−0.0050	0.0149	−0.0013	−0.0057	−0.0007	0.0002
Order 4	−0.0032	−0.0026	−0.0022	−0.0012	−0.0025	0.0108	−0.0030	−0.0028	−0.0010	−0.0002
Order 5	−0.0018	−0.0014	−0.0010	−0.0008	−0.0011	0.0081	−0.0017	−0.0018	−0.0010	0.0003
Error <0.004(0.001) at order	3(6)	0(6)	4(5)	3(5)	6	…	2(6)	0(−)	2(3)	2(3)
Convergent?	Yes	Yes	Yes?	Yes	Yes	No	Yes	No	Yes	No

the 2^1B_2, 2^1A_2, 3^3B_1, 2^3B_2, and 2^3A_2 states. The CPS(D) perturbation expansions will therefore diverge for these states, whereas the expansions are convergent for all the remaining excitation energies.

From the table, it is first noted that the second-order energy overshoots the correlation contributions for most of the excitation energies by 20%-50%. There are a few states where the second-order energies do not overestimate the full correction, but there does not seem to be any relation between symmetry, spin and position of the state and overshooting or undershooting of the full correction by the second-order energy. The third-order energies provide, in general, either no or very limited improvements of the energy. The errors of the fifth-order energies are smaller and are, in general, reduced by at least a factor of two compared to the second-order errors.

With respect to the stated thresholds, it is seen that second to fourth order is required to obtain an accuracy of 0.004 Hartree, whereas the corrections through sixth order typically are required to obtain an error of at most 0.001 Hartree. For many of the divergent expansions, these target accuracies are not obtained for any order.

The above results may seem somewhat unfavorable for the CPS(D) method, but it should be reiterated that the methylene molecule with the chosen reference state has a very complicated set of excited states, where many of the excited states are doubly excited with respect to the chosen reference state. To describe such states, a parent excitation space containing double excitations and a target excitation space containing triple excitations are needed. Note, however, that these complications are not, in general, caught by the diagnostic measure $|\mathbf{R}_{xS}^{(2)}|$, as many of the divergent states have diagnostics smaller than 0.1.

4. Calculations on F^-

For our final CPS(D) example, the fluorine anion, data are given in Table IV. We restrict ourselves to a single excitation for each spin and symmetry combination, as the other excitations in the aug-cc-pVDZ basis excite electrons from the 2s orbital and have large excitation energies. The table shows that all energy corrections are negative and in the range between −0.09 and −0.01 Hartree. The energy ordering of the states is identical in the parent and target spaces, and all expansions are convergent.

From the table, it is noted that the second order corrections overestimate the size of the correction to the excitation energies by a factor of about two, so the second-order excitation energies are, in general, not more accurate than the zeroth-order excitation energies. For the third- and higher-order corrections, the 1^1S state behaves in a different manner than the remaining five states. For these five states, the third-order correction results in significant reductions of the errors, leading to positive errors in the range between 0.0013 and 0.0039 Hartree, i.e., below our higher threshold. For these states, the fourth- and fifth-order contributions do not give a general improvement. For the 1^1S state, the third-order error is 0.03 Hartree, which is reduced in fifth order by a factor of about ten, giving an error of −0.0025 Hartree, corresponding to about 3% of the initial error.

With respect to the considered thresholds, it is seen from the table that up to order 16 is required to get the excitation energies with an accuracy of 0.001 Hartree, whereas the third order results are sufficient to obtain the excitation energies with an accuracy of 0.004 Hartree or better for all states except 1^1S. Thus, the perturbation expansions for the excitation energies are slowly convergent. This is not surprising as orders 8 and 23 are required to get the ground state energy correct within 0.004 and 0.001 Hartree, respectively.

The diagnostic $|\mathbf{R}_{xS}^{(2)}|$ is at most 0.05 for all the considered excitations, so it does not provide warnings about the slow convergence of the expansions. Nor is the diagnostic capable of predicting the very large errors in third order for the 1^1S state. However, considering that the second and third order excitation energy corrections, −0.2150 and 0.1538 Hartree, respectively, both are numerically large compared to the excitation energy correction of −0.0900 Hartree, the third-order energy correction is not expected to give an

TABLE IV. Convergence of the CPS(D) ground state and excitation energies for F^-. Energies, corrections, and errors in a.u. See text for details.

State	X^1S	1^1S	1^3S	1^1P	1^3P	1^1D	1^3D
Parent energy	−99.428282	0.5711	0.3303	0.3950	0.3598	0.3894	0.3658
Target energy	−99.662690	0.4801	0.3134	0.3465	0.3236	0.3548	0.3415
Target root	0	1	1	1	1	1	1
$\lvert\mathbf{R}_{xS}^{(2)}\rvert$	...	0.03	0.05	0.02	0.03	0.04	0.04
Correction	−0.234408	−0.0910	−0.0169	−0.0485	−0.0362	−0.0346	−0.0243
				Errors for various orders			
Order 2	−0.0033	−0.1239	−0.0191	−0.0335	−0.0278	−0.0303	−0.0254
Order 3	0.0060	0.0299	0.0015	0.0039	0.0035	0.0024	0.0013
Order 4	−0.0043	0.0077	−0.0036	−0.0047	−0.0051	−0.0031	−0.0034
Order 5	0.0028	−0.0025	0.0023	0.0053	0.0044	0.0035	0.0029
Error <0.004(0.001) at order	8(23)	5(15)	3(8)	3(16)	3(14)	3(10)	3(9)
Convergent?	Yes	Yes	Yes	Yes	Yes	Yes	Yes

accurate excitation energy. From the first and second order doubles correction to $\mathbf{R}_x^{(1)}$, $|\mathbf{R}_{xD}^{(1)}| = 0.496$, $|\mathbf{R}_{xD}^{(2)}| = 0.248$, it is clear that the 1^1S excitation is not single-replacement dominated and that the third-order excitation energy for this state therefore cannot be trusted. For comparison, for the excitation to the 1^3S state, the norm of the lowest order doubles correction is $|\mathbf{R}_{xD}^{(1)}| = 0.249$ and $|\mathbf{R}_{xD}^{(2)}| = 0.044$.

B. Excitation energies from the CPSD(T) expansion

1. Calculations on HF at R_e

The results of the CPSD(T) calculations for the ground and excited state energies of hydrogen fluoride at the equilibrium geometry are given in Table V. The triples corrections to the excitation energies are positive and are in the range of 0.0028-0.0063 Hartree, which is comparable to the size of the triples correction to the ground state energy, −0.0043 Hartree. The ordering of the states in the parent and target spaces is identical, and all perturbation calculations are found to converge.

The second-order energy correction underestimates in most cases the full triples corrections to the excitation energy and gives typically between 85% and 95% of the full triples correlation. It is noted that second order is sufficient to obtain errors of less than 0.001 Hartree for all excitation energies. The third-order corrections reduce, in general, the size of the triples correction and lead therefore to slightly larger errors. The fourth order corrections increase the size of the corrections and give rather accurate approximations to the full triples correction—the largest errors are now 0.00010 Hartree, and 97% or more of the full triples corrections are recovered at this order. The addition of the fifth-order contributions, in general, does not lead to an improved accuracy. Whereas the odd-order corrections lead to improvements of the ground state energy, it is the even-order corrections that lead to the major improvements in the excitation energies.

2. Calculations on HF at $1.5R_e$

We next consider the application of the CPSD(T) method to the more demanding case of the hydrogen fluoride molecule at the stretched bond length $1.5\mathrm{R}_e$, for which the results are given in

TABLE V. Convergence of the CPSD(T) ground state and excitation energies for hydrogen fluoride at R_e. Energies, corrections, and errors in a.u. See text for details.

State	$X^1\Sigma$	$1^1\Sigma$	$2^1\Sigma$	$1^3\Sigma$	$2^3\Sigma$	$3^3\Sigma$
Parent energy	−100.259434	0.5321	0.5985	0.4936	0.5240	0.6429
Target energy	−100.263767	0.5349	0.6014	0.4971	0.5303	0.6468
Target state	0	1	2	1	2	3
Correction	−0.0043	0.0028	0.0029	0.0035	0.0063	0.0039
Errors for various orders						
Order 2	0.00433	−0.00036	0.00065	−0.00094	−0.00086	−0.00046
Order 3	0.00034	−0.00042	−0.00043	−0.00059	−0.00092	−0.00054
Order 4	0.00029	−0.00003	0.00009	−0.00010	−0.00010	−0.00002
Order 5	0.00001	−0.00003	−0.00003	−0.00008	−0.00014	−0.00006
Error <0.004(0.001) at order	3(3)	0(2)	0(2)	0(2)	2(2)	0(2)
Convergent?	Yes	Yes	Yes	Yes	Yes	Yes
State	$1^1\Pi$	$2^1\Pi$	$1^3\Pi$	$2^3\Pi$	$1^1\Delta$	$1^3\Delta$
Parent exc. Energy	0.3788	0.5171	0.3638	0.5095	0.5525	0.5417
Target exc. Energy	0.3823	0.5209	0.3679	0.5136	0.5572	0.5472
Target state	1	2	1	2	1	1
Correction	0.0035	0.0038	0.0041	0.0041	0.0047	0.0055
Errors for various orders						
Order 2	−0.00026	−0.00022	−0.00044	−0.00020	−0.00039	−0.00058
Order 3	−0.00047	−0.00049	−0.00057	−0.00050	−0.00056	−0.00075
Order 4	−0.00005	−0.00003	−0.00005	−0.00001	−0.00005	−0.00005
Order 5	−0.00002	−0.00002	−0.00005	−0.00002	−0.00004	−0.00010
Error <0.004(0.001) at order	0(2)	0(2)	0(2)	2(2)	2(2)	2(2)
Convergent?	Yes	Yes	Yes	Yes	Yes	Yes

Table VI. It is seen that the triples correction to the excitation energies is in the range from −0.006 to 0.005 Hartree and may thus increase as well as decrease the total excitation energy.

From the table, it is seen that the second-order energies give very inaccurate approximation to the full triples corrections. For the excitation energies that have the largest triples corrections, the second-order correction does improve the accuracy and all excitation energies are within the 0.004 Hartree threshold at second order. The third-order corrections give significant improvements of the excitation energies, and the excitation energies are now within the smaller threshold of 0.001 Hartree for all states except the $2^3\Sigma$ state. The error of the latter state in third order is 0.00103 Hartree and is thus only marginally larger than the threshold. At fifth order, the largest errors are about 0.0004 Hartree, and more than 90% of the triples correction to the excitation energies is recovered.

3. Calculations on CH_2

The application of the CPSD(T) method to the methylene molecule allows us to test the performance of this method for excited parent states that are doubly excited with respect to the chosen reference state. The results are given in Table VII. In the entry in the table that specifies the target state, a (D) has been added for the six target states that are dominated by double excitations. The triples correction to the reference state energy is −0.004 Hartree.

For excited states that are dominated by double excitations, the contributions of the triples corrections to the excitation energy are large, typically of the order of −0.06 Hartree, and are thus more than an order of magnitude larger than the triples contribution to the reference state energy. For single-replacement dominated excited states, the triples contributions to the excitation energies are much smaller and are in the range of −0.001–0.002 Hartree.

The large reductions in the excitation energies for the states dominated by double excitations lead to several crossings in the energy order when going from the parent to the target excitation level. The states thus change position for the spin and point-group symmetries of $^1B_2$ and $^3B_2$. For the spin and symmetry $^1A_1$, the doubly excited state is the lowest state already at the parent level, so the reduction in this excitation energy does not lead to any change of the energy ordering. The perturbation expansion is divergent for

TABLE VI. Convergence of the CPSD(T) ground state and excitation energies for hydrogen fluoride at $1.5R_e$. Energies, corrections, and errors in a.u. See text for details.

State	$X^1\Sigma$	$1^1\Sigma$	$2^1\Sigma$	$1^3\Sigma$	$2^3\Sigma$	$3^3\Sigma$
Parent energy	−100.171773	0.3566	0.5065	0.2041	0.4714	0.4983
Target energy	−100.178960	0.3505	0.5071	0.2078	0.4761	0.5014
Target state	0	1	2	1	2	3
Correction	−0.007187	−0.0061	0.0006	0.0037	0.0047	0.0031
Errors for various orders						
Order 2	0.0072	−0.00171	−0.00154	−0.00423	−0.00189	−0.00204
Order 3	0.0007	0.00033	−0.00015	−0.00078	−0.00103	−0.00076
Order 4	0.0007	0.00001	−0.00007	−0.00057	−0.00031	−0.00007
Order 5	0.0000	0.00008	0.00012	−0.00008	−0.00020	−0.00013
Error <0.004(0.001) at order	2(3)	2(3)	0(4)	0(3)	2(3)	0(3)
Convergent?	Yes	Yes	Yes	Yes	Yes	Yes
State	$1^1\Pi$	$2^1\Pi$	$1^3\Pi$	$2^3\Pi$	$1^1\Delta$	$1^3\Delta$
Parent exc. Energy	0.1924	0.4212	0.1766	0.4187	0.4986	0.4881
Target exc. Energy	0.1882	0.4221	0.1746	0.4198	0.5007	0.4918
Target state	1	2	1	2	1	1
Correction	−0.0042	0.0009	−0.0020	0.0011	0.0021	0.0037
Errors for various orders						
Order 2	−0.00135	−0.00066	−0.00160	−0.00046	−0.00130	−0.00153
Order 3	0.00034	0.00021	0.00014	0.00024	−0.00021	−0.00069
Order 4	0.00002	−0.00034	0.00004	−0.00019	−0.00032	−0.00026
Order 5	0.00015	0.00038	0.00013	0.00037	0.00013	−0.00007
Error <0.004(0.001) at order	0(3)	0(0)	0(3)	0(0)	0(3)	0(3)
Convergent?	Yes	Yes	Yes	Yes	Yes	Yes

TABLE VII. Convergence of the CPSD(T) ground state and excitation energies for CH_2. Energies, corrections, and errors in a.u. See text for details. Note: A target state marked by D is a doubly excited state.

State	X^1A_1	1^1A_1	2^1A_1	3^1A_1	1^1B_1	2^1B_1	1^1B_2	2^1B_2	1^1A_2	2^1A_2
Parent energy	−39.027619	0.2219	0.2433	0.3276	0.0637	0.3130	0.2899	0.3473	0.2105	0.4404
Target energy	−39.031918	0.1681	0.2431	0.3269	0.0639	0.3118	0.2923	0.2846	0.2099	0.3777
Target state	0	1(D)	2	3	1	2	2	1(D)	1	2(D)
Correction	−0.004299	−0.0538	−0.0002	−0.0007	0.0002	−0.0012	0.0024	−0.0627	−0.0006	−0.0627
Errors for various orders										
Order 2	0.00430	0.01511	−0.00205	−0.00161	−0.00211	−0.00096	−0.00417	0.02965	−0.00167	0.01905
Order 3	0.00112	0.00630	−0.00057	−0.00026	−0.00052	0.00043	−0.00259	0.02163	−0.00025	0.00845
Order 4	0.00052	0.00019	0.00006	−0.00010	−0.00029	0.00034	−0.00252	−0.02102	−0.00016	0.00153
Order 5	0.00021	0.00030	0.00045	0.00005	−0.00012	0.00034	−0.00245	−0.04611	−0.00005	−0.00128
Error <0.004(0.001) at order	2(3)	4(5)	0(0)	0(0)	0(0)	0(0)	0(−)	−(−)	0(0)	4(6)
Convergent?	Yes	No	No	Yes	Yes	Yes	No	No	Yes	No
State	1^3A_1	2^3A_1	3^3A_1	1^3B_1	2^3B_1	3^3B_1	1^3B_2	2^3B_2	1^3A_2	2^3A_2
Parent exc. Energy	0.2354	0.3018	0.3638	−0.0015	0.3090	0.3891	0.2822	0.3040	0.1769	0.4356
Target exc. Energy	0.2356	0.3027	0.3633	−0.0004	0.3086	0.3259	0.2841	0.2391	0.1770	0.3722
Target state	1	2	3	1	2	3(D)	2	1(D)	1	2(D)
Correction	0.0002	0.0009	−0.0005	0.0011	−0.0004	−0.0632	0.0019	−0.0649	0.0001	−0.0634
Errors for various orders										
Order 2	−0.00191	−0.00215	−0.00148	−0.00233	−0.00120	0.01939	−0.00578	0.02505	−0.00188	0.01886
Order 3	−0.00035	−0.00043	−0.00005	−0.00068	0.00028	0.00815	−0.00487	0.01423	−0.00034	0.00770
Order 4	−0.00017	−0.00020	0.00003	−0.00037	0.00033	0.00155	−0.00887	0.01119	−0.00020	0.00254
Order 5	−0.00005	−0.00005	0.00010	−0.00017	0.00039	−0.00127	−0.01134	0.01051	−0.00007	0.00077
Error <0.004(0.001) at order	0(0)	0(0)	0(0)	0(0)	0(0)	5(−)	0(−)	−(−)	0(0)	4(5)
Convergent?	Yes	Yes	Yes	Yes	Yes	No	No	No	Yes	No

a number of states in addition to those changing position in the energy spectrum. In particular, the expansion is divergent for the two lowest ${}^1A_1$ states. We will return to an analysis of this divergence after we have discussed the accuracy of the perturbation expansions for the excitation energies.

Restricting the discussion to excitations dominated by double replacements, the second-order corrections give about 70% of the full correction for the four states that do not change position in the energy spectrum, 1^1A_1, 2^1A_2, 3^3B_1, and 2^3A_2, whereas 50%-60% of the full corrections is recovered for the two states that do change position. Increasing the order toward five leads to systematic improvements for the four states that do not change position, with the exception of the fifth-order correction for the 1^1A_1 state. Thus, at fifth order, the triple correction for the three states that do not change position recovers the full triples correction within 0.0013 Hartree, whereas the errors are up to 0.05 Hartree for the states that do change position.

With respect to the excitation energies to the single-excitation dominated states, the smallness of the corrections makes the lower-order corrections somewhat erratic. These excitation energies are within 0.002 Hartree of the full correction already at zeroth order for all such states except for the 1^1B_2 and 1^3B_2 states. The perturbation expansions for the latter two states are diverging, and the errors are within 0.004 Hartree at zeroth order but do not reach the lower threshold of 0.001 Hartree at any order.

We will now return to the divergence of the two lowest ${}^1A_1$ excited states. This divergence may be understood by observing that the large reduction in the energy of the first excited A_1 state, when going from the parent to the target space, implies that the energy of 1^1A_1 will rise significantly for negative values of the perturbation strength. By contrast, the excitation energy of the second excited state is nearly constant when going from the parent to the target space, which suggests that the excitation energy to this state is nearly constant for negative values of the perturbation strength. To quantify this, we assume that the excitation energies are simple linear functions of the perturbation parameter z. This linear approximation has been shown to be accurate for standard Møller-Plesset energies.[55,59] The parent excitation energies are obtained for $z = 0$, and the target excitation energies are obtained for $z = 1$. From the data in Table VII, we then obtain for the excitation energies as a function of z,

$$\begin{aligned} \omega(1^1A_1) &= 0.2219 - 0.0538z, \\ \omega(2^1A_1) &= 0.2433 - 0.0002z, \\ \omega(3^1A_1) &= 0.3276 - 0.0007z. \end{aligned} \tag{106}$$

These linearized excitation energies are plotted in Fig. 1 for $z \in [-1, 1]$. It is seen that the lines for the two lowest excitation energies cross around $z = -0.4$, whereas the third excitation energy is so large that no crossing is observed for this excitation energy. The perturbation expansions of the excitation energies for the two lowest excitations are thus divergent due to a degeneracy for negative perturbation strengths, much like the back-door intruders observed for the standard Møller-Plesset perturbation expansion,[55,59] whereas the third excitation energy is predicted to converge. These predictions are in agreement with the results of Table VII. The divergence of the doubly excited states ${}^1A_2$ and ${}^3A_2$ is similarly explained by the crossings, at negative perturbation strengths, of these states with singly excited states that have higher parent and target energies. These higher lying states are not included in the table, but they have been identified.

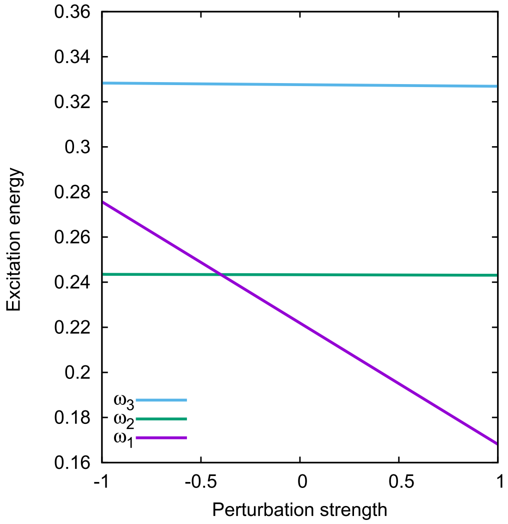

FIG. 1. Linearized excitation energies as functions of a real perturbation parameter for the excitation energies to the lowest three ${}^1A_1$ states of CH_2.

For the calculations of the methylene molecule, we conclude that double excited states represent a challenge to the CPSD(T) method: their large change in the excitation energy when going from the parent to the target state may lead to front- as well as back-door intruders. In the present calculations, the presence of the front-door intruders for the excitations to states of symmetry B_2 impairs the accuracy of the low-order results, whereas the back-door intruders do not impair the accuracy of the low-order results.

4. Calculations on F^-

The final test case for the the CPSD(T) method is the fluorine anion, for which the results are given in Table VIII. From the table, it is noted that the addition of triple excitations increases the excitation energies by up to 0.005 Hartree for all states except the 1^1S state, where the triples correction reduces the excitation energy by 0.01 Hartree. For comparison, the addition of triple excitations reduces the reference energy by 0.006 Hartree. It is also noted that all states keep their energy order when going from parent to target energies and that all expansions are convergent.

The corrections to the 1^1P and 1^1D states are so small that they are excluded from the following discussion. The second-order corrections underestimate in most cases the full triples corrections and recover 60%-100% of these. The third-order energies reduce the errors of the most inaccurate second-order corrections, and the errors are now 0.002 Hartree or less. When the fourth-order corrections are included, one obtains significant improvements of the excitation energies, whereas the fifth-order corrections improve the accuracy for three of the excitations.

The total corrections from the triples excitations are so small for two of the excitation energies that already the zeroth-order

TABLE VIII. Convergence of the CPSD(T) ground state and excitation energies for F^-. Energies, corrections, and errors in a.u. See text for details.

State	X^1S	1^1S	1^3S	1^1P	1^3P	1^1D	1^3D
Parent energy	−99.662 690	0.4801	0.3134	0.3465	0.3236	0.3548	0.3415
Target energy	−99.668 972	0.4699	0.3189	0.3468	0.3265	0.3557	0.3445
Target state	0	1	1	1	1	1	1
Correction	−0.006282	−0.01014	0.00550	0.00029	0.00291	0.00091	0.00307
			Errors for various orders				
Order 2	0.00628	0.00403	−0.00118	0.00052	0.00003	−0.00029	−0.00057
Order 3	0.00025	0.00202	−0.00092	0.00020	−0.00040	0.00024	−0.00031
Order 4	0.00089	−0.00048	−0.00019	0.00002	0.00005	−0.00022	−0.00012
Order 5	−0.00017	0.00124	−0.00013	0.00018	0.00000	0.00029	0.00008
Error <0.004(0.001) at order	3(3)	2(6)	2(2)	0(0)	0(2)	0(0)	0(2)
Convergent?	Yes	Yes	Yes	Yes	Yes	Yes	Yes

excitation energies are within the tighter error bound of 0.001 Hartree. For two of the remaining states, 1^3S and 1^3P, the tight error bound is obtained at second order, whereas this accuracy is obtained only at sixth order for the excitation energy to the 1^1S state.

C. The CPSDT(Q) method applied to the excitation energies of methylene

In Subsection IV B 3, it was noted that the CPSD(T) expansion of excitation energies for CH_2 diverged for several states due to the presence of states dominated by double excitations. It is of interest to investigate whether the next level of CP methods, CPSDT(Q), is sufficient to eliminate these divergence. For the A_1 and B_2 symmetries, where the presence of crossings led to divergence of the lowest excited states, we have thus performed calculations using the CPSDT(Q) method, and the relevant results are presented in Table IX. It is noted that all states retain the energy position when going from the parent to the target state and that all expansions converge.

Reflecting the higher accuracy of the CPSDT(Q) method, the thresholds in the table have been reduced to 0.00012 and 0.00048 Hartree. From the table, it is seen that the total quadruples correction is up to 0.0026 Hartree for excitations to doubly excited states. For excitations to singly excited states, the zeroth-order errors are within the looser threshold, and within the tighter threshold, at second or third order.

Restricting the discussion to the doubly excited states, it is seen that the second-order corrections give between 60% and 70% of the full corrections. As higher orders are added, the deviations decrease monotonically. At fifth order, all errors are less than 0.00012 Hartree and about 95% of the full quadruples corrections has been recovered. With respect to the chosen thresholds, it is seen that the 0.00012 Hartree deviation is obtained for the 1^1A_1 and 1^3B_2 states at fifth order, whereas this accuracy is obtained for the 1^1B_2 state at fourth order. The higher threshold of 0.00048 Hartree is obtained at second or third order for the three doubly excited states.

D. Summary of numerical calculations

For a single determinant reference state, the excited states may be divided into single and double replacement dominated excitations. For a closed shell single determinant reference state, the excitation energies of the CCSD response eigenvalue equation give good and robust approximations for single replacement dominated excitation energies. The CPS(D) excitation energy series that has the CCSD excitation energies as target excitation energies may therefore be used to obtain a good description of the single replacement dominated excitations. Double replacement dominated excitations cannot be described by the CPS(D) series as the CCSD target excitation energies cannot properly describe double replacement excitations. The description of double replacement excitations requires that parent excitation space contains double excitations and that the target excitation space contains at least triple excitations, and hence that the CPSD(T) or a higher correlation model is used.

We have carried out calculations of excitation energies using CP models for hydrogen fluoride at R_e and $1.5R_e$, and for F^-. These systems have a closed shell single determinant reference ground state. For HF at $1.5R_e$, the ground state has a minor multiconfiguration component. The lowest excitation energies for these systems are single replacement dominated and the CPS(D) model therefore can be used to obtain a good description of these excitation energies. We have explicitly reported the CPS(D) excitation energies through fifth order for these systems. The first order corrections vanish and the second order model, which is identical to the CIS(D) model, gives errors in the excitation energies in the range of 0.02-0.07 Hartree (0.54-1.90 eV). At third order, these errors are, in general, reduced by a factor of 4–10. Two outliers have been observed for the third order errors, the $3^1\Sigma$ state for hydrogen fluoride at $1.5R_e$ that has an error of −0.024 Hartree (−0.653 eV), and the 1^1S state for F^- that has an error of 0.030 Hartree (0.816 eV). For the $3^1\Sigma$ state of hydrogen fluoride, the $|\mathbf{R}_{xS}^{(2)}|$ diagnostic gives a warning that this excitation is not single replacement dominated and therefore cannot be trusted. For the 1^1S state of F^-, it is the size of the doubles component of the excitation eigenvector in the

TABLE IX. Convergence of the CPSDT(Q) ground state and excitation energies for CH_2. Energies, corrections, and errors in a.u. See text for details.

State	X^1A_1	1^1A	2^1A	3^1A	1^1B_2	2^1B_2
Parent energy	−39.031918	0.16809	0.24308	0.32686	0.28464	0.29229
Target energy	−39.032130	0.16579	0.24328	0.32700	0.28335	0.29210
Target state	0	1(D)	2	3	1(D)	2
Correction	−0.000212	−0.00230	0.00020	0.00014	−0.00129	−0.00019
			Errors for various orders			
Order 2	0.00021	0.00084	−0.00011	−0.00008	0.00042	−0.00004
Order 3	0.00009	0.00037	−0.00006	−0.00005	0.00020	−0.00008
Order 4	0.00003	0.00017	−0.00002	−0.00001	0.00009	−0.00003
Order 5	0.00001	0.00008	−0.00001	−0.00001	0.00003	−0.00001
Error <0.00048(0.00012) at order	1(3)	3(5)	0(2)	0(2)	2(4)	0(2)
Convergent?	Yes	Yes	Yes	Yes	Yes	Yes
State	1^3A	2^3A	3^3A	1^3B_2	2^3B_2	3^3B_2
Parent energy	0.23561	0.30268	0.36334	0.23913	0.28411	0.33210
Target energy	0.23582	0.30284	0.36351	0.23649	0.28426	0.33224
Target state	1	2	3	1(D)	2	3
Correction	0.00021	0.00016	0.00017	−0.00264	0.00015	0.00014
			Errors for various orders			
Order 2	−0.00012	−0.00013	−0.00009	0.00086	−0.00010	−0.00011
Order 3	−0.00006	−0.00006	−0.00005	0.00036	−0.00006	−0.00005
Order 4	−0.00002	−0.00002	−0.00001	0.00016	−0.00002	−0.00002
Order 5	−0.00001	−0.00001	−0.00001	0.00007	−0.00001	−0.00001
Error <0.00048(0.00012) at order	0(3)	0(3)	0(3)	3(5)	0(2)	0(2)
Convergent?	Yes	Yes	Yes	Yes	Yes	Yes

two lowest orders, $|\mathbf{R}_{xD}^{(1)}| = 0.496, |\mathbf{R}_{xD}^{(2)}| = 0.248$, which is so large that the third order excitation energy cannot be trusted. Excluding the two outliers, the errors of the third order excitation energies are all smaller than 0.0074 Hartree (0.2014 eV) and typical errors are below 0.004 Hartree (0.109 eV). This is also the case for the CPS(D) excitation energy series, which diverges for hydrogen fluoride at $1.5R_e$. The third order errors for hydrogen fluoride at R_e and $1.5R_e$ are, in general, of comparable size. If we restrict the diagnostic $|\mathbf{R}_{xS}^{(2)}|$ to be smaller than 0.3, the errors in the third order excitation energies are, in general, smaller than 0.004 Hartree (0.109 eV). The fourth order excitation energy correction does not improve the results, and in fifth order, some improvements are obtained. In Paper III,[40] a larger series of benchmark calculations is carried out of CPS(D-2) and CPS(D-3) excitation energies to investigate whether the accuracy that is obtained here for the test systems can generalized and the accuracy we have obtained for the CPS(D-2) and CPS(D-3) calculations is also obtained in the benchmark calculations.

For the CPSD(T) model, the lowest non vanishing second order correction gives typically about 85%-95% of the triples corrections for hydrogen fluoride at R_e, whereas at $1.5R_e$, where the reference state has a minor multi-configuration component, the third order correction is required to obtain this accuracy. The third order excitation energies all have an error that is smaller than 0.001 Hartree (0.027 eV).

We have also carried out calculations of CP excitation energies for CH_2, for which the single determinant reference state is chosen as a closed shell excited state and the ground state and many of the excited states are doubly excited compared to the closed shell reference state. The CH_2 state excitation energy spectrum therefore serves as a good test case for probing the accuracy obtainable with CP models for double replacement dominant excitations. Triple excitations are required in order to obtain a proper description of a double replacement excitation. Thus, even though it looks like the second order CPS(D) corrections in Table III give a reasonable description of the excitation spectrum, this is actually not the case because the target excitation energies are CCSD excitation energies that cannot properly describe double replacement dominant excitations. For the CPSD(T) model, we obtain a proper description of the double replacement dominant excitations when the position of the excitation is the same in the parent and target excitation space, whereas for excitations that shift position the CPSD(T) series diverge lowering also the accuracy obtainable for the lower order corrections. For these excitations, it is necessary to use the lower order corrections of the CPSDT(Q) model in order to achieve a good description of the excitation energies.

V. SUMMARY AND CONCLUSION

We have developed CP perturbation series for excitation energy corrections in orders of the CC parent state similarity transformed fluctuation potential, where the zeroth order term in the series is an excitation energy for the CC parent state response eigenvalue equation and where the series converge to an excitation energy of the CC target state response eigenvalue equation. CP perturbation series have also been derived for the energies of the excited states.

In CP theory, we have introduced a new generalized order concept in perturbation theory where internal relaxation in the parent excitation space is treated fully at zeroth order and hence it is removed from the perturbation calculation. For a CCS parent state, the singles cluster amplitudes vanish and the perturbation operator therefore becomes the standard fluctuation potential. Internal relaxation in the parent singles excitation space is not important compared to the effect of introducing a doubles auxiliary excitation space and CP and CCPT ground-state energy series therefore show similar local convergence. However, CP series may be determined for excitation energies with similar local convergence as for the ground-state energy series, whereas excitation energy series cannot be determined using CCPT. We have presented calculations for the CPS(D-n) model for excitation energies which show fast local convergence also for cases with close lying excited states where the CPS(D) excitation energy series diverge.

For a parent excitation space that contains a singles and doubles excitation space, the internal relaxation in the parent excitation space is large compared to the effect of introducing a triples excitation auxiliary space and the local convergence of the CP ground state energy series is greatly improved compared to CCPT ground-state energy series. The CP excitation energy series exhibit similar local convergence characteristic as for the CP ground state energy series. We have presented calculations for excitation energies for the CPSD(T-n) and CPSDT(Q-n) series which show a fast local convergence for the lower order corrections. Furthermore, the excitation energy series that are obtained for these excitation energy series are far less plagued by divergences than the CPS(D) excitation energy series.

CP excitation energy series may diverge for closely lying excited states. However, an important feature is that while the CP excitation energy series diverge, the divergence does not, in general, substantially affect the fast convergence of the lower-order correction in the CP excitation energy series. Furthermore, the divergence for closely lying excited states does not seem to affect substantially the convergence of the residual part of the excitation energy spectrum.

CP series may be determined for excitation energies and for total energies of the excited states. The total energy corrections for the excited states are size extensive and exhibit similar convergence patterns as for the ground state energy series. It therefore becomes interesting to examine potential energy surfaces that are obtained using lower order CP excited state energy corrections especially considering that these corrections can be obtained at a fraction of the cost required to calculate the excited state energies from full CC target state Jacobian response eigenvalue equation.

In a forthcoming publication, we will examine the global convergence of the excitation energy series for the CP models CPS(D), CPSD(T), and CPSDT(Q). We will examine the asymptotic convergence of the series that determines the convergence rate and the convergence patterns of the higher order terms in the series. Pilot calculations show that the asymptotic convergence of the CP excitation energy series effectively becomes a two state problem at higher orders.

Summarizing, we have developed an alternative way of solving the CC response eigenvalue equation in Eq. (8), where perturbative corrections to a CC parent state excitation energy targeting a CC target state excitation energy are determined. The excitation energy corrections are size-extensive at each order. In general, we only want to determine CC target state excitation energies to a precision where the excitation energy corrections are small compared to contributions that are not accounted for by the CC target state model. We therefore, in practice, need only to determine excitation energy corrections to low orders, thus reducing the computational effort for the determination of CC target state excitation energies to a small fraction of a conventional CC target state excitation energy calculation. Considering the fast local convergence, we have observed for the CP excitation energy series, it becomes computationally attractive to use low-order corrections in the CP series to obtain excitation energies of CC target state quality. In Paper III,[40] we have described an efficient implementation of the excitation energies for the CPS(D-n) series through third order and have carried out a series of benchmark calculations that demonstrate that excitation energies of CCSD quality are obtained with the CPS(D-3) model. The computational scaling of the lower-order corrections in the CPS(D-n) series has also been compared in Paper III,[40] with the scaling of a standard CCSD excitation energy calculation showing that a CPS(D-3) calculation can be carried out at a small fraction of the cost of a conventional CCSD excitation energy calculation. The efficient implementation of CPS(D-3) excitation energies, presented in Paper III,[40] has shown that the CPS(D-3) excitation energies can be determined for system sizes that are far beyond the ones that can be considered using a conventional CCSD excitation energy implementation. The derivation and the numerical results of this paper suggest that a similar behavior as for the CPS(D) series can be expected for efficient implementations of low order CP excitation energy corrections for CP models where the parent state also contains excitations higher than singles, e.g., the CPSD(T) series. We therefore expect that low-order excitation energy corrections in CP series soon will become state-of-the-art models for determining excitation energies of CP target state quality.

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