

Cluster perturbation theory. V. Theoretical foundation for cluster linear target states

Cite as: J. Chem. Phys. **150**, 134112 (2019); <https://doi.org/10.1063/1.5053627>

Submitted: 24 August 2018 . Accepted: 14 February 2019 . Published Online: 04 April 2019

Filip Pawłowski , Jeppe Olsen , and Poul Jørgensen



View Online



Export Citation



CrossMark

ARTICLES YOU MAY BE INTERESTED IN

[Cluster perturbation theory. I. Theoretical foundation for a coupled cluster target state and ground-state energies](#)

The Journal of Chemical Physics **150**, 134108 (2019); <https://doi.org/10.1063/1.5004037>

[Cluster perturbation theory. IV. Convergence of cluster perturbation series for energies and molecular properties](#)

The Journal of Chemical Physics **150**, 134111 (2019); <https://doi.org/10.1063/1.5053622>

[Cluster perturbation theory. III. Perturbation series for coupled cluster singles and doubles excitation energies](#)

The Journal of Chemical Physics **150**, 134110 (2019); <https://doi.org/10.1063/1.5046935>

Lock-in Amplifiers
up to 600 MHz



Cluster perturbation theory. V. Theoretical foundation for cluster linear target states

Cite as: *J. Chem. Phys.* **150**, 134112 (2019); doi: [10.1063/1.5053627](https://doi.org/10.1063/1.5053627)

Submitted: 24 August 2018 • Accepted: 14 February 2019 •

Published Online: 4 April 2019



View Online



Export Citation



CrossMark

Filip Pawłowski,^{1,a)}  Jeppe Olsen,²  and Poul Jørgensen²

AFFILIATIONS

¹Department of Chemistry and Biochemistry, Auburn University, Auburn, Alabama 36849-5312, USA

²Department of Chemistry, qLEAP Center for Theoretical Chemistry, Langelandsgade 140, DK-8000 Aarhus C, Denmark

^{a)}Electronic mail: filip.pawlowski1@gmail.com.

ABSTRACT

Cluster perturbation (CP) theory was developed in Paper I [F. Pawłowski *et al.*, *J. Chem. Phys.* **150**, 134108 (2019)] for a coupled cluster (CC) target state and is extended in this paper to comprehend a cluster linear (CL) target state, for which the embedding of a CC parent state in the target excitation space is described using a linear parametrization. The theory is developed for determining the energy and molecular properties for a CL state. When CP theory is applied to a CL target state, a series of corrections is determined in orders of the CC parent-state similarity-transformed fluctuation potential, where the zeroth-order term is the energy or molecular property of the CC parent state and where the series formally converges to the energy or molecular property of the CL target state. The determination of energies and molecular properties is simpler for a CL state than for a CC state because the CL state is linearly parametrized. The amplitude equations are quadratic for a CL target state, while quartic for a CC target state, and molecular property expressions for a CL target state have the same simple structure as for a configuration interaction state. The linear parametrization introduces non-size-extensive contributions in the energy and molecular property expressions. However, since the linear parametrization describes the embedding of the CC parent state in the target excitation space, the energy and molecular properties for a CL state are *weakly size-extensive*. For the energy, weak size-extensivity means that non-size-extensive contributions enter in sixth and higher orders in the CP energy series, whereas for molecular properties, weak size-extensivity means that non-size-extensive contributions enter in second and higher orders. Weak size-extensivity therefore has a little or vanishing effect on calculated energies or molecular properties. The determination of the CP energy and molecular property corrections does not require that amplitude or response equations are solved explicitly for the target state and it becomes computationally tractable to use low-order corrections from these series to obtain energies and molecular properties of CL target state quality. For three simple molecules, HF, N₂, and CH₂, the accuracy of the CL approach for ground-state energies is tested using a parent state including single and double excitations (i.e., the CC singles-and-doubles state, CCSD) and a target state that includes triple excitations. It is found that the size-extensive fifth-order CL energies deviate by less than 0.0001 hartree from the energies of a target CC that includes triple excitations (i.e., the CC singles-doubles-and-triples state, CCSDT). CP theory with a CL target state therefore becomes a very attractive replacement of standard CC theory for high-accuracy energy and molecular property calculations, in which triple and higher excitation levels are considered.

Published under license by AIP Publishing. <https://doi.org/10.1063/1.5053627>

I. INTRODUCTION

In Paper I,¹ we introduced a new class of perturbation models—the cluster perturbation (CP) models—for which 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 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. In CP theory, the zeroth-order state is a CC state in the parent excitation space. In Paper I,¹ the target state of CP theory was assumed to be a CC state in the target excitation space. In CP theory, we determine perturbation series for energies and molecular properties in orders of the perturbation—the CC parent-state

similarity-transformed fluctuation potential—where the zeroth-order term in the series is the energy or molecular property of the CC parent state and where the CP series formally converges to the energy or molecular property of the CP target state. Molecular properties in CP theory are determined using response function theory, where the response functions for the CC parent state determine the molecular property for the CC parent state and the response functions for the CP target state determine the molecular property for the CP target state. From the response functions and their residues, molecular properties can be determined for the ground state, for excited states, and for transitions between these states, including excitation energies.

In Paper I,¹ the theoretical foundation for CP theory is developed. CP series are described for the ground-state energy, and it is shown that CP series exist for molecular properties including excitation energies. Test calculations are reported in Paper I¹ for CP series for the ground-state energy. The test calculations show a great promise, and judging from the results of the test calculations, efficient implementations of low-order CP models will soon become state-of-the-art models for the determination of the correlation energy.

In Paper II,⁷ the CP series are developed for excitation energies. Test calculations of the CP excitation energy series are also presented in Paper II.⁷ The test calculations also show a great promise, as the test calculations for the CP series for the ground-state energy in Paper I.¹ In Paper III,⁸ the performance of the low-order members of the CP excitation energy series, CPS(D-n), is reported where excitation energy corrections to a CC singles (CCS) excitation energy are determined and where the series formally converges to a CC singles-and-doubles (CCSD) excitation energy. The first-order correction, CPS(D-1), vanishes and the second-order correction, CPS(D-2), gives the well-known configuration-interaction singles with a perturbative doubles correction [CIS(D)] model of Head-Gordon *et al.*⁹ In Paper III,⁸ we report an efficient implementation of the CPS(D-2) and CPS(D-3) models and carry out a sequence of benchmark calculations and statistical analysis of their errors for a test set of organic molecules¹⁰ containing 69 valence and Rydberg states. For single-configuration dominated excitations, the maximum and mean absolute errors (Δ_{\max} , $\bar{\Delta}_{\text{abs}}$), obtained by comparison with CCSD excitation energies, are (0.96 eV, 0.30 eV) for CPS(D-2) and (0.14 eV, 0.07 eV) for CPS(D-3). The CPS(D-3) model can therefore be used to obtain excitation energies of CCSD quality in the sense that the difference between CPS(D-3) and CCSD excitation energies is of the same size or smaller than the effect of adding triples corrections to CCSD excitation energies. The computational cost of a CPS(D-3) excitation energy calculation is only a few percent of the cost of a conventional CCSD excitation energy calculation. CPS(D-3) calculations were also reported in Paper III⁸ for system sizes that are far beyond the size for which a conventional CCSD calculation can be carried out. We also note that the CPS(D-3) calculations are well suited for an efficient massively parallel implementation as will be described in a coming publication.

The promises that CP series have given for an efficient and cost effective determination of the energy and molecular properties make it natural to ask whether CP theory can further be simplified without compromising the performance of the CP series. It is this question that will be addressed in the present article.

In CP theory, the molecular system is described at zeroth-order by a CC state in the parent excitation space and the corrections to the CC parent state description then will converge towards the CC target state description. The CC target state description can in CP theory be viewed as a CC parent state description that is embedded in an exponentially parametrized target excitation space. The CC parent state description is size-extensive, and the disconnected contributions in the CC target state are therefore described to high accuracy by the CC parent state. The embedding of the CC parent state using an exponential parametrization can therefore be replaced by an embedding in a linearly parametrized target excitation space without compromising the accuracy of the calculation. In this paper, we describe how this can be done by introducing a *cluster linear (CL) state* where the CC parent state is embedded in a linearly parametrized target excitation space.

The advantage of using a CL target state with a linearly parametrized target excitation space, over a CC target state with an exponentially parametrized target excitation space, is that the series of perturbation corrections simplifies due to the linear parametrization. The amplitude equations are thus quadratic for a CL state, whereas they are quartic for a CC state, and the molecular properties for a CL state have the same simple structure as for a conventional linearly parametrized configuration interaction (CI) state.¹¹ These simplifications come at the price of the energy and molecular properties becoming not size-extensive. However, since the linear parametrization of the CL target state describes an embedding of a CC parent state, which is exponentially parametrized, in a target excitation space, the non-size-extensive contributions to the energy and molecular properties become much smaller than for a conventional linearly parametrized CI state. In fact, the energy and molecular properties for a CL target state are *weakly size-extensive*, where the weak size-extensivity is defined in terms of the CP series for the energy and molecular properties. For the energy, weak size-extensivity means that non-size-extensive contributions enter in sixth and higher orders in CP theory, while for molecular properties, weak size-extensivity means that non-size-extensive contributions enter in second and higher orders. The fact that energies and molecular properties are weakly size-extensive means that the non-size-extensive contributions have little effect on the calculated energy or molecular properties.

For a CL target state, the CC parent state must contain at least the singles-and-doubles excitation space in order for the CL state to describe the important disconnected contributions in the wave function through the CC parent state, for example, the disconnected quadruple excitation formed by a product of two double excitations.^{12,13} In general, CL target states will further be restricted to have an auxiliary space that contains only one excitation level. The reason is that when auxiliary spaces contain more than one excitation level, too much effort is spent on optimizing amplitudes at the highest excitation levels, which are computationally most demanding, for amplitudes that are far from converged at the lower excitation levels.

CL states have not been previously considered in electronic structure theory and their features, described above, may make them an attractive alternative to CC states even outside the CP framework (i.e., even without considering perturbative approximations to CL states). Therefore, before embarking on the development of CP theory for CL target states, we will describe in the initial

part of this paper the theoretical foundation for the CL states. The theoretical development for determining the energy and molecular properties for a CL state follows an outline similar to the one for a CC state (see, for example, Refs. 12 and 13 for the CC energy and Refs. 11 and 14–16 for CC molecular properties). In particular, molecular properties are determined from the response functions for the CL state and are derived in this article following an outline similar to the one used in Ref. 11 for deriving response functions for a CC state.

The CL state is linearly parametrized, and the time evolution of the CL state is also linearly parametrized when the response functions are determined. In order to determine the response functions for a CL state, it is imperative to use the developments in response function theory described in Ref. 11. However, when this is done, CL states can be used as target states in CP theory and perturbation series in orders of the CC parent-state similarity-transformed fluctuation potential can be determined for molecular properties, where the zeroth-order term is the molecular property for the CC parent state and where the series formally converges to a molecular property for the CL target state. Because the parent state is a CC state and because the time evolution of the CL target state is linearly parametrized, the zeroth-order molecular properties (the molecular properties of the CC parent state) become equation-of-motion coupled cluster (EOM-CC) molecular properties expressed in the form described by Coriani *et al.*¹⁷ EOM-CC molecular properties were introduced by Stanton and Bartlett¹⁸ for calculation of dipole moments of excited states and dipole transition strengths and obtained by replacing the exact states in the exact-state molecular property expressions with states determined by solving the EOM-CC Hamiltonian eigenvalue equation.

CP models are characterized by a CC parent state defined in the parent excitation space and by an auxiliary excitation space. This can be expressed using a notation, in which the parent excitation space is followed by the auxiliary excitation 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 the CP target state is exponentially parametrized and that molecular properties are determined from a time evolving target state that is exponentially parametrized. If the time evolution is linearly parametrized, EOM-CC molecular properties^{17–19} are obtained and the CP model will be labeled with an overline. For example, $\overline{\text{CPSD(T)}}$ denotes that energy corrections are determined using an exponential parametrization of the target state, whereas molecular properties are determined using a linear parametrization of the time evolution of the target state. For a CL target state, the auxiliary space label is preceded with a label L to emphasize that the effect of introducing an auxiliary space is described in terms of a linearly parametrized excitation space. For example, CPSD(LT) denotes a model with an exponentially parametrized CCSD parent state embedded in a linearly parametrized target space and with a linear parametrization of the time evolution. In this model, CP energy corrections are determined, starting with CCSD energy as zeroth-order, which formally converge to the CPSD(LT) target-state energy. Similarly, CP molecular property corrections are determined in this model, with EOM-CCSD molecular properties as zeroth-order, which formally converge to CPSD(LT) target-state molecular properties. We also note that if the auxiliary excitation space is followed by a number, as, for example, in CPSD(LT), the number

denotes that perturbation corrections are determined through that order.

In Sec. II, we describe the theoretical foundation for introducing CL states. In Sec. III, the energy and amplitude equations are derived for a CL state. In Sec. IV, the energy Lagrangian^{20,21} is set up for a CL state and used to determine a perturbation series for the energy. In particular, the perturbation series for the energy is determined for the CPSD(LT) model, for which the target state is a CL state with a CCSD parent state embedded in a linearly parametrized singles-doubles-and-triples target excitation space. We show that the ground-state energy corrections of this series are identical through fourth order to the energy corrections for the series CPSD(T) derived in Paper I¹ and that non-size-extensive contributions for the CPSD(LT) energy series first enter at sixth order. Section IV includes numerical tests of the accuracy of the CPSD(LT) ground-state energy corrections through sixth order for the simple molecules HF, N₂, and CH₂. For these molecules, it is shown that the accuracy of the energies obtained through fifth order using the CPSD(LT) method is equal to the accuracy obtained using the CPSD(T) method through fifth order. We describe in Sec. V how response functions can be determined for a CL target state and how molecular properties obtain the simple structure of CI molecular properties. In Sec. VI, we determine, for the CPSD(LT) model, explicit expressions for the lowest-order corrections for the excitation energies and for the linear response function. Section VII contains a summary and conclusions.

II. CLUSTER LINEAR (CL) TARGET STATE

A. Standard coupled cluster theory

In CC theory,^{12,13} the wave function is exponentially parametrized

$$|\text{CC}\rangle = e^T |\text{HF}\rangle, \quad (1)$$

where the cluster operator

$$T = \sum_{\mu_i} t_{\mu_i} \theta_{\mu_i} \quad (2)$$

contains the cluster amplitudes t_{μ_i} and the many-body excitation operators θ_{μ_i} that act on the Hartree-Fock state $|\text{HF}\rangle$ producing its orthogonal complement set of states

$$|\mu_i\rangle = \theta_{\mu_i} |\text{HF}\rangle. \quad (3)$$

In Eqs. (2) and (3), i denotes an excitation level and μ_i denotes an excitation at this level.

The CC Schrödinger equation can be expressed as

$$e^{-T} H_0 e^T |\text{HF}\rangle = E_0 |\text{HF}\rangle, \quad (4)$$

where H_0 is the Hamiltonian and E_0 is the ground-state energy. The CC Schrödinger equation can be solved by projection against the basis $\langle \mathcal{B} | = \langle \mathcal{B} \rangle^\dagger$, where

$$|\mathcal{B}\rangle = \{ |\text{HF}\rangle, |\mu_i\rangle \}, \quad i = 1, 2, \dots, \quad (5)$$

leading to the CC energy and amplitude equations

$$E_0 = \langle \text{HF} | e^{-T} H_0 e^T | \text{HF} \rangle = \langle \text{HF} | H_0 | \text{HF} \rangle + \langle \text{HF} | H_0 T_2 | \text{HF} \rangle + \frac{1}{2} \langle \text{HF} | H_0 T_1^2 | \text{HF} \rangle, \quad (6)$$

$$\langle \mu_i | e^{-T} H_0 e^T | \text{HF} \rangle = 0, \quad (7)$$

where we have used the Brillouin theorem to obtain the energy in Eq. (6). In a standard CC calculation, a CC state is determined for a truncated excitation space, denoted as the *target excitation space*. The amplitude equations in Eq. (7) are solved in the target excitation space and the energy is determined from Eq. (6).

B. Linearly parametrized CL target state

In CP theory, we partition a target excitation space ($1 \leq i \leq t$) into a *parent excitation space* ($1 \leq i \leq p$) and an *auxiliary excitation space* ($p < i \leq t$). The zeroth-order state in CP theory is a CC state in the parent excitation space

$$|\text{CC}^*\rangle = e^{*T} |\text{HF}\rangle, \quad (8)$$

where the cluster amplitudes satisfy the CC amplitude equations in the parent excitation space

$$\langle \mu_i | e^{-*T} H_0 e^{*T} | \text{HF} \rangle = 0, \quad 1 \leq i \leq p, \quad (9)$$

$$*T = *T_1 + \dots + *T_p, \quad (10)$$

$$*T_i = \sum_{\mu_i} *t_{\mu_i} \theta_{\mu_i}, \quad 1 \leq i \leq p, \quad (11)$$

with the energy

$$*E_0 = \langle \text{HF} | e^{-*T} H_0 e^{*T} | \text{HF} \rangle. \quad (12)$$

The target state in Paper I¹ was a CC state parametrized with the CC parent state as the expansion point

$$|\text{CC}\rangle = e^{\delta T + *T} |\text{HF}\rangle = e^{\delta T} |\text{CC}^*\rangle, \quad (13)$$

where

$$\delta T = \sum_{i=1}^t \sum_{\mu_i} \delta t_{\mu_i} \theta_{\mu_i}. \quad (14)$$

The CC target state in Eq. (13) can be viewed as a CC parent state embedded in an exponentially parametrized target excitation space. In this paper, we extend CP theory to encompass CP target states, for which the embedding of the CC parent state in the target excitation space is described using a linear parametrization. We refer to such CP target states as CL target states.

To understand how the CP model can be extended to include a CL target state, we expand the CC target state wave function in Eq. (13) as

$$|\text{CC}\rangle = e^{*T + \delta T} |\text{HF}\rangle = e^{*T} \left(1 + \delta T + \frac{1}{2!} \delta T^2 + \frac{1}{3!} \delta T^3 + \dots \right) |\text{HF}\rangle. \quad (15)$$

The CC target state can thus be viewed as a CP parent state, $e^{*T} |\text{HF}\rangle$, that is corrected due to the effect of introducing an auxiliary space.

In Paper I,¹ we described how the cluster amplitudes δt_{μ_i} in Eq. (14) can be determined using CP theory. The perturbation analysis in Paper I¹ shows that the cluster amplitudes δt_{μ_i} vanish in zeroth order and that the only δt_{μ_i} amplitudes that contribute in first order are the amplitudes in the auxiliary space, $p < i \leq t$. Relaxation of the parent state amplitudes δt_{μ_i} , $1 \leq i \leq p$, due to the presence of auxiliary space amplitudes, enters in second order. The amplitudes in the δT operator are therefore small, and the terms that are quadratic and higher in δT in Eq. (15) and represent disconnected contributions hence are very small. With only small changes in the parameters of the wave function in Eq. (15), we can therefore re-parametrize Eq. (15) in terms of a linear expansion and obtain the CL target state

$$|\text{CL}\rangle = e^{*T} \left(1 + \sum_{i=1}^t \sum_{\mu_i} z_{\mu_i} |\mu_i\rangle \langle \text{HF} | \right) |\text{HF}\rangle = e^{*T} e^Z |\text{HF}\rangle, \quad (16)$$

where

$$Z = \sum_{i=1}^t \sum_{\mu_i} |\mu_i\rangle \langle \text{HF} | z_{\mu_i}, \quad (17)$$

recalling that the action of the state-transfer operator $|\mu_i\rangle \langle \text{HF} |$ on the $|\text{HF}\rangle$ state is equal to the action of the many-body orbital-excitation operator θ_{μ_i} on the $|\text{HF}\rangle$ state,

$$|\mu_i\rangle = \left(|\mu_i\rangle \langle \text{HF} | \right) |\text{HF}\rangle = \theta_{\mu_i} |\text{HF}\rangle, \quad (18)$$

and that

$$Z^2 = 0. \quad (19)$$

The $|\text{CL}\rangle$ state in Eq. (16) is intermediate normalized against the $|\text{HF}\rangle$ state and has the parent CC state as its dominant component. Furthermore, the expansion coefficients z_{μ_i} in Eq. (16), which describe the effect of the auxiliary space, are small and similar in size to the δt_{μ_i} amplitudes in Eq. (15).

The linear parametrization of the $|\text{CL}\rangle$ state in Eq. (16) leads to energies and molecular properties that are not size-extensive. However, the size-extensivity problems are due to the fact that the small disconnected terms that are quadratic and higher in δT in Eq. (15) are neglected. The size-extensivity problems that arise when using the $|\text{CL}\rangle$ state to calculate energies and molecular properties are therefore weak compared to the size-extensivity problems that arise for standard truncated CI linear expansions, where large disconnected contributions are neglected. To see this, we Taylor expand the operator e^{*T} in the $|\text{CL}\rangle$ wave function of Eq. (16)

$$|\text{CL}\rangle = \left(1 + *T + \frac{1}{2!} *T^2 + \dots \right) (1 + Z) |\text{HF}\rangle \quad (20)$$

and compare this expansion with a conventional CI intermediate-normalized linearly expanded wave function

$$|\text{CI}\rangle = (1 + Z) |\text{HF}\rangle. \quad (21)$$

The $|\text{CL}\rangle$ wave function does contain disconnected higher-excitation contributions, e.g., a large $*T^2 |\text{HF}\rangle$ disconnected contribution, which are not present in the $|\text{CI}\rangle$ wave function. It is these disconnected contributions in the $|\text{CL}\rangle$ wave function that make the non-size-extensivity of energies and molecular properties weak

compared to the non-size-extensivity that is encountered when a conventional linearly expanded CI wave function is used. In another perspective, in CC theory, the disconnected contributions of a CC wave function ensure that CC energies and molecular properties are size-extensive. For the $|\text{CL}\rangle$ wave function, these disconnected contributions are described to high accuracy by the parent CC state, and energies and molecular properties that are determined using the $|\text{CL}\rangle$ wave function therefore become size-extensive to high accuracy.

From the expansion in Eq. (20), we also see that the first large disconnected contribution that arises from the parent state is the disconnected quadruples contribution, ${}^*T_2^2|\text{HF}\rangle$. We therefore restrict $|\text{CL}\rangle$ target states to states where the parent CC state contains at least doubles excitations, i.e., where $p \geq 2$. If the parent CC state is restricted to contain only single excitations, i.e., $p = 1$, the $|\text{CL}\rangle$ target state gives a conventional CI description of the molecular system, but using a non-conventional parametrization.

III. ENERGY AND AMPLITUDE EQUATIONS FOR A CL TARGET STATE

In Sec. II, we introduced CL target states. In Sec. III A, we describe how the amplitudes and the energy can be determined for CL target states. In Sec. III B, a perturbation analysis is carried out for the amplitude equations of the CL state and it is discussed through which order in CP perturbation theory the CL amplitudes are size-extensive. In particular, we discuss in Sec. III C that for CL models, for which the auxiliary space is restricted to contain only one excitation level, the CL ground-state energy is size-extensive through fifth order.

A. Energy and amplitude equations

The similarity-transformed Schrödinger equation for the CL target state in Eq. (16) becomes

$$e^{-Z}e^{-*T}H_0e^{*T}e^Z|\text{HF}\rangle = E_0|\text{HF}\rangle \quad (22)$$

and can be solved by projecting Eq. (22) against the basis $\langle \mathcal{B} | = |\mathcal{B}\rangle^\dagger$ [cf. Eq. (5)], giving the energy and amplitude equations

$$E_0 = \langle \text{HF} | e^{-Z}H_0^*T e^Z | \text{HF} \rangle = {}^*E_0 + \sum_{i=1}^2 \sum_{\mu_i} \langle \text{HF} | H_0^*T | \mu_i \rangle z_{\mu_i}, \quad (23)$$

$$\langle \mu_i | e^{-Z}H_0^*T e^Z | \text{HF} \rangle = 0, \quad 1 \leq i \leq t, \quad (24)$$

where we have used Eq. (12) and introduced the similarity-transformed Hamiltonian

$$H_0^{*T} = e^{-*T}H_0e^{*T}. \quad (25)$$

To obtain the last term in Eq. (23), we have used the vector $\langle \text{HF} | H_0^*T | \mu_i \rangle$ which has non-vanishing components only in the singles-and-doubles space.

Applying a Baker-Campbell-Hausdorff (BCH) expansion, the amplitude equations in Eq. (24) can be written as

$$\langle \mu_i | H_0^*T | \text{HF} \rangle S_{ip} + \sum_{j=1}^t \sum_{\nu_j} \langle \mu_i | [H_0^*T, | \nu_j \rangle \langle \text{HF} |] | \text{HF} \rangle z_{\nu_j} - z_{\mu_i} \left(\sum_{j=1}^2 \sum_{\nu_j} \langle \text{HF} | H_0^*T | \nu_j \rangle z_{\nu_j} \right) = 0, \quad 1 \leq i \leq t, \quad (26)$$

where to obtain the first term we have used Eq. (9) and introduced the integer step function S_{ab}

$$S_{ab} = \begin{cases} 0, & \text{for } a \leq b \\ 1, & \text{for } a > b. \end{cases} \quad (27)$$

To obtain the last term in Eq. (26), we have used $Z^2 = 0$. To determine the energy E_0 for a CL target ground state [Eq. (23)], we thus have to solve the *quadratic* amplitude equations in Eq. (26).

B. Perturbation analysis of amplitude equations for a CL target state

To get an insight into the structure of the amplitude equations and the size-extensivity problems that arise due to the linear parametrization of the CL state, we perform a perturbation analysis for the energy and the amplitude equations in Eqs. (23) and (26), respectively. Introducing a Møller-Plesset partitioning of the similarity-transformed Hamiltonian H_0^{*T} of Eq. (25)

$$H_0^{*T} = f^{*T} + \Phi^{*T}, \quad (28)$$

where f is the Fock operator in the canonical Hartree-Fock basis and Φ is the fluctuation potential, Eqs. (23) and (26) become

$$E_0 = {}^*E_0 + \sum_{i=1}^2 \sum_{\mu_i} \langle \text{HF} | \Phi^{*T} | \mu_i \rangle z_{\mu_i}, \quad (29)$$

$$\langle \mu_i | \Phi^{*T} | \text{HF} \rangle S_{ip} + \sum_{j=1}^t \sum_{\nu_j} \langle \mu_i | [H_0^*T, | \nu_j \rangle \langle \text{HF} |] | \text{HF} \rangle z_{\nu_j} - z_{\mu_i} \left(\sum_{j=1}^2 \sum_{\nu_j} \langle \text{HF} | \Phi^{*T} | \nu_j \rangle z_{\nu_j} \right) = 0, \quad 1 \leq i \leq t, \quad (30)$$

where we have used

$$\langle \text{HF} | f^{*T} | \mu_i \rangle = 0, \quad 1 \leq i \leq t, \quad (31)$$

$$\langle \mu_i | f^{*T} | \text{HF} \rangle = 0, \quad p < i \leq t. \quad (32)$$

The second term in Eq. (30) contains the extended parent-state Jacobian (i.e., the Jacobian that has a structure of the parent-state Jacobian but indices referencing the whole target space) for a linearly parametrized excitation space

$$\begin{aligned} \mathcal{A}_{\mu_i \nu_j} &= \frac{\partial}{\partial z_{\nu_j}} \langle \mu_i | e^{-Z} H_0^*T e^Z | \text{HF} \rangle \Big|_{z_{\mu_i}=0} = \langle \mu_i | [H_0^*T, | \nu_j \rangle \langle \text{HF} |] | \text{HF} \rangle \\ &= \langle \mu_i | H_0^*T | \nu_j \rangle - \delta_{\mu_i \nu_j} \langle \text{HF} | H_0^*T | \text{HF} \rangle, \quad 1 \leq i, j \leq t. \end{aligned} \quad (33)$$

The extended parent-state Jacobian for a linearly parametrized excitation space can be expressed in terms of the extended parent-state Jacobian for an exponentially parametrized excitation space.¹ To do this, we write Eq. (33) as

$$\mathcal{A}_{\mu_i v_j} = \langle \mu_i | [H_0^{*T}, \theta_{v_j}] | \text{HF} \rangle + \langle \mu_i | \theta_{v_j} H_0^{*T} | \text{HF} \rangle - \delta_{\mu_i v_j} \langle \text{HF} | H_0^{*T} | \text{HF} \rangle, \quad 1 \leq i, j \leq t, \quad (34)$$

and introduce in the second term of Eq. (34) the resolution of the identity in the complete orthonormal basis $|\mathcal{B}\rangle$ of Eq. (5)

$$\begin{aligned} \langle \mu_i | \theta_{v_j} H_0^{*T} | \text{HF} \rangle &= \langle \mu_i | \theta_{v_j} | \text{HF} \rangle \langle \text{HF} | H_0^{*T} | \text{HF} \rangle \\ &+ \langle \mu_i | \theta_{v_j} \sum_{r=1}^{\infty} \sum_{\lambda_r} |\lambda_r\rangle \langle \lambda_r | H_0^{*T} | \text{HF} \rangle \\ &= \delta_{\mu_i v_j} \langle \text{HF} | H_0^{*T} | \text{HF} \rangle + \langle \mu_i | \theta_{v_j} \sum_{r=p+1}^{\infty} \\ &\times \sum_{\lambda_r} |\lambda_r\rangle \langle \lambda_r | \Phi^{*T} | \text{HF} \rangle, \quad 1 \leq i, j \leq t, \quad (35) \end{aligned}$$

where to obtain the second equality we have used Eqs. (9) and (32). Substituting Eq. (35) into Eq. (34) gives

$$\mathcal{A}_{\mu_i v_j} = \langle \mu_i | [H_0^{*T}, \theta_{v_j}] | \text{HF} \rangle + \sum_{r=p+1}^{\infty} \sum_{\lambda_r} \langle \mu_i | \theta_{v_j} | \lambda_r \rangle \langle \lambda_r | \Phi^{*T} | \text{HF} \rangle, \quad 1 \leq i, j \leq t. \quad (36)$$

The extended parent-state Jacobian for an exponentially parametrized space is given in Eq. (27) of Paper I¹

$$A_{\mu_i v_j} = \langle \mu_i | [H_0^{*T}, \theta_{v_j}] | \text{HF} \rangle, \quad 1 \leq i, j \leq t. \quad (37)$$

Introducing Eq. (37) in Eq. (36) gives

$$\mathcal{A}_{\mu_i v_j} = A_{\mu_i v_j} + \sum_{r=p+1}^{\infty} \sum_{\lambda_r} \langle \mu_i | \theta_{v_j} | \lambda_r \rangle \langle \lambda_r | \Phi^{*T} | \text{HF} \rangle, \quad 1 \leq i, j \leq t. \quad (38)$$

The extended parent-state Jacobian for an exponentially parametrized state is in CP theory partitioned using the parent-state Jacobian partitioning as described in Sec. II D of Paper I.¹ Using the parent-state Jacobian partitioning, the extended parent-state Jacobian for an exponentially parametrized space can be written as [cf. Eqs. (29) and (39) of Paper I¹]

$$A_{\mu_i v_j} = A_{\mu_i v_j}^{(0)} + A_{\mu_i v_j}^{(1)}, \quad (39)$$

where

$$A_{\mu_i v_j}^{(0)} = \langle \mu_i | [H_0^{*T}, \theta_{v_j}] | \text{HF} \rangle (1 - S_{ip})(1 - S_{jp}) + \varepsilon_{v_j} \delta_{\mu_i v_j} S_{ip} S_{jp}, \quad 1 \leq i, j \leq t, \quad (40a)$$

$$A_{\mu_i v_j}^{(1)} = \langle \mu_i | [\Phi^{*T}, \theta_{v_j}] | \text{HF} \rangle (1 - S_{ip}) S_{jp} + \langle \mu_i | [\Phi^{*T}, \theta_{v_j}] | \text{HF} \rangle S_{ip} (1 - S_{jp}) + \langle \mu_i | [\Phi^{*T}, \theta_{v_j}] | \text{HF} \rangle S_{ip} S_{jp}, \quad 1 \leq i, j \leq t. \quad (40b)$$

Using Eq. (39), we can write Eq. (38) as

$$\mathcal{A}_{\mu_i v_j} = A_{\mu_i v_j}^{(0)} + A_{\mu_i v_j}^{(1)} + \sum_{r=p+1}^{\infty} \sum_{\lambda_r} \langle \mu_i | \theta_{v_j} | \lambda_r \rangle \langle \lambda_r | \Phi^{*T} | \text{HF} \rangle, \quad 1 \leq i, j \leq t. \quad (41)$$

Introducing Eq. (41) in the amplitude equations in Eq. (30), we obtain

$$\begin{aligned} \sum_{j=1}^t \sum_{v_j} A_{\mu_i v_j}^{(0)} z_{v_j} &= -\langle \mu_i | \Phi^{*T} | \text{HF} \rangle S_{ip} - \sum_{j=1}^t \sum_{v_j} A_{\mu_i v_j}^{(1)} z_{v_j} \\ &+ z_{\mu_i} \left(\sum_{j=1}^2 \sum_{v_j} \langle \text{HF} | \Phi^{*T} | v_j \rangle z_{v_j} \right) \\ &- \sum_{j=1}^t \sum_{v_j} \sum_{r=p+1}^{\infty} \sum_{\lambda_r} \langle \mu_i | \theta_{v_j} | \lambda_r \rangle \langle \lambda_r | \Phi^{*T} | \text{HF} \rangle z_{v_j}, \\ &1 \leq i \leq t, \quad p \geq 2. \quad (42) \end{aligned}$$

Both the last and the second to the last term in Eq. (42) give rise to non-size-extensive contributions. The non-size-extensive contributions from the last term arise due to an inadequate description of the Jacobian, and hence of the excitation space, in the case of a truncated excitation manifold for a linear parametrization. The non-size-extensive contributions from the second to the last term arise more directly due to the linear parametrization of the wave function.

The quadratic amplitude equations for the CL target ground state in Eq. (42) should be contrasted to quartic amplitude equations for the CC target state, which in Eq. (30) of Paper I¹ are given as

$$\begin{aligned} \sum_{j=1}^t \sum_{v_j} A_{\mu_i v_j}^{(0)} \delta t_{v_j} &= -\langle \mu_i | \Phi^{*T} | \text{HF} \rangle S_{ip} - \sum_{j=1}^t \sum_{v_j} A_{\mu_i v_j}^{(1)} \delta t_{v_j} \\ &- \frac{1}{2} \langle \mu_i | [[\Phi^{*T}, \delta T], \delta T] | \text{HF} \rangle \\ &- \frac{1}{6} \langle \mu_i | [[[\Phi^{*T}, \delta T], \delta T], \delta T] | \text{HF} \rangle \\ &- \frac{1}{24} \langle \mu_i | [[[[\Phi^{*T}, \delta T], \delta T], \delta T], \delta T] | \text{HF} \rangle, \\ &1 \leq i \leq t, \quad (43) \end{aligned}$$

where δT is the cluster operator of Eq. (14) that contains the cluster amplitudes δt_{μ_i} of Eq. (43). The CL amplitude equations differ from the CC amplitude equations by the last two non-size-extensive terms in the CL equations which are replaced with the three last term-wise size-extensive commutator terms in the CC amplitude equations.¹²

Equations (42) and (43) give vanishing zeroth-order amplitudes, and the first-order amplitudes from the two equations are identical

$$z_{\mu_i}^{(1)} = 0, \quad 1 \leq i \leq p, \quad (44a)$$

$$z_{\mu_i}^{(1)} = -\varepsilon_{\mu_i}^{-1} \langle \mu_i | \Phi^{*T} | \text{HF} \rangle, \quad p < i \leq t. \quad (44b)$$

At second order, the amplitudes become

$$\begin{aligned} \sum_{j=1}^t \sum_{v_j} A_{\mu_i v_j}^{(0)} z_{v_j}^{(2)} &= -\sum_{j=p+1}^t \sum_{v_j} A_{\mu_i v_j}^{(1)} z_{v_j}^{(1)} - \sum_{j=p+1}^t \sum_{v_j} \sum_{r=p+1}^{\infty} \sum_{\lambda_r} \\ &\times \langle \mu_i | \theta_{v_j} | \lambda_r \rangle \langle \lambda_r | \Phi^{*T} | \text{HF} \rangle z_{v_j}^{(1)}, \quad 1 \leq i \leq t, \quad (45) \end{aligned}$$

where the last term is non-size-extensive and contributes to high excitations, $(2p + 2) \leq i \leq t$, in the auxiliary space, since $\langle \mu_i | \theta_{v_j} | \lambda_r \rangle$

in Eq. (45) is non-vanishing only for this excitation range. For the third-order amplitudes, $z_{v_j}^{(3)}$, we obtain

$$\sum_{j=1}^t \sum_{v_j} A_{\mu_i v_j}^{(0)} z_{v_j}^{(3)} = - \sum_{j=1}^t \sum_{v_j} A_{\mu_i v_j}^{(1)} z_{v_j}^{(2)} - \sum_{j=1}^t \sum_{v_j} \sum_{r=p+1}^{\infty} \sum_{\lambda_r} \times \langle \mu_i | \theta_{v_j} | \lambda_r \rangle \langle \lambda_r | \Phi^{*T} | \text{HF} \rangle z_{v_j}^{(2)}, \quad 1 \leq i \leq t, \quad (46)$$

since the third term in Eq. (42) does not contribute at third order

$$z_{\mu_i}^{(1)} \left(\sum_{j=1}^2 \sum_{v_j} \langle \text{HF} | \Phi^{*T} | v_j \rangle z_{v_j}^{(1)} \right) = 0, \quad 1 \leq i \leq t, \quad p \geq 2, \quad (47)$$

as follows from Eq. (44a). The last term in Eq. (46) is non-size-extensive and has non-vanishing contributions only in the auxiliary space, since in Eq. (46) $\langle \mu_i | \theta_{v_j} | \lambda_r \rangle \neq 0$ only for $i \geq (p+2)$. In addition, the first term in Eq. (46) can contain non-size-extensive contributions originating from the second-order amplitudes in the auxiliary space [see Eq. (45)]. The third term on the right-hand side of Eq. (42) gives non-size-extensive contributions, which enter for first time at fourth order,

$$z_{\mu_i}^{(1)} \left(\sum_{j=1}^2 \sum_{v_j} \langle \text{HF} | \Phi^{*T} | v_j \rangle z_{v_j}^{(2)} \right) \neq 0, \quad p < i \leq t, \quad (48)$$

and have non-vanishing components only in the auxiliary space, due to Eq. (44). The second- and third-order amplitudes, $\delta t_{\mu_i}^{(2)}$ and $\delta t_{\mu_i}^{(3)}$, can be obtained from Eq. (43) and become identical to $z_{\mu_i}^{(2)}$ and $z_{\mu_i}^{(3)}$, respectively, if the last non-size-extensive term in Eq. (45) is neglected and the last non-size-extensive term in Eq. (46) is replaced by the connected size-extensive contribution $-\frac{1}{2} \langle \mu_i | [[\Phi^{*T}, \delta T^{(1)}], \delta T^{(1)}] | \text{HF} \rangle$.

C. The choice of auxiliary space for a CL state

Using the above observations, we see that the third right-hand side term in Eq. (42) can first contribute to fifth-order primary-space amplitudes, and therefore, the non-size-extensive contributions originating from this term can enter in the energy of Eq. (29) in the sixth order. Similarly, non-size-extensive contributions originating from the last term in Eq. (42) enter in the energy at the fourth order [cf. Eq. (46)]. If, however, we restrict the auxiliary space to contain only one excitation level, the last term in Eq. (42) vanishes

$$\sum_{j=1}^t \sum_{v_j} \sum_{r=p+1}^{\infty} \sum_{\lambda_r} \langle \mu_i | \theta_{v_j} | \lambda_r \rangle \langle \lambda_r | \Phi^{*T} | \text{HF} \rangle z_{v_j} = 0, \quad \text{for } t = p+1, \quad (49)$$

the second-order amplitudes $z_{\mu_i}^{(2)}$ then become identical to $\delta t_{\mu_i}^{(2)}$, and the third-order amplitudes $z_{\mu_i}^{(3)}$ become size-extensive, and therefore, non-size-extensive contributions first start to enter in sixth order in the energy. We also note that auxiliary spaces containing more than one excitation level are computationally intractable, since too much effort is then spent on optimizing amplitudes at the highest excitation levels, which are computationally most demanding, for amplitudes that are far from being converged at the lower

excitation levels. Unless otherwise specified, CL target states are in the following restricted to contain only one excitation level in the auxiliary space and non-size-extensive energy contributions therefore first enter in sixth order.

IV. CLUSTER PERTURBATION (CP) ENERGY FROM THE ENERGY LAGRANGIAN SERIES

In Sec. II, we introduced CL target states, and in Sec. III, we described how the amplitudes and the energy can be determined for a CL target state. In addition, we described in Sec. III how a series of CP energy corrections can be obtained for a CL target state. In this section, we describe how the series of CP energy corrections can be determined in a simpler manner using the energy Lagrangian^{20,21} for the CL target state. In this way, we also pave the road for the determination of response functions for a CL target state, as this determination is simplified by employing an energy which is bi-variational in the limit where the time-periodic perturbation operator vanishes. To simplify the derivation in this section, we consider specifically the CPSD(LT) model, for which the CC parent state is a CCSD state and the effect of introducing triple excitations in the CP wave function is described by a linear parametrization.

A. The energy Lagrangian for the CPSD(LT) model

For the CPSD(LT) model, we have $p = 2$ and $t = 3$, and the energy Lagrangian can be written as

$$L_{\text{CPSD(LT)}}(\mathbf{z}, \bar{\mathbf{z}}) = \langle \text{HF} | e^{-Z} H_0^{*T} e^Z | \text{HF} \rangle + \sum_{i=1}^3 \sum_{\mu_i} \bar{z}_{\mu_i} \times \langle \mu_i | e^{-Z} H_0^{*T} e^Z | \text{HF} \rangle, \quad (50)$$

where the amplitude equations [Eq. (24)] are added to the energy [Eq. (23)] using undetermined Lagrangian multipliers, \bar{z}_{μ_i} . Substituting the energy [Eq. (23)] and amplitude equations [Eq. (30)] into Eq. (50) gives

$$L_{\text{CPSD(LT)}}(\mathbf{z}, \bar{\mathbf{z}}) = E_{\text{CCSD}} + \sum_{i=1}^2 \sum_{\mu_i} \langle \text{HF} | \Phi^{*T} | \mu_i \rangle z_{\mu_i} + \sum_{i=1}^3 \sum_{\mu_i} \bar{z}_{\mu_i} \times \left(\sum_{j=1}^3 \sum_{v_j} A_{\mu_i v_j} z_{v_j} + \langle \mu_i | \Phi^{*T} | \text{HF} \rangle \delta_{i3} - z_{\mu_i} \left(\sum_{j=1}^2 \sum_{v_j} \langle \text{HF} | \Phi^{*T} | v_j \rangle z_{v_j} \right) \right), \quad (51)$$

where we have used Eqs. (33) and that (38) and the last term in Eq. (38) vanishes because the auxiliary space is restricted to contain only one excitation level [cf. Sec. III C].

The Lagrangian $L_{\text{CPSD(LT)}}(\mathbf{z}, \bar{\mathbf{z}})$ is variational with respect to the multipliers and amplitudes, giving the amplitude and multiplier equations

$$\frac{\partial L_{\text{CPSD(LT)}}(\mathbf{z}, \bar{\mathbf{z}})}{\partial \bar{z}_{\mu_i}} = \sum_{j=1}^3 \sum_{v_j} A_{\mu_i v_j} z_{v_j} + \langle \mu_i | \Phi^{*T} | \text{HF} \rangle \delta_{i3} - z_{\mu_i} \left(\sum_{j=1}^2 \sum_{v_j} \langle \text{HF} | \Phi^{*T} | v_j \rangle z_{v_j} \right) = 0, \quad i = 1, 2, 3, \quad (52)$$

$$\begin{aligned} \frac{\partial L_{\text{CPSD(LT)}}(\mathbf{z}, \bar{\mathbf{z}})}{\partial z_{\mu_i}} &= \langle \text{HF} | \Phi^{*T} | \mu_i \rangle (\delta_{i1} + \delta_{i2}) + \sum_{j=1}^3 \sum_{v_j} \bar{z}_{v_j} \\ &\times \left(A_{v_j \mu_i} - \delta_{v_j \mu_i} \left(\sum_{q=1}^2 \sum_{\lambda_q} \langle \text{HF} | \Phi^{*T} | \lambda_q \rangle z_{\lambda_q} \right) \right. \\ &\left. - z_{v_j} \langle \text{HF} | \Phi^{*T} | \mu_i \rangle (\delta_{i1} + \delta_{i2}) \right) = 0, \quad i = 1, 2, 3. \end{aligned} \quad (53)$$

B. Perturbative corrections to the energy Lagrangian

The amplitudes and multipliers of the target state can be determined by solving Eqs. (52) and (53), using perturbation theory with the parent-state similarity-transformed fluctuation potential Φ^{*T} as the perturbation operator. To do this, we write Eqs. (52) and (53) in the form

$$\sum_{j=1}^3 \sum_{v_j} A_{\mu_i v_j} z_{v_j} = -\langle \mu_i | \Phi^{*T} | \text{HF} \rangle \delta_{i3} + z_{\mu_i} \left(\sum_{j=1}^2 \sum_{v_j} \langle \text{HF} | \Phi^{*T} | v_j \rangle z_{v_j} \right), \quad i = 1, 2, 3, \quad (54)$$

$$\begin{aligned} \sum_{j=1}^3 \sum_{v_j} \bar{z}_{v_j} A_{v_j \mu_i} &= -\langle \text{HF} | \Phi^{*T} | \mu_i \rangle (\delta_{i1} + \delta_{i2}) + \bar{z}_{\mu_i} \\ &\times \left(\sum_{j=1}^2 \sum_{v_j} \langle \text{HF} | \Phi^{*T} | v_j \rangle z_{v_j} \right) + \left(\sum_{j=1}^3 \sum_{v_j} \bar{z}_{v_j} z_{v_j} \right) \\ &\times \langle \text{HF} | \Phi^{*T} | \mu_i \rangle (\delta_{i1} + \delta_{i2}), \quad i = 1, 2, 3. \end{aligned} \quad (55)$$

In CP theory, the amplitude and multiplier corrections are determined using the parent-state Jacobian partitioning of the extended parent-state Jacobian. This partitioning is given in Eqs. (39) and (40) and can for the CPSD(LT) model be written as

$$A_{\mu_i v_j} = A_{\mu_i v_j}^{(0)} + A_{\mu_i v_j}^{(1)}, \quad i, j = 1, 2, 3, \quad (56)$$

where

$$\begin{aligned} A_{\mu_i v_j}^{(0)} &= \langle \mu_i | [H_0^{*T}, \theta_{v_j}] | \text{HF} \rangle \left(\delta_{i1} \delta_{j1} + \delta_{i1} \delta_{j2} + \delta_{i2} \delta_{j1} + \delta_{i2} \delta_{j2} \right) \\ &+ \varepsilon_{v_j} \delta_{\mu_i v_j} \delta_{i3} \delta_{j3}, \quad i, j = 1, 2, 3, \end{aligned} \quad (57a)$$

$$\begin{aligned} A_{\mu_i v_j}^{(1)} &= \langle \mu_i | [\Phi^{*T}, \theta_{v_j}] | \text{HF} \rangle \left(\delta_{i1} \delta_{j3} + \delta_{i2} \delta_{j3} + \delta_{i3} \delta_{j1} + \delta_{i3} \delta_{j2} + \delta_{i3} \delta_{j3} \right), \\ &i, j = 1, 2, 3. \end{aligned} \quad (57b)$$

The singles-and-doubles component of the matrix $\mathbf{A}^{(0)}$ is equal to the parent-state CCSD Jacobian

$$J_{\mu_i v_j}^{\text{CCSD}} = \langle \mu_i | [H_0^{*T}, \theta_{v_j}] | \text{HF} \rangle, \quad i, j = 1, 2. \quad (58)$$

In the two-component form, the matrix $\mathbf{A}^{(0)}$ can be written as

$$\mathbf{A}^{(0)} = \begin{pmatrix} J^{\text{CCSD}} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\varepsilon}_T \end{pmatrix}, \quad (59)$$

where $\boldsymbol{\varepsilon}_T$ is a diagonal matrix containing orbital energy differences in the triples space

$$(\boldsymbol{\varepsilon}_T)_{\mu_3 v_3} = \varepsilon_{v_3} \delta_{\mu_3 v_3}. \quad (60)$$

The matrix $\mathbf{A}^{(1)}$ contains only terms that are of first order in Φ^{*T} . Expanding the amplitudes and multipliers in orders of Φ^{*T} ,

$$z_{\mu_i} = z_{\mu_i}^{(0)} + z_{\mu_i}^{(1)} + z_{\mu_i}^{(2)} + \dots, \quad (61)$$

$$\bar{z}_{\mu_i} = \bar{z}_{\mu_i}^{(0)} + \bar{z}_{\mu_i}^{(1)} + \bar{z}_{\mu_i}^{(2)} + \dots, \quad (62)$$

substituting Eqs. (57a) and (57b) into Eqs. (54) and (55), and using Eq. (58), we obtain the k th order corrections for the amplitudes and multipliers expressed in the two-component form

$$\begin{aligned} \sum_{j=1}^2 \sum_{v_j} J_{\mu_i v_j}^{\text{CCSD}} z_{v_j}^{(k)} &= -\sum_{v_3} A_{\mu_i v_3}^{(1)} z_{v_3}^{(k-1)} \\ &+ \left\{ z_{\mu_i} \left(\sum_{j=1}^2 \sum_{v_j} \langle \text{HF} | \Phi^{*T} | v_j \rangle z_{v_j} \right) \right\}^{\{k\}}, \quad i = 1, 2, \end{aligned} \quad (63a)$$

$$\begin{aligned} \varepsilon_{\mu_3} z_{\mu_3}^{(k)} &= -\langle \mu_3 | \Phi^{*T} | \text{HF} \rangle \delta_{k1} - \sum_{j=1}^3 \sum_{v_j} A_{\mu_3 v_j}^{(1)} z_{v_j}^{(k-1)} \\ &+ \left\{ z_{\mu_3} \left(\sum_{j=1}^2 \sum_{v_j} \langle \text{HF} | \Phi^{*T} | v_j \rangle z_{v_j} \right) \right\}^{\{k\}}, \end{aligned} \quad (63b)$$

$$\begin{aligned} \sum_{j=1}^2 \sum_{v_j} \bar{z}_{v_j}^{(k)} J_{v_j \mu_i}^{\text{CCSD}} &= -\langle \text{HF} | \Phi^{*T} | \mu_i \rangle \delta_{k1} - \sum_{v_3} \bar{z}_{v_3}^{(k-1)} A_{v_3 \mu_i}^{(1)} \\ &+ \left\{ \bar{z}_{\mu_i} \left(\sum_{j=1}^2 \sum_{v_j} \langle \text{HF} | \Phi^{*T} | v_j \rangle z_{v_j} \right) \right. \\ &\left. + \left(\sum_{j=1}^3 \sum_{v_j} \bar{z}_{v_j} z_{v_j} \right) \langle \text{HF} | \Phi^{*T} | \mu_i \rangle \right\}^{\{k\}}, \quad i = 1, 2, \end{aligned} \quad (64a)$$

$$\bar{z}_{\mu_3}^{(k)} \varepsilon_{\mu_3} = -\sum_{j=1}^3 \sum_{v_j} \bar{z}_{v_j}^{(k-1)} A_{v_j \mu_3}^{(1)} + \left\{ \bar{z}_{\mu_3} \left(\sum_{j=1}^2 \sum_{v_j} \langle \text{HF} | \Phi^{*T} | v_j \rangle z_{v_j} \right) \right\}^{\{k\}}, \quad (64b)$$

where we have used that the zeroth-order amplitudes and multipliers vanish

$$z_{\mu_i}^{(0)} = \bar{z}_{\mu_i}^{(0)} = 0, \quad i = 1, 2, 3, \quad (65)$$

and where $\{ \cdot \}^{\{k\}}$ denotes that from the whole expression in parentheses only terms of order k in Φ^{*T} are retained.

The first-, second-, and third-order amplitudes can be obtained from Eq. (63) as

$$z_{\mu_i}^{(1)} = 0, \quad i = 1, 2, \quad (66a)$$

$$\varepsilon_{\mu_3} z_{\mu_3}^{(1)} = -\langle \mu_3 | \Phi^{*T} | \text{HF} \rangle, \quad (66b)$$

$$\sum_{j=1}^2 \sum_{\nu_j} J_{\mu_i \nu_j}^{\text{CCSD}} z_{\nu_j}^{(2)} = - \sum_{\nu_3} \langle \mu_i | [\Phi^{*T}, \theta_{\nu_3}] | \text{HF} \rangle z_{\nu_3}^{(1)}, \quad i = 1, 2, \quad (67a)$$

$$\varepsilon_{\mu_3} z_{\mu_3}^{(2)} = - \sum_{\nu_3} \langle \mu_3 | [\Phi^{*T}, \theta_{\nu_3}] | \text{HF} \rangle z_{\nu_3}^{(1)}, \quad (67b)$$

$$\sum_{j=1}^2 \sum_{\nu_j} J_{\mu_i \nu_j}^{\text{CCSD}} z_{\nu_j}^{(3)} = - \sum_{\nu_3} \langle \mu_i | [\Phi^{*T}, \theta_{\nu_3}] | \text{HF} \rangle z_{\nu_3}^{(2)}, \quad i = 1, 2, \quad (68a)$$

$$\varepsilon_{\mu_3} z_{\mu_3}^{(3)} = - \sum_{j=1}^3 \sum_{\nu_j} \langle \mu_3 | [\Phi^{*T}, \theta_{\nu_j}] | \text{HF} \rangle z_{\nu_j}^{(2)}, \quad (68b)$$

where to obtain Eq. (68) we have used Eq. (66a).

Similarly, for the first- and second-order multipliers, we obtain from Eq. (64)

$$\sum_{j=1}^2 \sum_{\nu_j} \bar{z}_{\nu_j}^{(1)} J_{\nu_j \mu_i}^{\text{CCSD}} = - \langle \text{HF} | \Phi^{*T} | \mu_i \rangle, \quad i = 1, 2, \quad (69a)$$

$$\bar{z}_{\mu_3}^{(1)} = 0, \quad (69b)$$

$$\sum_{j=1}^2 \sum_{\nu_j} \bar{z}_{\nu_j}^{(2)} J_{\nu_j \mu_i}^{\text{CCSD}} = - \sum_{\nu_3} \bar{z}_{\nu_3}^{(1)} \langle \nu_3 | [\Phi^{*T}, \theta_{\mu_i}] | \text{HF} \rangle = 0, \quad i = 1, 2, \quad (70a)$$

$$\varepsilon_{\mu_3} \bar{z}_{\mu_3}^{(2)} = - \sum_{j=1}^2 \sum_{\nu_j} \bar{z}_{\nu_j}^{(1)} \langle \nu_j | [\Phi^{*T}, \theta_{\mu_3}] | \text{HF} \rangle, \quad (70b)$$

where to obtain the last equality in Eq. (70a) we have used Eq. (69b). Equation (70a) implies that

$$\bar{z}_{\mu_i}^{(2)} = 0, \quad i = 1, 2. \quad (71)$$

The energy Lagrangian in Eq. (50) may be expanded in orders of the perturbation

$$L_{\text{CPSD(LT)}} = \sum_{q=0} L_{\text{CPSD(LT)}}^{(q)}. \quad (72)$$

We now determine the energy corrections of the CPSD(LT) series from Eq. (50) using the $2n + 1$ rule for the amplitudes and the $2n + 2$ rule for the multipliers (see, for example, Refs. 20–22). The energy corrections through sixth order become

$$L_{\text{CPSD(LT)}}^{(0)} = E_{\text{CCSD}}, \quad (73)$$

$$L_{\text{CPSD(LT)}}^{(1)} = 0, \quad (74)$$

$$L_{\text{CPSD(LT)}}^{(2)} = 0, \quad (75)$$

$$L_{\text{CPSD(LT)}}^{(3)} = \sum_{i=1}^2 \sum_{\mu_i} \sum_{\nu_3} \bar{z}_{\mu_i}^{(1)} \langle \mu_i | [\Phi^{*T}, \theta_{\nu_3}] | \text{HF} \rangle z_{\nu_3}^{(1)}, \quad (76)$$

$$L_{\text{CPSD(LT)}}^{(4)} = \sum_{i=1}^2 \sum_{\mu_i} \sum_{\nu_3} \bar{z}_{\mu_i}^{(1)} \langle \mu_i | [\Phi^{*T}, \theta_{\nu_3}] | \text{HF} \rangle z_{\nu_3}^{(2)}, \quad (77)$$

$$L_{\text{CPSD(LT)}}^{(5)} = \sum_{\mu_3} \sum_{j=1}^3 \sum_{\nu_j} \bar{z}_{\mu_3}^{(2)} \langle \mu_3 | [\Phi^{*T}, \theta_{\nu_j}] | \text{HF} \rangle z_{\nu_j}^{(2)}, \quad (78)$$

$$L_{\text{CPSD(LT)}}^{(6)} = \sum_{\mu_3} \sum_{j=1}^3 \sum_{\nu_j} \bar{z}_{\mu_3}^{(2)} \langle \mu_3 | [\Phi^{*T}, \theta_{\nu_j}] | \text{HF} \rangle z_{\nu_j}^{(3)} + \left(\sum_{\mu_3} \bar{z}_{\mu_3}^{(2)} z_{\mu_3}^{(1)} + \sum_{i=1}^2 \sum_{\mu_i} \bar{z}_{\mu_i}^{(1)} z_{\mu_i}^{(2)} \right) \sum_{j=1}^2 \sum_{\nu_j} \langle \text{HF} | \Phi^{*T} | \nu_j \rangle z_{\nu_j}^{(2)}. \quad (79)$$

C. Comparison of energy corrections for the CPSD(LT) and CPSD(T) models

We will now compare the lowest-order energy corrections for the CPSD(LT) and CPSD(T) models. The energy series for the CPSD(T) model was derived in Paper I.¹ The lowest-order energy and cluster amplitude corrections for the CPSD(T) series were determined in Paper I¹ and are given in Appendixes A and B, respectively. In Appendix B, ${}^* \bar{t}^{\text{CCSD}}$ is the solution to the CCSD parent-state multiplier equation

$$\langle \text{HF} | [H_0^{*T}, \theta_{\nu_j}] | \text{HF} \rangle + \sum_{i=1}^2 \sum_{\mu_i} {}^* \bar{t}_{\mu_i}^{\text{CCSD}} J_{\mu_i \nu_j}^{\text{CCSD}} = 0, \quad j = 1, 2. \quad (80)$$

To compare the lowest-order CPSD(LT) energy corrections in Eqs. (73)–(79) with the CPSD(T) energy corrections given in Appendix A, we first note that the CPSD(LT) amplitudes $z_{\mu_i}^{(1)}$, $z_{\mu_i}^{(2)}$, $z_{\mu_i}^{(3)}$ in Eqs. (66)–(68) are identical to the corresponding CPSD(T) amplitudes in Appendix B

$$z_{\mu_i}^{(q)} = \delta t_{\mu_i}^{(q)}, \quad i = 1, 2, 3, \quad q = 1, 2, 3. \quad (81)$$

Comparing Eqs. (69a) and (80), we see that $\bar{z}_{\mu_i}^{(1)} = {}^* \bar{t}_{\mu_i}^{\text{CCSD}}$, $i = 1, 2$, and the multipliers in Eqs. (69) and (70) therefore may be expressed as

$$\bar{z}_{\mu_i}^{(1)} = {}^* \bar{t}_{\mu_i}^{\text{CCSD}}, \quad i = 1, 2, \quad (82a)$$

$$\bar{z}_{\mu_3}^{(1)} = 0, \quad (82b)$$

$$\bar{z}_{\mu_i}^{(2)} = 0, \quad i = 1, 2, \quad (83a)$$

$$\varepsilon_{\mu_3} \bar{z}_{\mu_3}^{(2)} = - \langle {}^* \bar{t}^{\text{CCSD}} | [\Phi^{*T}, \theta_{\mu_3}] | \text{HF} \rangle. \quad (83b)$$

Comparing the CPSD(LT) and CPSD(T) energy series, we see that both series have the CCSD energy as the zeroth-order energy and that the first- and second-order corrections vanish. Using Eqs. (80) and (81), the third- and fourth-order CPSD(LT) energy corrections in Eqs. (76) and (77), respectively, may be written as

$$L_{\text{CPSD(LT)}}^{(3)} = \langle {}^* \bar{t}^{\text{CCSD}} | [\Phi^{*T}, \delta T^{(1)}] | \text{HF} \rangle, \quad (84)$$

$$L_{\text{CPSD(LT)}}^{(4)} = \langle {}^* \bar{t}^{\text{CCSD}} | [\Phi^{*T}, \delta T_3^{(2)}] | \text{HF} \rangle. \quad (85)$$

These energy contributions are identical to the third- and fourth-order CPSD(T) energy corrections in Appendix A. The fifth-order CPSD(LT) energy correction in Eq. (78) becomes

$$L_{\text{CPSD(LT)}}^{(5)} = - \sum_{\mu_3} \langle {}^* \bar{t}^{\text{CCSD}} | [\Phi^{*T}, \theta_{\mu_3}] | \text{HF} \rangle \varepsilon_{\mu_3}^{-1} \langle \mu_3 | [\Phi^{*T}, \delta T^{(2)}] | \text{HF} \rangle = \langle {}^* \bar{t}^{\text{CCSD}} | [\Phi^{*T}, \delta T_3^{(3)}] | \text{HF} \rangle, \quad (86)$$

where to obtain the first equality, we have used Eqs. (81) and (83b) and to obtain the last equality, we have used Eq. (B3b) in Appendix B. Compared to $E_0^{(5)}$ in Eq. (A6) in Appendix A, the last two contributions in $E_0^{(5)}$ are absent in the expression for $L_{\text{CPSD(LT)}}^{(5)}$. The fifth-order term $L_{\text{CPSD(LT)}}^{(5)}$ is size-extensive.

The sixth-order term in Eq. (79) contains a first term, $L_{\text{CPSD(LT)}}^{(6,ext)}$, that is size-extensive and a second term, $L_{\text{CPSD(LT)}}^{(6,non-ext)}$, that is not size-extensive

$$L_{\text{CPSD(LT)}}^{(6)} = L_{\text{CPSD(LT)}}^{(6,ext)} + L_{\text{CPSD(LT)}}^{(6,non-ext)}. \quad (87)$$

The size-extensive term may be expressed as

$$L_{\text{CPSD(LT)}}^{(6,ext)} = - \sum_{j=1,3} \sum_{\mu_3} \langle \hat{t}^{* \text{CCSD}} | [\Phi^{*T}, \theta_{\mu_3}] | \text{HF} \rangle \epsilon_{\mu_3}^{-1} \langle \mu_3 | [\Phi^{*T}, \delta T^{(3)}] | \text{HF} \rangle. \quad (88)$$

The size-extensive term in Eq. (88) is a part of the first term of the sixth-order energy $E_0^{(6)}$ in Eq. (A7) in Appendix A

$$\begin{aligned} \langle \hat{t}^{* \text{CCSD}} | [\Phi^{*T}, \delta T_3^{(4)}] | \text{HF} \rangle &= - \sum_{\mu_3} \langle \hat{t}^{* \text{CCSD}} | [\Phi^{*T}, \theta_{\mu_3}] | \text{HF} \rangle \epsilon_{\mu_3}^{-1} \\ &\quad \times \langle \mu_3 | [\Phi^{*T}, \delta T^{(3)}] | \text{HF} \rangle \\ &\quad - \sum_{\mu_3} \langle \hat{t}^{* \text{CCSD}} | [\Phi^{*T}, \theta_{\mu_3}] | \text{HF} \rangle \epsilon_{\mu_3}^{-1} \\ &\quad \times \langle \mu_3 | [[\Phi^{*T}, \delta T^{(1)}], \delta T^{(2)}] | \text{HF} \rangle. \end{aligned} \quad (89)$$

The second term in Eq. (89) and the last three terms of $E_0^{(6)}$ in Eq. (A7) in Appendix A are the terms that occur only in $E_0^{(6)}$ and are replaced in $L_{\text{CPSD(LT)}}^{(6)}$ by the non-size-extensive term

$$L_{\text{CPSD(LT)}}^{(6,non-ext)} = \left(\sum_{\mu_3} z_{\mu_3}^{(2)} z_{\mu_3}^{(1)} + \sum_{i=1}^2 \sum_{\mu_i} z_{\mu_i}^{(1)} z_{\mu_i}^{(2)} \right) \sum_{j=1}^2 \sum_{\nu_j} \langle \text{HF} | \Phi^{*T} | \nu_j \rangle z_{\nu_j}^{(2)}. \quad (90)$$

Summarizing, the CPSD(LT) and CPSD(T) energy series are identical through fourth order. In fifth order, the CPSD(LT) energy contributions are included in the fifth-order CPSD(T) contribution that in addition contains two connected contributions. In sixth

order, the CPSD(LT) energy corrections $L_{\text{CPSD(LT)}}^{(6)}$ contain a size-extensive term, $L_{\text{CPSD(LT)}}^{(6,ext)}$, and a non-size-extensive term, $L_{\text{CPSD(LT)}}^{(6,non-ext)}$. The size-extensive term is contained in the sixth-order CPSD(T) energy, $E_0^{(6)}$, that in addition contains four connected contributions that replace the non-size-extensive term, $L_{\text{CPSD(LT)}}^{(6,non-ext)}$.

D. Numerical comparison of the accuracy of the energy corrections for the CPSD(LT) and CPSD(T) models

We now report calculations of the CPSD(LT) and CPSD(T) energy series through sixth order, which allow us to compare the attainable accuracy of the two series. Our test systems are the HF molecule at three bond lengths using the aug-cc-pVTZ basis, the CH₂ molecule using the cc-pVTZ basis, and the N₂ molecule using the cc-pVTZ basis. The three bond distances for HF are chosen as R_e , $1.5R_e$, and $2R_e$ with $R_e = 0.91680 \text{ \AA}$, the geometry of CH₂ is chosen as the equilibrium geometry given in Ref. 23, and the bond length of N₂ is the equilibrium bond length of 1.09768 \AA . The calculations employ the lowest closed-shell restricted Hartree-Fock determinant as a reference state, so the reference state corresponds to the ground state for HF and N₂ and the lowest excited state for CH₂. The 1s core on atoms different from H is kept doubly occupied in all calculations. The calculations were carried out using the tools of the general coupled cluster codes²⁴ as implemented in LUCIA.²⁵

The HF molecule has been selected to examine the corrections for a molecule containing an electron-rich atom, and the three bond lengths allow us to examine the size of the corrections for a system without static correlation at R_e , a small degree of static correlation at $1.5R_e$, and a moderate degree of static correlation at $2R_e$. The N₂ molecule provides an example of a molecule without electron-rich atoms and a triple bond, whereas the CH₂ molecule is a molecule without electron-rich atoms and a low-lying doubly excited state that leads to a slow convergence.

For the CPSD(T) energy series, it is known from Paper I¹ that the lower odd-order corrections lead to significant improvements of the ground-state energies, whereas the lower even-order corrections lead only to marginal improvements for molecules containing electron-rich atoms, including the fluorine atom. It is therefore generally advisable to use an odd order as the largest calculated order. For that reason, we give in Table I the deviations of the CPSD(T)

TABLE I. Summary of the CPSD(T) and CPSD(LT) ground-state energy corrections (in Hartree) through fifth order.

	HF at R_e	HF at $1.5R_e$	HF at $2R_e$	N ₂	CH ₂
Deviations compared to CCSDT energies (recovered percentage of the full triples correlation energy in parentheses)					
$E_0^{(3)}, L_{\text{CPSD(LT)}}^{(3)}$	0.000573 (92.4%)	0.000969 (91.2%)	0.001890 (88.6%)	0.001770 (90.3%)	0.001220 (78.3%)
$E_0^{(4)}, L_{\text{CPSD(LT)}}^{(4)}$	0.000459 (93.9%)	0.000995 (90.9%)	0.001961 (88.1%)	0.001436 (92.1%)	0.000620 (89.0%)
$E_0^{(5)}$	0.000021 (99.7%)	0.000017 (99.8%)	-0.000035 (100.2%)	0.000138 (99.2%)	0.000230 (95.9%)
$L_{\text{CPSD(LT)}}^{(5)}$	0.000019 (99.8%)	0.000012 (99.9%)	-0.000067 (100.4%)	0.000128 (99.3%)	0.000229 (95.9%)
$\Delta E(\text{T})$	-0.007550	-0.010986	-0.016518	-0.018201	-0.005622
$E(\text{CCSDT})$	-100.349593	-100.260133	-100.175189	-109.373560	-39.062181

TABLE II. Summary of the $E_0^{(6)}$ and $L_{\text{CPSD(LT)}}^{(6)}$ ground-state energy corrections (in Hartree).

	HF at R_e	HF at $1.5 R_e$	HF at $2 R_e$	N_2	CH_2
Deviations compared to CCSDT energies (recovered percentage of the full triples correlation energy in parentheses)					
$E_0^{(6)}$	0.000043 (99.4%)	0.000151 (98.6%)	0.000369 (97.8%)	0.000134 (99.3%)	0.000124 (97.8%)
$L_{\text{CPSD(LT)}}^{(6)}$	0.000020 (99.7%)	0.000129 (99.4%)	-0.000063 (100.4%)	-0.000068 (100.4%)	0.000084 (98.5%)
Contributions to $L_{\text{CPSD(LT)}}^{(6)}$ energy					
$L_{\text{CPSD(LT)}}^{(6,ext)}$	0.000021	0.000117	0.000259	-0.000050	-0.000121
$L_{\text{CPSD(LT)}}^{(6,non-ext)}$	-0.000019	-0.000060	-0.000255	-0.000146	-0.000024
Total	0.000001	0.000057	0.000004	-0.000196	-0.000145

and CPSD(LT) energies through order five, as compared to the full CC singles-doubles-and-triples (CCSDT) energies, as well as the recovered percentage of the full triples correlation energy. For completeness, the full CCSDT energies and the full triple correlation energy calculated as $\Delta E(T) = E(\text{CCSDT}) - E(\text{CCSD})$ are also given. Since the sixth-order energies are the first energy corrections where the CPSD(LT) method gives a non-size-extensive contribution, we give these energies in Table II, although sixth-order methods, as even-order methods, are not expected to provide a useful computational scheme, as discussed above.

Consider first the results for orders three and four (Table I), for which the CPSD(T) and CPSD(LT) energy corrections are identical. The third-order energies provide about 90% of the full triples correlation energy for the three inter-nuclear distances of HF and N_2 , whereas only about 80% is recovered for CH_2 . In absolute terms, the deviation at third order is less than 0.001 hartree for HF at R_e and $1.5 R_e$, whereas the deviation is between 0.001 and 0.002 Hartree for the remaining three cases. For HF, the deviation increases by about a factor of two when the bond length is increased by $0.5 R_e$. Going from order three to four leads only to a significant improvement in accuracy for CH_2 , where the fourth order correction gives a triples correlation energy that is about 90% of the full triples correlation energy.

The fifth-order CPSD(LT) energy correction is given by Eq. (78). The correction is size-extensive, but includes only the first of the three terms of the CPSD(T) energy correction in Eq. (A6) of Appendix A. The fifth-order CPSD(T) energies were shown in Paper I¹ to be very accurate, and this is also observed for the calculations reported in Table I: the deviations from the CCSDT results are 1% or less for all cases except CH_2 , where the deviation is about 4%. In absolute terms, the size of the deviations is less than 0.0001 Hartree for HF at the three distances, about 0.0001 Hartree for N_2 , and about 0.0002 Hartree for CH_2 . It is worth seeing that the fifth-order energies of the CPSD(LT) model give the same improvement in accuracy as the CPSD(T) ones. As a matter of fact, the absolute deviations from the CCSDT energies are slightly smaller for the CPSD(LT) model. The size of the fifth-order energy $L_{\text{CPSD(LT)}}^{(5)}$ must therefore be much larger than the size of the two terms occurring only in $E_0^{(5)}$. Indeed, the size of $L_{\text{CPSD(LT)}}^{(5)}$ is about two orders

of magnitude or more larger than the size of the two terms occurring only in $E_0^{(5)}$. With respect to the performance of the CPSD(LT) method at fifth order, it is concluded that the accuracy of this method equals that of the fifth-order CPSD(T) calculations for the considered examples.

The sixth-order CPSD(LT) energy correction, $L_{\text{CPSD(LT)}}^{(6)}$, is given in Eqs. (79) and (87). The first term in Eq. (87), $L_{\text{CPSD(LT)}}^{(6,ext)}$, is size-extensive and is also contained in the sixth-order CPSD(T) energy, $E_0^{(6)}$ given in Eq. (A7), but the second, and non-size-extensive, term, $L_{\text{CPSD(LT)}}^{(6,non-ext)}$, is not a part of $E_0^{(6)}$. From Table II, it is noticed that including the sixth-order CPSD(T) or CPSD(LT) energy corrections only gives a sizable reduction of the deviation for CH_2 , where the deviations for both methods are reduced from about 4% to about 2%. The CPSD(LT) energies through sixth order are actually slightly closer to the full triples correction than the CPSD(T) energies through sixth order. The size-extensive and non-size-extensive sixth-order terms in CPSD(LT), $L_{\text{CPSD(LT)}}^{(6,ext)}$ and $L_{\text{CPSD(LT)}}^{(6,non-ext)}$, are given in Table II. For HF, the size-extensive terms are positive and the non-size-extensive terms are negative, which leads to cancellations in the sum of these terms. For N_2 and CH_2 , both terms are negative and their relative sizes vary. As the non-size-extensive terms are significant already for the present calculations, where only 6-10 electrons are correlated, it is obvious that the sixth-order CPSD(LT) ground-state energies will not provide accurate approximations for larger molecules.

V. RESPONSE FUNCTIONS FOR A CL TARGET STATE

In this section, we apply a time-periodic perturbation to a molecular system described by a CL target state in order to determine the response functions for the target state. As the target state is linearly parametrized, we also use a linear parametrization to describe the time evolution of the CL target state. The response functions for the target state simplify if the time evolution is expressed in a basis, in which the energy is bi-variational. This can be accomplished by introducing the bi-orthonormal basis defined by the energy Lagrangian. In Subsection V A, we determine this bi-orthonormal basis. Response function theory, as developed

in Ref. 11, is then applied to determine the response functions for the CL target state. Explicit expressions will be given for the linear, quadratic, and cubic response functions.

A. Bi-variational energy Lagrangian for a CL target state

To determine a bi-orthonormal basis in which the energy is bi-variational, we introduce the energy Lagrangian for the energy and amplitude equations in Eqs. (23) and (24)

$$L_0(\mathbf{z}, \bar{\mathbf{z}}) = \langle \text{HF} | e^{-Z} H_0^* e^Z | \text{HF} \rangle + \sum_{i=1}^t \bar{z}_{\mu_i} \langle \mu_i | e^{-Z} H_0^* e^Z | \text{HF} \rangle \\ = \langle \text{HF} | e^{\bar{Z}} e^{-Z} e^{-*T} H_0 e^{*T} e^Z e^{-\bar{Z}} | \text{HF} \rangle, \quad (91)$$

where

$$\bar{Z} = \sum_{i=1}^t \sum_{\mu_i} \bar{z}_{\mu_i} | \text{HF} \rangle \langle \mu_i |. \quad (92)$$

To obtain the last equality in Eq. (91), we have used that

$$\langle \text{HF} | e^{\bar{Z}} = \langle \text{HF} | + \sum_{i=1}^t \sum_{\mu_i} \bar{z}_{\mu_i} \langle \mu_i | \quad (93)$$

and

$$e^{-\bar{Z}} | \text{HF} \rangle = | \text{HF} \rangle. \quad (94)$$

The energy Lagrangian in Eq. (91) is a generalized Hamiltonian expectation value for the bi-orthonormal ket |CL⟩ and bra ⟨CL| state

$$| \text{CL} \rangle = e^{*T} e^Z e^{-\bar{Z}} | \text{HF} \rangle, \quad (95a)$$

$$\langle \text{CL} | = \langle \text{HF} | e^{\bar{Z}} e^{-Z} e^{-*T}, \quad (95b)$$

where the amplitudes and multipliers satisfy the variational conditions

$$\frac{\partial L_0(\mathbf{z}, \bar{\mathbf{z}})}{\partial \bar{z}_{\mu_i}} = \langle \mu_i | e^{-Z} e^{-*T} H_0 e^{*T} e^Z | \text{HF} \rangle = 0, \quad (96)$$

$$\frac{\partial L_0(\mathbf{z}, \bar{\mathbf{z}})}{\partial z_{\mu_i}} = \langle \text{HF} | \left[e^{-Z} e^{-*T} H_0 e^{*T} e^Z, | \mu_i \rangle \langle \text{HF} | \right] | \text{HF} \rangle \\ + \sum_{j=1}^t \sum_{\nu_j} \bar{z}_{\nu_j} \langle \nu_j | \left[e^{-Z} e^{-*T} H_0 e^{*T} e^Z, | \mu_i \rangle \langle \text{HF} | \right] | \text{HF} \rangle = 0. \quad (97)$$

The energy Lagrangian is bi-variational in the bi-orthonormal basis

$$| \mathcal{B}^{*TZ\bar{Z}} \rangle = \left\{ e^{*T} e^Z e^{-\bar{Z}} | \text{HF} \rangle, e^{*T} e^Z e^{-\bar{Z}} | \mu_i \rangle \right\}, \quad i = 1, 2, \dots, t, \quad (98a)$$

$$\langle \mathcal{B}^{\bar{Z}Z^*T} | = \left\{ \langle \text{HF} | e^{\bar{Z}} e^{-Z} e^{-*T}, \langle \mu_i | e^{\bar{Z}} e^{-Z} e^{-*T} \right\}, \quad i = 1, 2, \dots, t. \quad (98b)$$

To see this, consider the Hamiltonian matrix in the bi-orthonormal basis in Eq. (98). The HF-HF component of the Hamiltonian matrix is equal to the energy Lagrangian in Eq. (91), and the Hamiltonian interaction elements between the |CL⟩ ground state and its orthogonal complement set of states vanish

$$\langle \mu_i | e^{\bar{Z}} e^{-Z} e^{-*T} H_0 e^{*T} e^Z e^{-\bar{Z}} | \text{HF} \rangle = 0, \quad (99)$$

$$\langle \text{HF} | e^{\bar{Z}} e^{-Z} e^{-*T} H_0 e^{*T} e^Z e^{-\bar{Z}} | \mu_i \rangle = 0. \quad (100)$$

To obtain Eqs. (99) and (100), the variational conditions in Eqs. (96) and (97) must be used.

B. Response function theory for the time-evolving CL target state

We now determine response functions for the |CL⟩ ground state following the outline of Ref. 11. The time evolution of the |CL⟩ state is linearly expanded in the bi-orthonormal basis of Eq. (98), in which the energy is bi-variational. We determine the linear, quadratic, and cubic response functions and show that the response functions have the same simple structure as the response functions for a linearly parametrized variational CI state.¹¹

1. The time-periodic Hamiltonian and its eigenvalue equation

We consider a system described by a time-dependent bounded Hermitian Hamiltonian $H(t, \epsilon)$ ¹¹

$$H(t, \epsilon) = H_0 + V(t, \epsilon), \quad (101)$$

where H_0 is the unperturbed time-independent Hamiltonian of Eq. (22) and $V(t, \epsilon)$ is a physical²⁶ perturbation operator that is Hermitian and periodic in time with a period T

$$V(t + T, \epsilon) = V(t, \epsilon). \quad (102)$$

$V(t, \epsilon)$ can be expanded in a sum over Fourier components

$$V(t, \epsilon) = \sum_j X_j \epsilon_{X_j}(\omega_{X_j}) \exp(-i\omega_{X_j} t), \quad (103)$$

where X_j is a Hermitian time-independent operator and $\epsilon_{X_j}(\omega_{X_j})$ is the associated perturbation strength for the real frequency ω_{X_j} . ϵ denotes a set of perturbation strengths $\epsilon_{X_j}(\omega_{X_j})$. It follows from the Hermiticity of $V(t, \epsilon)$ that the sum in Eq. (103) includes for each term $X_j \epsilon_{X_j}(\omega_{X_j}) \exp(-i\omega_{X_j} t)$ also its adjoint $X_j^\dagger \epsilon_{X_j}(-\omega_{X_j}) \exp(i\omega_{X_j} t)$ with

$$\epsilon_{X_j}(-\omega_{X_j}) = \epsilon_{X_j}^*(\omega_{X_j}). \quad (104)$$

From the periodicity of $V(t, \epsilon)$ [Eq. (102)], we can determine a fundamental frequency ω_T

$$\omega_T = \frac{2\pi}{T} \quad (105)$$

such that the frequencies in Eq. (103) become integers multiplied on the fundamental frequency

$$\omega_{X_j} = n_{X_j} \omega_T. \quad (106)$$

We now consider the solution to the time-dependent Schrödinger equation for the time-periodic Hamiltonian, $H(t, \epsilon)$ of Eq. (101),

$$H(t, \epsilon) \tilde{0}(t, \epsilon) = i \frac{\partial}{\partial t} \tilde{0}(t, \epsilon). \quad (107)$$

It has been shown in Ref. 11 that for the time-periodic Hamiltonian in Eq. (101), the time-dependent wave function, $|\tilde{0}(t, \epsilon)\rangle$, can be written in the phase-isolated form

$$|\tilde{0}(t, \epsilon)\rangle = \exp\left(-i(\mathcal{E}(\epsilon)t + \mathcal{F}_{P_0}(t, \epsilon))\right)|0_R(t, \epsilon)\rangle, \quad (108)$$

where $\mathcal{E}(\epsilon)$ is a real time-independent eigenvalue (referred to as the quasi-energy) of the steady-state time-dependent Schrödinger equation,^{11,27} $\mathcal{F}_{P_0}(t, \epsilon)$ is a real time-periodic phase, and $|0_R(t, \epsilon)\rangle$ is a unit-normalized time-periodic regular wave function that can be written as

$$|0_R(t, \epsilon)\rangle = N(t, \epsilon)|0_I(t, \epsilon)\rangle, \quad (109)$$

where $N(t, \epsilon)$ is a time-periodic real normalization constant

$$N(t, \epsilon) = \langle 0_I(t, \epsilon) | 0_I(t, \epsilon) \rangle^{-1/2}, \quad (110)$$

and where $|0_I(t, \epsilon)\rangle$ is time-periodic and intermediate-normalized against a bra reference state. We will determine response functions for the state $|\text{CL}\rangle$ of Eq. (95a), using a linear parametrization of the time evolution of this CL state. Identifying the $|\text{CL}(t)\rangle$ state with the intermediate-normalized state $|0_I(t, \epsilon)\rangle$ of Eq. (109) and expanding $|\text{CL}(t)\rangle$ linearly in the ket component of the bi-orthonormal basis of Eqs. (98), we obtain

$$\begin{aligned} |0_I(t, \epsilon)\rangle &= |\text{CL}(t)\rangle = e^{*T} e^Z e^{-\bar{Z}} |\text{HF}\rangle + \sum_{\mu_k} c_{\mu_k}(t, \epsilon) e^{*T} e^Z e^{-\bar{Z}} |\mu_k\rangle \\ &= e^{*T} e^Z e^{-\bar{Z}} e^{C(t, \epsilon)} |\text{HF}\rangle, \end{aligned} \quad (111)$$

where the operator

$$C(t, \epsilon) = \sum_{\mu_k} |\mu_k\rangle \langle \text{HF} | c_{\mu_k}(t, \epsilon) \quad (112)$$

vanishes in the limit of no perturbation and where the time-evolving state in Eq. (111) is intermediate normalized against the unperturbed bra ground state of Eq. (95b) [the first component of the bra basis in Eq. (98b)]

$$\langle \text{CL} | 0_I(t, \epsilon) \rangle = 1. \quad (113)$$

In the limit of no perturbation, $|0_I(t, \epsilon)\rangle$ therefore satisfies

$$\lim_{\epsilon \rightarrow 0} |0_I(t, \epsilon)\rangle = |\text{CL}\rangle = e^{*T} e^Z e^{-\bar{Z}} |\text{HF}\rangle. \quad (114)$$

2. Solution to the time-dependent eigenvalue equation for the CL target state via projection

Substituting Eqs. (108), (109) and (111) into the time-dependent Schrödinger equation in Eq. (107), we obtain the time-dependent eigenvalue equation

$$\begin{aligned} \left(H(t, \epsilon) - i \frac{\partial}{\partial t} - \dot{\mathcal{F}}_{P_0}(t, \epsilon) - \left(i \frac{d}{dt} \ln N(t, \epsilon) \right) \right) e^{*T} e^Z e^{-\bar{Z}} e^{C(t, \epsilon)} |\text{HF}\rangle \\ = \mathcal{E}(\epsilon) e^{*T} e^Z e^{-\bar{Z}} e^{C(t, \epsilon)} |\text{HF}\rangle, \end{aligned} \quad (115)$$

which is satisfied at each time. Solving the eigenvalue equation in Eq. (115) is equivalent to solving the time-dependent Schrödinger equation in Eq. (107) (see Ref. 11).

Multiplying Eq. (115) by $e^{-C(t, \epsilon)} e^{\bar{Z}} e^{-Z} e^{-*T}$ on the left, the time-dependent Schrödinger equation can be written as

$$\begin{aligned} e^{-C(t, \epsilon)} e^{\bar{Z}} e^{-Z} e^{-*T} \left(H(t, \epsilon) - i \frac{\partial}{\partial t} - \dot{\mathcal{F}}_{P_0}(t, \epsilon) - \left(i \frac{d}{dt} \ln N(t, \epsilon) \right) \right) \\ \times e^{*T} e^Z e^{-\bar{Z}} e^{C(t, \epsilon)} |\text{HF}\rangle = \mathcal{E}(\epsilon) |\text{HF}\rangle. \end{aligned} \quad (116)$$

The time-dependent Schrödinger equation in Eq. (116) can be solved by projection against the basis $\langle \mathcal{B} |$ [cf. Eq. (5)] in the composite Hilbert space,²⁷ giving (see Sec. IV B of Ref. 11 for the detailed route of derivation)

$$\mathcal{E}(\epsilon) = \text{Re} \left\{ \left\langle \text{HF} \left| e^{-C(t, \epsilon)} \left(e^{\bar{Z}} e^{-Z} H^{*T}(t, \epsilon) e^Z e^{-\bar{Z}} - i \frac{\partial}{\partial t} \right) e^{C(t, \epsilon)} \right| \text{HF} \right\rangle_T \right\}, \quad (117)$$

$$\left\{ \left\langle \mu_k \left| e^{-C(t, \epsilon)} \left(e^{\bar{Z}} e^{-Z} H^{*T}(t, \epsilon) e^Z e^{-\bar{Z}} - i \frac{\partial}{\partial t} \right) e^{C(t, \epsilon)} \right| \text{HF} \right\rangle_T \right\} = 0, \quad (118)$$

where the similarity-transformed perturbed Hamiltonian, $H^{*T}(t, \epsilon)$, is defined analogously to Eq. (25) and where $\{\cdot\}_T$ denotes a time average over the period T . To obtain Eqs. (117) and (118), we have used that the operator $e^{*T} e^Z e^{-\bar{Z}}$ is time-independent. Equations (117) and (118) show that the quasi-energy and the time-dependent amplitudes are independent of the normalization constant, $N(t, \epsilon)$, and of the real time-periodic phase, $\mathcal{F}_{P_0}(t, \epsilon)$.

Comparing Eqs. (91) and (99) for the unperturbed system with Eqs. (117) and (118) for the perturbed system, we see that Eqs. (117) and (118) describe a time-dependent generalization of Eqs. (91) and (99) where the Hamiltonian is replaced by the time-dependent Hamiltonian and where the Hilbert space is extended with a time-dependent component.

The quasi-energy can be determined by solving Eq. (118) for the amplitudes, $c_{\mu_k}(t, \epsilon)$, and substituting these amplitudes in Eq. (117). However, to get variational flexibility, which simplifies the determination of molecular response functions, we introduce the Lagrangian,²⁰ where the amplitude equations are added as a constraint to the quasi-energy using time-dependent undetermined Lagrangian multipliers. As the Hamiltonian, $H(t, \epsilon)$ [Eq. (101)], is time-periodic, this is most conveniently done in the frequency domain. The amplitudes in the time domain, $c_{\mu_k}(t, \epsilon)$, can in the frequency domain be expressed as^{11,16}

$$c_{\mu_k}(t, \epsilon) = \sum_K c_{\mu_k}(\omega_K) e^{-i\omega_K t}, \quad (119)$$

where $c_{\mu_k}(\omega_K)$ are the frequency-dependent amplitudes that can be expanded in the perturbation strength as^{11,16}

$$\begin{aligned} c_{\mu_k}(\omega_K) &= \sum_{n=1}^{\infty} \frac{1}{n!} \sum_{j_1 \dots j_n} c_{\mu_k}^{X_{j_1} \dots X_{j_n}}(\omega_{X_{j_1}}, \dots, \omega_{X_{j_n}}) \left[\prod_{m=1}^n \epsilon_{X_{j_m}}(\omega_{X_{j_m}}) \right] \\ &\times \Delta \left(\sum_{m=1}^n \omega_{X_{j_m}} - \omega_K \right), \end{aligned} \quad (120)$$

where $c_{\mu_k}^{X_{j_1} \dots X_{j_n}}(\omega_{X_{j_1}}, \dots, \omega_{X_{j_n}})$ is a derivative of the amplitude $c_{\mu_k}(t, \epsilon)$ with respect to the perturbation strengths, taken at zeroth perturbation strengths,

$$c_{\mu_k}^{X_{j_1} \dots X_{j_n}}(\omega_{X_{j_1}}, \dots, \omega_{X_{j_n}}) = \left. \frac{d^n c_{\mu_k}(t, \epsilon)}{d\epsilon_{X_{j_1}}(\omega_{X_{j_1}}) \dots d\epsilon_{X_{j_n}}(\omega_{X_{j_n}})} \right|_{\epsilon=0}, \quad (121)$$

and

$$\Delta(x) = \begin{cases} 0, & x \neq 0 \\ 1, & x = 0. \end{cases} \quad (122)$$

Equations (120) and (122) show that the frequency-dependent amplitudes, $c_{\mu_k}(\omega_K)$, are only non-vanishing when ω_K is equal to a sum of the physical perturbation frequencies of Eq. (103). Furthermore, in the limit of no physical perturbation, where all the perturbation strengths and frequencies of Eq. (103) are set to zero, the time-dependent amplitudes $c_{\mu_k}(t, \epsilon)$ [Eq. (119)] vanish.

Adding the amplitude equation as a constraint to the quasi-energy in terms of time-dependent Lagrangian multipliers, $\bar{c}_{\mu_k}(t, \epsilon)$, and transforming to the frequency domain, we obtain the complex quasi-energy Lagrangian¹¹

$$\begin{aligned} {}^c\mathcal{L} = & \left\{ \langle \text{HF} | e^{-C(t, \epsilon)} \left(e^{\bar{z}} e^{-Z} H^* T(t, \epsilon) e^Z e^{-\bar{z}} - i \frac{\partial}{\partial t} \right) e^{C(t, \epsilon)} | \text{HF} \rangle \right\}_T \\ & + \sum_{\mu_k K} \bar{c}_{\mu_k}(\omega_K) \left\{ \langle \mu_k | e^{-C(t, \epsilon)} \left(e^{\bar{z}} e^{-Z} H^* T(t, \epsilon) e^Z e^{-\bar{z}} - i \frac{\partial}{\partial t} \right) \right. \\ & \left. \times e^{C(t, \epsilon)} | \text{HF} \rangle e^{-i\omega_K t} \right\}, \quad (123) \end{aligned}$$

where $\bar{c}_{\mu_k}(\omega_K)$ are frequency-dependent multipliers, which can be expanded as in Eq. (120). To obtain Eq. (123), we have used that the imaginary part of $\left\{ \langle \text{HF} | e^{C(t, \epsilon)} \left(e^{\bar{z}} e^{-Z} H^* T(t, \epsilon) e^Z e^{-\bar{z}} - i \frac{\partial}{\partial t} \right) e^{-C(t, \epsilon)} | \text{HF} \rangle \right\}_T$ vanishes.¹¹ We refer to Ref. 11, where details concerning the derivation of Eq. (123) can be found.

It has been shown in Ref. 11 (Secs. IV C and IV D therein) that solving the eigenvalue equation for the intermediate-normalized ket state [Eq. (115)] via projection in the frequency domain is equivalent to determining stationary points of the quasi-energy Lagrangian ${}^c\mathcal{L}$ in Eq. (123)

$$\frac{\partial {}^c\mathcal{L}}{\partial c_{\mu_k}(\omega_K)} = 0, \quad (124)$$

$$\frac{\partial {}^c\mathcal{L}}{\partial \bar{c}_{\mu_k}(\omega_K)} = 0. \quad (125)$$

The frequency-dependent multipliers, $\bar{c}_{\mu_k}(\omega_K)$, and amplitudes, $c_{\mu_k}(\omega_K)$, can be determined from Eqs. (124) and (125), respectively, and the unperturbed multipliers, \bar{z}_{μ_k} , and amplitudes, z_{μ_k} , from Eqs. (97) and (96), respectively. In the limit of no perturbation, where all frequencies and perturbation strengths of Eq. (103) are set to zero and hence $c_{\mu_k}(\omega_K)$ and $\bar{c}_{\mu_k}(\omega_K)$ vanish, the quasi-energy Lagrangian, ${}^c\mathcal{L}$ [Eq. (123)], recovers the Lagrangian for the unperturbed system, $L_0(\mathbf{z}, \bar{\mathbf{z}})$ [Eq. (91)].

3. Response functions for the CL target ground state

Following the development of Ref. 11, molecular response properties can be obtained by differentiating the quasi-energy Lagrangian, ${}^c\mathcal{L}$ [Eq. (123)], with respect to the perturbation strengths. The n th-order molecular response property can then be expressed as¹¹

$$\begin{aligned} \langle \langle X_{j_1}; X_{j_2}, \dots, X_{j_n} \rangle \rangle_{\omega_{X_{j_2}}, \dots, \omega_{X_{j_n}}} &= \frac{1}{2} C^{\pm\omega} {}^c\mathcal{L}^{X_{j_1} \dots X_{j_n}}(\omega_{X_{j_1}}, \dots, \omega_{X_{j_n}}), \\ \sum_{m=1}^n \omega_{X_{j_m}} &= 0, \end{aligned} \quad (126)$$

where the perturbation components of the quasi-energy Lagrangian are defined as derivatives of ${}^c\mathcal{L}$ with respect to perturbation strengths

$${}^c\mathcal{L}^{X_{j_1} \dots X_{j_n}}(\omega_{X_{j_1}}, \dots, \omega_{X_{j_n}}) = \left. \frac{d^n {}^c\mathcal{L}}{d\epsilon_{X_{j_1}}(\omega_{X_{j_1}}) \dots d\epsilon_{X_{j_n}}(\omega_{X_{j_n}})} \right|_{\epsilon=0}, \quad (127)$$

and where $C^{\pm\omega}$ is the complex conjugation and frequency sign inversion operator

$$\begin{aligned} C^{\pm\omega} {}^c\mathcal{L}^{X_{j_1} \dots X_{j_n}}(\omega_{X_{j_1}}, \dots, \omega_{X_{j_n}}) &= {}^c\mathcal{L}^{X_{j_1} \dots X_{j_n}}(\omega_{X_{j_1}}, \dots, \omega_{X_{j_n}}) \\ &+ {}^c\mathcal{L}^{X_{j_1} \dots X_{j_n}*}(-\omega_{X_{j_1}}, \dots, -\omega_{X_{j_n}}). \end{aligned} \quad (128)$$

4. The Jacobian for the CL target ground state

The Jacobian plays a central role in response function theory as its eigenvalues occur at the excitation energies of the unperturbed molecular system.¹¹ Furthermore, the inverse of the Jacobian enters in the response amplitudes (and multipliers) and the Jacobian thereby determines the pole structure of the response functions.^{15,16} The Jacobian is defined as the derivative of the quasi-energy Lagrangian with respect to frequency-dependent amplitudes and multipliers taken at the zeroth perturbation strengths

$$\begin{aligned} \mathcal{J}_{\mu_k v_m} &= \left. \frac{\partial^2 {}^c\mathcal{L}}{\partial \bar{c}_{\mu_k}(\omega_K) \partial c_{v_m}(\omega_M)} \right|_{\epsilon=0} \\ &= \langle \mu_k | [e^{\bar{z}} e^{-Z} H_0^* T e^Z e^{-\bar{z}}, |v_m\rangle \langle \text{HF} |] | \text{HF} \rangle. \end{aligned} \quad (129)$$

To obtain the second equality in Eq. (129), we have used Eqs. (112), (119), and (123), and that the frequencies are zero at the zeroth perturbation strength.

C. The quasi-energy Lagrangian for the CL target ground-state

In this section, we simplify the quasi-energy Lagrangian for the time-evolving ket state, ${}^c\mathcal{L}$ [Eq. (123)], to a form that is convenient for deriving response functions. First, in Sec. V C 1, we perform a BCH expansion of the Lagrangian in the time domain and show that the expansion terminates after the double commutator term. Next, the bi-variational conditions for the unperturbed system [Eqs. (99) and (100)] are used to simplify the Lagrangian, and finally, further simplifications are obtained in Sec. V C 2 by using Eqs. (119)–(122) to transform the Lagrangian to the frequency domain. The flow of derivation in this subsection is similar to the one in Sec. V of Ref. 11.

1. Quasi-energy Lagrangian in the time domain

Substituting Eqs. (101) and (103) into Eq. (123), we can write the quasi-energy Lagrangian in the form

$${}^c\mathcal{L} = {}^c\mathcal{L}_{H_0} + {}^c\mathcal{L}_F + \sum_{j_1} {}^c\mathcal{L}_{X_{j_1}} \epsilon_{X_{j_1}}(\omega_{X_{j_1}}), \quad (130)$$

where

$${}^c\mathcal{L}_{H_0} = \left\{ \langle \text{HF} | e^{-C(t,\epsilon)} e^{\bar{Z}} e^{-Z} H_0^* T e^Z e^{-\bar{Z}} e^{C(t,\epsilon)} | \text{HF} \rangle \right\}_T + \sum_{\mu_k K} \bar{c}_{\mu_k}(\omega_K) \times \left\{ \langle \mu_k | e^{-C(t,\epsilon)} e^{\bar{Z}} e^{-Z} H_0^* T e^Z e^{-\bar{Z}} e^{C(t,\epsilon)} | \text{HF} \rangle e^{-i\omega_K t} \right\}_T, \quad (131)$$

$${}^c\mathcal{L}_{X_{j_1}} = \left\{ \langle \text{HF} | e^{-C(t,\epsilon)} e^{\bar{Z}} e^{-Z} X_{j_1}^* T e^Z e^{-\bar{Z}} e^{C(t,\epsilon)} | \text{HF} \rangle e^{-i\omega_{X_{j_1}} t} \right\}_T + \sum_{\mu_k K} \bar{c}_{\mu_k}(\omega_K) \left\{ \langle \mu_k | e^{-C(t,\epsilon)} e^{\bar{Z}} e^{-Z} X_{j_1}^* T e^Z e^{-\bar{Z}} e^{C(t,\epsilon)} | \text{HF} \rangle \times e^{-i(\omega_K + \omega_{X_{j_1}})t} \right\}_T, \quad (132)$$

and

$${}^c\mathcal{L}_F = -i \sum_{\mu_k K} \bar{c}_{\mu_k}(\omega_K) \left\{ \langle \mu_k | e^{-C(t,\epsilon)} \frac{\partial}{\partial t} e^{C(t,\epsilon)} | \text{HF} \rangle e^{-i\omega_K t} \right\}_T. \quad (133)$$

To obtain Eq. (133), we have used that

$$\frac{\partial}{\partial t} e^{C(t,\epsilon)} = e^{C(t,\epsilon)} \sum_{\mu_k} \dot{c}_{\mu_k}(t,\epsilon) |\mu_k\rangle \langle \text{HF}| \quad (134)$$

and therefore $\left\{ \langle \text{HF} | e^{-C(t,\epsilon)} \frac{\partial}{\partial t} e^{C(t,\epsilon)} | \text{HF} \rangle \right\}_T$ vanishes.

In the following, we will carry out BCH expansions with respect to $C(t, \epsilon)$ for the individual terms of ${}^c\mathcal{L}$ in Eq. (130). To simplify the expansion, we note that the double commutator of $C(t, \epsilon)$ [Eq. (112)] with an arbitrary operator O becomes

$$\begin{aligned} & \left[[O, C(t, \epsilon)], C(t, \epsilon) \right] \\ &= \sum_{\mu_k \nu_m} \left[[O, |\mu_k\rangle \langle \text{HF}|], |\nu_m\rangle \langle \text{HF}| \right] c_{\mu_k}(t, \epsilon) c_{\nu_m}(t, \epsilon) \\ &= - \sum_{\mu_k \nu_m} \left(|\mu_k\rangle \langle \text{HF}| O |\nu_m\rangle \langle \text{HF}| + |\nu_m\rangle \langle \text{HF}| O |\mu_k\rangle \langle \text{HF}| \right) \\ & \quad \times c_{\mu_k}(t, \epsilon) c_{\nu_m}(t, \epsilon) \\ &= -2 \sum_{\mu_k \nu_m} |\mu_k\rangle \langle \text{HF}| O |\nu_m\rangle \langle \text{HF}| c_{\mu_k}(t, \epsilon) c_{\nu_m}(t, \epsilon). \end{aligned} \quad (135)$$

Equation (135) simplifies the double commutator term in the BCH expansion of $e^{-C(t,\epsilon)} O e^{C(t,\epsilon)}$ and further implies that the triple, quadruple, and higher commutator terms in this expansion vanish.

Applying initially the BCH expansion to the ${}^c\mathcal{L}_{H_0}$ term in Eq. (131), we obtain

$${}^c\mathcal{L}_{H_0} = {}^c\mathcal{L}_{H_0}^L + {}^c\mathcal{L}_{H_0}^{NL}, \quad (136)$$

where ${}^c\mathcal{L}_{H_0}^L$ denotes the terms that are constant or linear in the $c_{\mu_k}(t, \epsilon)$ amplitudes, and ${}^c\mathcal{L}_{H_0}^{NL}$ denotes the terms that are non-linear in these amplitudes. The linear term becomes

$$\begin{aligned} {}^c\mathcal{L}_{H_0}^L &= \langle \text{HF} | e^{\bar{Z}} e^{-Z} H_0^* T e^Z e^{-\bar{Z}} | \text{HF} \rangle \\ &+ \left\{ \langle \text{HF} | [e^{\bar{Z}} e^{-Z} H_0^* T e^Z e^{-\bar{Z}}, C(t, \epsilon)] | \text{HF} \rangle \right\}_T \\ &+ \sum_{\mu_k K} \bar{c}_{\mu_k}(\omega_K) \left\{ \langle \mu_k | e^{\bar{Z}} e^{-Z} H_0^* T e^Z e^{-\bar{Z}} | \text{HF} \rangle e^{-i\omega_K t} \right\}_T \\ &+ \sum_{\mu_k K} \bar{c}_{\mu_k}(\omega_K) \left\{ \langle \mu_k | [e^{\bar{Z}} e^{-Z} H_0^* T e^Z e^{-\bar{Z}}, C(t, \epsilon)] | \text{HF} \rangle e^{-i\omega_K t} \right\}_T. \end{aligned} \quad (137)$$

For the non-linear term, we recall that the BCH expansion terminates after the double commutator, giving

$$\begin{aligned} {}^c\mathcal{L}_{H_0}^{NL} &= \frac{1}{2} \left\{ \langle \text{HF} | [[e^{\bar{Z}} e^{-Z} H_0^* T e^Z e^{-\bar{Z}}, C(t, \epsilon)], C(t, \epsilon)] | \text{HF} \rangle \right\}_T \\ &+ \frac{1}{2} \sum_{\mu_k K} \bar{c}_{\mu_k}(\omega_K) \left\{ \langle \mu_k | [[e^{\bar{Z}} e^{-Z} H_0^* T e^Z e^{-\bar{Z}}, C(t, \epsilon)], C(t, \epsilon)] \right. \\ & \quad \left. \times | \text{HF} \rangle e^{-i\omega_K t} \right\}_T \\ &= - \sum_{\mu_k \nu_m K} \bar{c}_{\mu_k}(\omega_K) \langle \text{HF} | e^{\bar{Z}} e^{-Z} H_0^* T e^Z e^{-\bar{Z}} | \nu_m \rangle \\ & \quad \times \left\{ c_{\mu_k}(t, \epsilon) c_{\nu_m}(t, \epsilon) e^{-i\omega_K t} \right\}_T, \end{aligned} \quad (138)$$

where to obtain the last equality we have used Eq. (135). The ${}^c\mathcal{L}_{H_0}^L$ term of Eq. (137) and the ${}^c\mathcal{L}_{H_0}^{NL}$ term of Eq. (138) can be simplified using the bi-variational conditions of Eqs. (99) and (100) which are satisfied for the unperturbed system. Using the variational condition in Eq. (99), the third term in Eq. (137) vanishes and we obtain

$$\begin{aligned} {}^c\mathcal{L}_{H_0}^L &= L_0 + \left\{ \langle \text{HF} | [e^{\bar{Z}} e^{-Z} H_0^* T e^Z e^{-\bar{Z}}, C(t, \epsilon)] | \text{HF} \rangle \right\}_T \\ &+ \sum_{\mu_k K} \bar{c}_{\mu_k}(\omega_K) \left\{ \langle \mu_k | [e^{\bar{Z}} e^{-Z} H_0^* T e^Z e^{-\bar{Z}}, C(t, \epsilon)] \right. \\ & \quad \left. \times | \text{HF} \rangle e^{-i\omega_K t} \right\}_T, \end{aligned} \quad (139)$$

where we have introduced L_0 of Eq. (91). Substituting Eq. (112) into Eq. (139), we further obtain that

$$\begin{aligned} {}^c\mathcal{L}_{H_0}^L &= L_0 + \sum_{\nu_m} \left\{ \langle \text{HF} | [e^{\bar{Z}} e^{-Z} H_0^* T e^Z e^{-\bar{Z}}, |\nu_m\rangle \langle \text{HF}|] | \text{HF} \rangle c_{\nu_m}(t, \epsilon) \right\}_T \\ &+ \sum_{\mu_k \nu_m K} \bar{c}_{\mu_k}(\omega_K) \left\{ \langle \mu_k | [e^{\bar{Z}} e^{-Z} H_0^* T e^Z e^{-\bar{Z}}, |\nu_m\rangle \langle \text{HF}|] \right. \\ & \quad \left. \times | \text{HF} \rangle c_{\nu_m}(t, \epsilon) e^{-i\omega_K t} \right\}_T. \end{aligned} \quad (140)$$

The second term in Eq. (140) vanishes by the variational condition in Eq. (100) for the unperturbed system, giving

$${}^c\mathcal{L}_{H_0}^L = L_0 + \sum_{\mu_k \nu_m K} \bar{c}_{\mu_k}(\omega_K) \langle \mu_k | [e^{\bar{Z}} e^{-Z} H_0^{*T} e^Z e^{-\bar{Z}}, |v_m\rangle \langle \text{HF} |] | \text{HF} \rangle \times \left\{ c_{\nu_m}(t, \epsilon) e^{-i\omega_K t} \right\}_T. \quad (141)$$

Substituting the definition of the Jacobian [Eq. (129)] into Eq. (141), we obtain

$${}^c\mathcal{L}_{H_0}^L = L_0 + \sum_{\mu_k \nu_m K} \bar{c}_{\mu_k}(\omega_K) \mathcal{J}_{\mu_k \nu_m} \left\{ c_{\nu_m}(t, \epsilon) e^{-i\omega_K t} \right\}_T. \quad (142)$$

We now turn to the non-linear term, ${}^c\mathcal{L}_{H_0}^{NL}$, of Eq. (138). Using the variational condition in Eq. (100), we obtain that ${}^c\mathcal{L}_{H_0}^{NL}$ vanishes

$${}^c\mathcal{L}_{H_0}^{NL} = 0. \quad (143)$$

For the ${}^c\mathcal{L}_{X_{j_1}}$ term [Eq. (132)], we apply the BCH expansion and use Eq. (135), giving

$$\begin{aligned} {}^c\mathcal{L}_{X_{j_1}} = & \langle \text{HF} | e^{\bar{Z}} e^{-Z} X_{j_1}^{*T} e^Z e^{-\bar{Z}} | \text{HF} \rangle \left\{ e^{-i\omega_{X_{j_1}} t} \right\}_T + \sum_{\nu_m} \langle \text{HF} | [e^{\bar{Z}} e^{-Z} X_{j_1}^{*T} e^Z e^{-\bar{Z}}, |v_m\rangle \langle \text{HF} |] | \text{HF} \rangle \left\{ c_{\nu_m}(t, \epsilon) e^{-i\omega_{X_{j_1}} t} \right\}_T \\ & + \sum_{\mu_k K} \bar{c}_{\mu_k}(\omega_K) \langle \mu_k | e^{\bar{Z}} e^{-Z} X_{j_1}^{*T} e^Z e^{-\bar{Z}} | \text{HF} \rangle \left\{ e^{-i(\omega_{X_{j_1}} + \omega_K) t} \right\}_T + \sum_{\mu_k \nu_m K} \bar{c}_{\mu_k}(\omega_K) \langle \mu_k | [e^{\bar{Z}} e^{-Z} X_{j_1}^{*T} e^Z e^{-\bar{Z}}, |v_m\rangle \langle \text{HF} |] | \text{HF} \rangle \\ & \times \left\{ c_{\nu_m}(t, \epsilon) e^{-i(\omega_{X_{j_1}} + \omega_K) t} \right\}_T - \sum_{\mu_k \nu_m K} \bar{c}_{\mu_k}(\omega_K) \langle \text{HF} | e^{\bar{Z}} e^{-Z} X_{j_1}^{*T} e^Z e^{-\bar{Z}} | v_m \rangle \left\{ c_{\mu_k}(t, \epsilon) c_{\nu_m}(t, \epsilon) e^{-i(\omega_{X_{j_1}} + \omega_K) t} \right\}_T. \end{aligned} \quad (144)$$

The ${}^c\mathcal{L}_F$ term can be simplified substituting Eq. (134) into Eq. (133)

$${}^c\mathcal{L}_F = -i \sum_{\mu_k K} \bar{c}_{\mu_k}(\omega_K) \left\{ \dot{c}_{\mu_k}(t, \epsilon) e^{-i\omega_K t} \right\}_T. \quad (145)$$

2. Quasi-energy Lagrangian in the frequency domain

In this section, we transform the quasi-energy Lagrangian, derived in Sec. V C 1, to the frequency domain. To do this, we use the relation derived in Ref. 11

$$\begin{aligned} & \left\{ e^{-i \left[\left(\sum_{K \in \Gamma_1} \omega_K - \sum_{L \in \Gamma_2} \omega_L \right) + \left(\sum_{m \in \Gamma_3} \omega_{X_{j_m}} - \sum_{n \in \Gamma_4} \omega_{X_{j_n}} \right) \right] t} \right\}_T \\ & = \Delta \left(\left(\sum_{K \in \Gamma_1} \omega_K - \sum_{L \in \Gamma_2} \omega_L \right) + \left(\sum_{m \in \Gamma_3} \omega_{X_{j_m}} - \sum_{n \in \Gamma_4} \omega_{X_{j_n}} \right) \right), \end{aligned} \quad (146)$$

where $\Delta(x)$ has been defined in Eq. (122) and where Γ_1 , Γ_2 , Γ_3 , and Γ_4 are sets of frequency indices. We also use Eq. (119) for $c_{\mu_k}(t, \epsilon)$ amplitudes,

$$c_{\mu_k}(t, \epsilon) = \sum_K c_{\mu_k}(\omega_K) e^{-i\omega_K t}, \quad (147)$$

and its time derivative,

$$\dot{c}_{\mu_k}(t, \epsilon) = -i \sum_K \omega_K c_{\mu_k}(\omega_K) e^{-i\omega_K t}. \quad (148)$$

Substituting Eq. (147) into ${}^c\mathcal{L}_{H_0}^L$ of Eq. (142), we obtain

$${}^c\mathcal{L}_{H_0}^L = L_0 + \sum_{\mu_k \nu_m KM} \bar{c}_{\mu_k}(\omega_K) \mathcal{J}_{\mu_k \nu_m} c_{\nu_m}(\omega_M) \left\{ e^{-i(\omega_K + \omega_M) t} \right\}_T. \quad (149)$$

By applying Eq. (146), the explicit time dependence in Eq. (149) is removed, giving ${}^c\mathcal{L}_{H_0}^L$ in the frequency domain

$${}^c\mathcal{L}_{H_0}^L = L_0 + \sum_{\mu_k \nu_m KM} \bar{c}_{\mu_k}(\omega_K) \mathcal{J}_{\mu_k \nu_m} c_{\nu_m}(\omega_M) \Delta(\omega_K + \omega_M). \quad (150)$$

To obtain ${}^c\mathcal{L}_F$ in the frequency domain, we substitute Eq. (148) into Eq. (145) and apply Eq. (146), giving

$${}^c\mathcal{L}_F = - \sum_{\mu_k KM} \omega_M \bar{c}_{\mu_k}(\omega_K) c_{\mu_k}(\omega_M) \Delta(\omega_K + \omega_M). \quad (151)$$

For further convenience in the derivation of response functions, we combine ${}^c\mathcal{L}_F$ with ${}^c\mathcal{L}_{H_0}^L$ in

$$\begin{aligned} {}^c\mathcal{L}_{\mathcal{H}} = & {}^c\mathcal{L}_{H_0}^L + {}^c\mathcal{L}_F = L_0 + \sum_{\mu_k \nu_m KM} \bar{c}_{\mu_k}(\omega_K) \left(\mathcal{J}_{\mu_k \nu_m} - \omega_M \delta_{\mu_k \nu_m} \right) \\ & \times c_{\nu_m}(\omega_M) \Delta(\omega_K + \omega_M). \end{aligned} \quad (152)$$

Applying the same technique as for deriving Eq. (150), we transform the ${}^c\mathcal{L}_{X_{j_1}}$ term of Eq. (144) to the frequency domain, giving

$$\begin{aligned}
 {}^c\mathcal{L}_{X_{j_1}} &= \langle \text{HF} | e^{\bar{Z}} e^{-Z} X_{j_1}^{*T} e^Z e^{-\bar{Z}} | \text{HF} \rangle \Delta(\omega_{X_{j_1}}) + \sum_{v_m M} \langle \text{HF} | e^{\bar{Z}} e^{-Z} X_{j_1}^{*T} e^Z e^{-\bar{Z}} | v_m \rangle c_{v_m}(\omega_M) \Delta(\omega_{X_{j_1}} + \omega_M) \\
 &+ \sum_{\mu_k K} \bar{c}_{\mu_k}(\omega_K) \langle \mu_k | e^{\bar{Z}} e^{-Z} X_{j_1}^{*T} e^Z e^{-\bar{Z}} | \text{HF} \rangle \Delta(\omega_{X_{j_1}} + \omega_K) \\
 &+ \sum_{\mu_k v_m K M} \bar{c}_{\mu_k}(\omega_K) \langle \mu_k | [e^{\bar{Z}} e^{-Z} X_{j_1}^{*T} e^Z e^{-\bar{Z}} | v_m \rangle \langle \text{HF} |] | \text{HF} \rangle c_{v_m}(\omega_M) \Delta(\omega_{X_{j_1}} + \omega_K + \omega_M) \\
 &- \sum_{KLM} \left(\sum_{\mu_k} \bar{c}_{\mu_k}(\omega_K) c_{\mu_k}(\omega_L) \right) \left(\sum_{v_m} \langle \text{HF} | e^{\bar{Z}} e^{-Z} X_{j_1}^{*T} e^Z e^{-\bar{Z}} | v_m \rangle c_{v_m}(\omega_M) \right) \Delta(\omega_{X_{j_1}} + \omega_K + \omega_L + \omega_M). \quad (153)
 \end{aligned}$$

Summarizing, the quasi-energy Lagrangian in the frequency domain can be expressed as [cf. Eq. (130)]

$${}^c\mathcal{L} = {}^c\mathcal{L}_{\mathcal{H}} + \sum_{j_1} {}^c\mathcal{L}_{X_{j_1}} \epsilon_{X_{j_1}}(\omega_{X_{j_1}}), \quad (154)$$

where ${}^c\mathcal{L}_{\mathcal{H}}$ is given in Eq. (152) and ${}^c\mathcal{L}_{X_{j_1}}$ is given in Eq. (153).

D. Response functions for the CL target state

In this section, we show how molecular response property expressions can be derived for the time-evolving state $|\text{CL}(t)\rangle$ of Eq. (111), using the quasi-energy Lagrangian derived in Sec. V C. We start in Sec. V D 1 with a brief summary outlining the strategy that we have developed in Ref. 11 for the derivation of the response functions. We then apply this strategy in Secs. V D 2–V D 5 to determine the first- through fourth-order molecular response property expressions for the time-evolving state $|\text{CL}(t)\rangle$.

1. Outline for deriving response functions

It follows from Eq. (126) that response functions can be determined once ${}^c\mathcal{L}^{X_{j_1} \dots X_{j_n}}(\omega_{X_{j_1}}, \dots, \omega_{X_{j_n}})$ of Eq. (127) has been determined. ${}^c\mathcal{L}^{X_{j_1} \dots X_{j_n}}(\omega_{X_{j_1}}, \dots, \omega_{X_{j_n}})$ can be written as (see Sec. IV E of Ref. 11 for details of the derivation)

$${}^c\mathcal{L}^{X_{j_1} \dots X_{j_n}}(\omega_{X_{j_1}}, \dots, \omega_{X_{j_n}}) = P_{\omega_{X_{j_1}} \dots \omega_{X_{j_n}} \omega_{X_{j_1}} \dots \omega_{X_{j_n}}}^{X_{j_1} \dots X_{j_n}} \bar{f}_{X_{j_1} \dots X_{j_n}}^{X_{j_1} \dots X_{j_n}}, \quad \sum_{m=1}^n \omega_{X_{j_m}} = 0, \quad (155)$$

where the permutation operator $P_{\omega_{X_{j_1}} \dots \omega_{X_{j_n}} \omega_{X_{j_1}} \dots \omega_{X_{j_n}}}^{X_{j_1} \dots X_{j_n}}$ generates $n!$ (distinct and non-distinct) permutations of the operator–frequency pairs $(X_{j_k}, \omega_{X_{j_k}})$, where the operators and the corresponding frequencies are simultaneously permuted, and $\bar{f}_{X_{j_1} \dots X_{j_n}}^{X_{j_1} \dots X_{j_n}}$ is an n th-order contribution to Eq. (154) that is permutation-distinct with respect to the operator–frequency pairs. We have shown in Ref. 11 how $\bar{f}_{X_{j_1} \dots X_{j_n}}^{X_{j_1} \dots X_{j_n}}$ can be identified by substituting the expansion of $c_{\mu_k}(\omega_K)$ [Eq. (120)] and a similar expansion of $\bar{c}_{\mu_k}(\omega_K)$ into ${}^c\mathcal{L}_{\mathcal{H}}$ [Eq. (152)] and ${}^c\mathcal{L}_{X_{j_1}}$ [Eq. (153)], and collecting terms of the same order in the physical perturbation. While carrying out this substitution, the summation over the upper-case indices (K, L, M, \dots) is performed explicitly in Eqs. (152) and (153) such that $\Delta(x)$ of Eq. (122) gives only the contributions that satisfy the frequency constraint in Eq. (126).¹¹

We have further shown in Sec. IV E 2 of Ref. 11 that the stationary conditions of Eqs. (124) and (125) imply that ${}^c\mathcal{L}^{X_{j_1} \dots X_{j_n}}(\omega_{X_{j_1}}, \dots, \omega_{X_{j_n}})$ [Eq. (127)] is stationary with respect to $c_{\mu_k}^{X_{j_1} \dots X_{j_n}}(\omega_{X_{j_1}}, \dots, \omega_{X_{j_n}})$ and $\bar{c}_{\mu_k}^{X_{j_1} \dots X_{j_n}}(\omega_{X_{j_1}}, \dots, \omega_{X_{j_n}})$

$$\frac{\partial {}^c\mathcal{L}^{X_{j_1} \dots X_{j_n}}(\omega_{X_{j_1}}, \dots, \omega_{X_{j_n}})}{\partial c_{\mu_k}^{X_{j_1} \dots X_{j_n}}(\omega_{X_{j_1}}, \dots, \omega_{X_{j_n}})} = 0, \quad \sum_{q=1}^n \omega_{X_{j_q}} = 0, \quad (156)$$

$$\frac{\partial {}^c\mathcal{L}^{X_{j_1} \dots X_{j_n}}(\omega_{X_{j_1}}, \dots, \omega_{X_{j_n}})}{\partial \bar{c}_{\mu_k}^{X_{j_1} \dots X_{j_n}}(\omega_{X_{j_1}}, \dots, \omega_{X_{j_n}})} = 0, \quad \sum_{q=1}^n \omega_{X_{j_q}} = 0. \quad (157)$$

Equations (156) and (157) can be used to obtain response equations that determine the Lagrangian multipliers $\bar{c}_{\mu_k}^{X_{j_1} \dots X_{j_n}}(\omega_{X_{j_1}}, \dots, \omega_{X_{j_n}})$ and the amplitudes $c_{\mu_k}^{X_{j_1} \dots X_{j_n}}(\omega_{X_{j_1}}, \dots, \omega_{X_{j_n}})$, respectively.

Summarizing, ${}^c\mathcal{L}^{X_{j_1} \dots X_{j_n}}(\omega_{X_{j_1}}, \dots, \omega_{X_{j_n}})$ can be identified using Eq. (155). Next, response equations can be obtained by differentiating ${}^c\mathcal{L}^{X_{j_1} \dots X_{j_n}}(\omega_{X_{j_1}}, \dots, \omega_{X_{j_n}})$ with respect to $c_{\mu_k}^{X_{j_1} \dots X_{j_n}}(\omega_{X_{j_1}}, \dots, \omega_{X_{j_n}})$ and $\bar{c}_{\mu_k}^{X_{j_1} \dots X_{j_n}}(\omega_{X_{j_1}}, \dots, \omega_{X_{j_n}})$ [Eqs. (156) and (157)]. The response equations can then be used to obtain a simplified expression for ${}^c\mathcal{L}^{X_{j_1} \dots X_{j_n}}(\omega_{X_{j_1}}, \dots, \omega_{X_{j_n}})$, which can be inserted into Eq. (126) giving the response functions. In the following, we use the outline described in this section to derive first- through fourth-order molecular property expressions.

2. First-order molecular properties

We initially identify the first-order²⁸ component of the Lagrangian, ${}^c\mathcal{L}$ [Eq. (154)], as

$${}^c\mathcal{L}^{X_{j_1}}(\omega_{X_{j_1}}) = \langle \text{HF} | e^{\bar{Z}} e^{-Z} X_{j_1}^{*T} e^Z e^{-\bar{Z}} | \text{HF} \rangle, \quad \omega_{X_{j_1}} = 0, \quad (158)$$

where we have used that $c_{v_m}(\omega_M)$ and $\bar{c}_{v_m}(\omega_M)$ do not have a zeroth-order contribution [cf. Eq. (120)]. Substituting Eq. (158) into Eq. (126), we obtain the first-order molecular property expression for the time-evolving CL state of Eq. (111)

$$\langle \langle X_{j_1} \rangle \rangle_0 = \frac{1}{2} C^{\pm\omega} \langle \text{HF} | e^{\bar{Z}} e^{-Z} X_{j_1}^{*T} e^Z e^{-\bar{Z}} | \text{HF} \rangle, \quad (159)$$

where the zeroth-order amplitudes, z_{μ_k} , and multipliers, \bar{z}_{μ_k} , are obtained by solving Eqs. (96) and (97), respectively.

3. Second-order molecular properties

The second-order Lagrangian can be identified as

$$\begin{aligned} & \mathcal{L}^{X_{j_1} X_{j_2}}(\omega_{X_{j_1}}, \omega_{X_{j_2}}) \\ &= P_{\omega_{X_{j_1}} \omega_{X_{j_2}}}^{X_{j_1} X_{j_2}} \left(\sum_{\mu_k \nu_m} \bar{c}_{\mu_k}^{X_{j_1}}(\omega_{X_{j_1}}) (\mathcal{J}_{\mu_k \nu_m} - \omega_{X_{j_2}} \delta_{\mu_k \nu_m}) c_{\nu_m}^{X_{j_2}}(\omega_{X_{j_2}}) \right. \\ &+ \sum_{\nu_m} \langle \text{HF} | e^{\bar{Z}} e^{-Z} X_{j_1}^* T e^Z e^{-\bar{Z}} | \nu_m \rangle c_{\nu_m}^{X_{j_2}}(\omega_{X_{j_2}}) \\ &+ \left. \sum_{\mu_k} \bar{c}_{\mu_k}^{X_{j_2}}(\omega_{X_{j_2}}) \langle \mu_k | e^{\bar{Z}} e^{-Z} X_{j_1}^* T e^Z e^{-\bar{Z}} | \text{HF} \rangle \right), \quad \omega_{X_{j_1}} + \omega_{X_{j_2}} = 0. \end{aligned} \quad (160)$$

Applying the stationary condition of Eq. (157) to $\mathcal{L}^{X_{j_1} X_{j_2}}(\omega_{X_{j_1}}, \omega_{X_{j_2}})$ of Eq. (160),

$$\frac{\partial \mathcal{L}^{X_{j_1} X_{j_2}}(\omega_{X_{j_1}}, \omega_{X_{j_2}})}{\partial \bar{c}_{\mu_k}^{X_{j_2}}(\omega_{X_{j_2}})} = 0, \quad (161)$$

gives

$$\sum_{\nu_m} (\mathcal{J}_{\mu_k \nu_m} - \omega_{X_{j_1}} \delta_{\mu_k \nu_m}) c_{\nu_m}^{X_{j_1}}(\omega_{X_{j_1}}) + \langle \mu_k | e^{\bar{Z}} e^{-Z} X_{j_1}^* T e^Z e^{-\bar{Z}} | \text{HF} \rangle = 0. \quad (162)$$

Equation (162) is the first-order response equation for the first-order amplitudes $c_{\nu_m}^{X_{j_1}}(\omega_{X_{j_1}})$. Similarly, applying the stationary condition of Eq. (156) gives the response equation for the first-order multipliers $\bar{c}_{\nu_m}^{X_{j_1}}(\omega_{X_{j_1}})$,

$$\sum_{\mu_k} \bar{c}_{\mu_k}^{X_{j_1}}(\omega_{X_{j_1}}) (\mathcal{J}_{\mu_k \nu_m} + \omega_{X_{j_1}} \delta_{\mu_k \nu_m}) + \langle \text{HF} | e^{\bar{Z}} e^{-Z} X_{j_1}^* T e^Z e^{-\bar{Z}} | \nu_m \rangle = 0, \quad (163)$$

where for the first term we have used the frequency constraint, $\omega_{X_{j_1}} + \omega_{X_{j_2}} = 0$.

Using the $2n + 1$ rule for the amplitudes and the $2n + 2$ rule for the multipliers (see, for example, Refs. 20–22), the linear response function becomes

$$\begin{aligned} \langle \langle X_{j_1}; X_{j_2} \rangle \rangle_{\omega_{X_{j_2}}} &= \frac{1}{2} C^{\pm\omega} P_{\omega_{X_{j_1}} \omega_{X_{j_2}}}^{X_{j_1} X_{j_2}} \sum_{\nu_m} \langle \text{HF} | e^{\bar{Z}} e^{-Z} X_{j_1}^* T e^Z e^{-\bar{Z}} | \nu_m \rangle \\ &\times c_{\nu_m}^{X_{j_2}}(\omega_{X_{j_2}}), \quad \omega_{X_{j_1}} + \omega_{X_{j_2}} = 0, \end{aligned} \quad (164)$$

where $c_{\nu_m}^{X_{j_2}}(\omega_{X_{j_2}})$ amplitudes are obtained from Eq. (162).

4. Third-order molecular properties

Third-order molecular properties can be determined from the quadratic response function. To determine the quadratic response function, we initially identify the third-order quasi-energy Lagrangian

$$\begin{aligned} & \mathcal{L}^{X_{j_1} X_{j_2} X_{j_3}}(\omega_{X_{j_1}}, \omega_{X_{j_2}}, \omega_{X_{j_3}}) = P_{\omega_{X_{j_1}} \omega_{X_{j_2}} \omega_{X_{j_3}}}^{X_{j_1} X_{j_2} X_{j_3}} \left(\sum_{\mu_k \nu_m} \bar{c}_{\mu_k}^{X_{j_1} X_{j_2}}(\omega_{X_{j_1}}, \omega_{X_{j_2}}) (\mathcal{J}_{\mu_k \nu_m} - \omega_{X_{j_3}} \delta_{\mu_k \nu_m}) c_{\nu_m}^{X_{j_3}}(\omega_{X_{j_3}}) \right. \\ &+ \sum_{\mu_k \nu_m} \bar{c}_{\mu_k}^{X_{j_1}}(\omega_{X_{j_1}}) (\mathcal{J}_{\mu_k \nu_m} - (\omega_{X_{j_2}} + \omega_{X_{j_3}}) \delta_{\mu_k \nu_m}) c_{\nu_m}^{X_{j_2} X_{j_3}}(\omega_{X_{j_2}}, \omega_{X_{j_3}}) + \sum_{\nu_m} \langle \text{HF} | e^{\bar{Z}} e^{-Z} X_{j_1}^* T e^Z e^{-\bar{Z}} | \nu_m \rangle c_{\nu_m}^{X_{j_2} X_{j_3}}(\omega_{X_{j_2}}, \omega_{X_{j_3}}) \\ &+ \left. \sum_{\mu_k} \bar{c}_{\mu_k}^{X_{j_2} X_{j_3}}(\omega_{X_{j_2}}, \omega_{X_{j_3}}) \langle \mu_k | e^{\bar{Z}} e^{-Z} X_{j_1}^* T e^Z e^{-\bar{Z}} | \text{HF} \rangle + \sum_{\mu_k \nu_m} \bar{c}_{\mu_k}^{X_{j_2}}(\omega_{X_{j_2}}) \langle \mu_k | [e^{\bar{Z}} e^{-Z} X_{j_1}^* T e^Z e^{-\bar{Z}} | \nu_m \rangle \langle \text{HF} |] | \text{HF} \rangle c_{\nu_m}^{X_{j_3}}(\omega_{X_{j_3}}) \right), \\ & \omega_{X_{j_1}} + \omega_{X_{j_2}} + \omega_{X_{j_3}} = 0. \end{aligned} \quad (165)$$

Differentiating $\mathcal{L}^{X_{j_1} X_{j_2} X_{j_3}}(\omega_{X_{j_1}}, \omega_{X_{j_2}}, \omega_{X_{j_3}})$ with respect to the first-order response multipliers, $\bar{c}_{\mu_k}^{X_{j_1}}(\omega_{X_{j_1}})$, and using the stationarity condition in Eq. (157), gives the second-order response amplitude equation needed for constructing the cubic response function in Subsection V D 5,

$$\begin{aligned} & \sum_{\nu_m} (\mathcal{J}_{\mu_k \nu_m} - (\omega_{X_{j_1}} + \omega_{X_{j_2}}) \delta_{\mu_k \nu_m}) c_{\nu_m}^{X_{j_1} X_{j_2}}(\omega_{X_{j_1}}, \omega_{X_{j_2}}) \\ &= -P_{\omega_{X_{j_1}} \omega_{X_{j_2}}}^{X_{j_1} X_{j_2}} \sum_{\nu_m} \langle \mu_k | [e^{\bar{Z}} e^{-Z} X_{j_1}^* T e^Z e^{-\bar{Z}} | \nu_m \rangle \langle \text{HF} |] | \text{HF} \rangle c_{\nu_m}^{X_{j_2}}(\omega_{X_{j_2}}). \end{aligned} \quad (166)$$

Applying the $2n + 1$ and $2n + 2$ rules to the third-order Lagrangian, $\mathcal{L}^{X_{j_1} X_{j_2} X_{j_3}}(\omega_{X_{j_1}}, \omega_{X_{j_2}}, \omega_{X_{j_3}})$ of Eq. (165), gives the quadratic response

function [cf. Eq. (126)]

$$\begin{aligned} & \langle \langle X_{j_1}; X_{j_2}, X_{j_3} \rangle \rangle_{\omega_{X_{j_2}}, \omega_{X_{j_3}}} \\ &= \frac{1}{2} C^{\pm\omega} P_{\omega_{X_{j_1}} \omega_{X_{j_2}} \omega_{X_{j_3}}}^{X_{j_1} X_{j_2} X_{j_3}} \sum_{\mu_k \nu_m} \bar{c}_{\mu_k}^{X_{j_2}}(\omega_{X_{j_2}}) \langle \mu_k | [e^{\bar{Z}} e^{-Z} X_{j_1}^* T e^Z e^{-\bar{Z}} | \nu_m \rangle \langle \text{HF} |] \\ &\times | \text{HF} \rangle c_{\nu_m}^{X_{j_3}}(\omega_{X_{j_3}}) \\ &= \frac{1}{2} C^{\pm\omega} P_{\omega_{X_{j_1}} \omega_{X_{j_2}} \omega_{X_{j_3}}}^{X_{j_1} X_{j_2} X_{j_3}} \sum_{\mu_k \nu_m} \bar{c}_{\mu_k}^{X_{j_2}}(\omega_{X_{j_2}}) \mathcal{J}_{\mu_k \nu_m}^X c_{\nu_m}^{X_{j_3}}(\omega_{X_{j_3}}), \\ & \omega_{X_{j_1}} + \omega_{X_{j_2}} + \omega_{X_{j_3}} = 0, \end{aligned} \quad (167)$$

where $c_{v_m}^{X_{j_1}}(\omega_{X_{j_1}})$ amplitudes and $\bar{c}_{\mu_k}^{X_{j_1}}(\omega_{X_{j_1}})$ multipliers are obtained from Eqs. (162) and (163), respectively, and where

$$\mathcal{J}_{\mu_k v_m}^X = \langle \mu_k | [e^{\bar{Z}} e^{-Z} X^{*T} e^Z e^{-\bar{Z}} |v_m\rangle \langle \text{HF} |] | \text{HF} \rangle \quad (168)$$

is the *property Jacobian*, which can be viewed as the Jacobian of Eq. (129) with H_0^{*T} replaced by X^{*T} .

5. Fourth-order molecular properties

The fourth-order molecular properties can be obtained from the cubic response function. Applying the $2n + 1$ rule for the amplitudes and the $2n + 2$ rule for the multipliers, the cubic response function can be obtained from the fourth-order quasi-energy Lagrangian ${}^c\mathcal{L}^{X_{j_1} X_{j_2} X_{j_3} X_{j_4}}(\omega_{X_{j_1}}, \omega_{X_{j_2}}, \omega_{X_{j_3}}, \omega_{X_{j_4}})$ as

$$\begin{aligned} \langle (X_{j_1}; X_{j_2}, X_{j_3}, X_{j_4}) \rangle_{\omega_{X_{j_2}}, \omega_{X_{j_3}}, \omega_{X_{j_4}}} &= \frac{1}{2} C^{\pm\omega} P_{\omega_{X_{j_1}} \omega_{X_{j_2}} \omega_{X_{j_3}} \omega_{X_{j_4}}}^{X_{j_1} X_{j_2} X_{j_3} X_{j_4}} \left(\sum_{\mu_k v_m} \bar{c}_{\mu_k}^{X_{j_2}}(\omega_{X_{j_2}}) \langle \mu_k | [e^{\bar{Z}} e^{-Z} X_{j_1}^{*T} e^Z e^{-\bar{Z}} |v_m\rangle \langle \text{HF} |] | \text{HF} \rangle c_{v_m}^{X_{j_3} X_{j_4}} \right. \\ &\times (\omega_{X_{j_3}}, \omega_{X_{j_4}}) - \left. \left(\sum_{\mu_k} \bar{c}_{\mu_k}^{X_{j_2}}(\omega_{X_{j_2}}) c_{\mu_k}^{X_{j_3}}(\omega_{X_{j_3}}) \right) \left(\sum_{v_m} \langle \text{HF} | e^{\bar{Z}} e^{-Z} X_{j_1}^{*T} e^Z e^{-\bar{Z}} |v_m\rangle c_{v_m}^{X_{j_4}}(\omega_{X_{j_4}}) \right) \right), \\ &\omega_{X_{j_1}} + \omega_{X_{j_2}} + \omega_{X_{j_3}} + \omega_{X_{j_4}} = 0, \end{aligned} \quad (169)$$

where $c_{v_m}^{X_{j_1}}(\omega_{X_{j_1}})$, $\bar{c}_{\mu_k}^{X_{j_1}}(\omega_{X_{j_1}})$, and $c_{v_m}^{X_{j_1} X_{j_2}}(\omega_{X_{j_1}}, \omega_{X_{j_2}})$ are obtained from Eqs. (162), (163), and (166), respectively.

The route of derivation outlined here can straightforwardly be followed to determine higher-order response functions for the CL state.

E. Structural simplicity of molecular property expressions for CL states

Comparing the response functions obtained for CL and CC states (for the latter, see, for example, Sec. VIII of Ref. 11), we see that the response functions for the CL state contain contributions only from the ${}^c\mathcal{L}_{X_{j_1}}$ term [Eq. (153)] of the quasi-energy Lagrangian, whereas the response functions for the CC state contain contributions from both the ${}^c\mathcal{L}_{X_{j_1}}$ and ${}^c\mathcal{L}_{H_0}^{NL}$ terms.¹¹ The contributions that arise from ${}^c\mathcal{L}_{H_0}^{NL}$ contain the two-electron Hamiltonian H_0 , and therefore, their leading-order computational scaling is one order of magnitude larger than for corresponding contributions that arise from ${}^c\mathcal{L}_{X_{j_1}}$ and contain only one-electron operators X . Hence, the determination of response functions for a CL state is greatly simplified, both in terms of the structure of the equations and the computational scaling, compared to response functions for a CC state.

For calculating the response functions and right-hand sides of the response equations for a CL state, we have to determine two property vectors

$$\Omega_{\mu_i}^X = \langle \mu_i | e^{\bar{Z}} e^{-Z} X^{*T} e^Z e^{-\bar{Z}} | \text{HF} \rangle, \quad i = 1, 2, \dots, t, \quad (170)$$

$$j_{v_j}^X = \langle \text{HF} | e^{\bar{Z}} e^{-Z} X^{*T} e^Z e^{-\bar{Z}} | v_j \rangle, \quad j = 1, 2, \dots, t, \quad (171)$$

and linear transformations of the property Jacobian in Eq. (168) with the amplitude and multiplier response vectors, e.g.,

$$\begin{aligned} (\mathcal{J}^X c^Y)_{\mu_i} &= \sum_{j=1}^t \sum_{v_j} \mathcal{J}_{\mu_i v_j}^X c_{v_j}^Y \\ &= \sum_{j=1}^t \sum_{v_j} \langle \mu_i | [e^{\bar{Z}} e^{-Z} X^{*T} e^Z e^{-\bar{Z}} | v_j \rangle \langle \text{HF} |] | \text{HF} \rangle c_{v_j}^Y, \\ &i = 1, 2, \dots, t. \end{aligned} \quad (172)$$

The property vectors in Eqs. (170) and (171) enter, for example, in the right-hand sides of the first-order response equations for the amplitudes and multipliers, Eqs. (162) and (163), respectively. The linear transformation of the property Jacobian with first-order response vectors arises, for example, when the quadratic response function in Eq. (167) is evaluated. Response functions for a CI state (see Sec. VI of Ref. 11) contain only ${}^c\mathcal{L}_{X_{j_1}}$ term, as for the CL target state. Similarly, CI response functions and right-hand sides of CI response equations, as determined in Sec. VI of Ref. 11, contain only two property vectors and linear transformations of the property Jacobian with the response vectors, which are structurally analogous to Eqs. (170)–(172) for the CL state. The same structural simplifications thus occur for determining response functions for a CL and a CI state.

When evaluating response functions for a CL state, we have to solve response equations, e.g., Eqs. (162) and (163). These equations are solved using iterative algorithms and require linear transformations of the Jacobian \mathcal{J} of Eq. (129) on trial vectors \mathbf{b} , i.e., $\mathcal{J}\mathbf{b}$ and $\mathbf{b}^\top \mathcal{J}$. Since the Jacobian contains the two-electron operator H_0 , the leading-order scaling for the evaluation of these linear transformations is an order of magnitude larger than for constructing the response functions and the right-hand sides of the response equations. The leading-order computational scaling for determining CL response functions therefore arises from solving the response equations. When CP theory is used for a CL target state, we do not need to solve the response equations iteratively. Instead, we can determine a series of corrections in orders of the CC parent-state

similarity-transformed fluctuation potential, where the zeroth-order term is equal to the response function for the CC parent state and where the series formally converges to the response functions for the CL target state. In particular, it becomes computationally attractive to use CP theory if low-order corrections can reproduce the target quantities to high accuracy. Recall that the time evolution of the CL state is linearly parametrized and zeroth-order molecular properties therefore become EOM-CC molecular properties.^{17–19} In Sec. VI, we use CP theory to determine the lowest-order perturbative corrections for excitation energies and linear response function in the CPSD(LT) model.

VI. LOWEST-ORDER CORRECTIONS FOR THE CPSD(LT) MODEL

In Sec. IV, a series of energy corrections were determined for the CP model CPSD(LT), where the zeroth-order energy was the energy of the CCSD parent state and where the series formally converges to the energy of the CL target state. Using CP theory, series of molecular property corrections can also be determined, where the zeroth-order molecular properties are the molecular properties of the CCSD parent state and where the series formally converges to the molecular properties of the CL target state. The theoretical foundation for determining such a series is the same for a CL target state as for a CC target state and is described in Paper I¹ for a CC target state. For the CPSD(LT) model, we determine first- and second-order corrections to parent state excitation energies in Secs. VI A and VI B and the first-order correction to the linear response function in Sec. VI C.

A. Lowest-order corrections for excitation energies

In this subsection, we consider how an excitation energy can be determined for the CPSD(LT) model using CP theory, where a series of excitation-energy corrections to a CCSD excitation energy is determined in orders of the parent-state similarity-transformed fluctuation potential, and where the series formally converges to the excitation energy of the CL target state. We derive explicit expressions for the lowest-order corrections and use these corrections to analyze the size-extensivity of the CPSD(LT) excitation energies.

1. Perturbative approach to determination of excitation energies

Excitation energies are obtained from the response eigenvalue equation^{13,14,29,30}

$$\mathcal{J}\mathcal{R}_x = \omega_x \mathcal{R}_x, \quad (173a)$$

$$\mathcal{L}_x \mathcal{J} = \mathcal{L}_x \omega_x, \quad (173b)$$

$$\mathcal{L}_x \mathcal{R}_y = \delta_{xy}, \quad (173c)$$

where \mathcal{R}_x and \mathcal{L}_x are right and left eigenvectors for an excited state x , and ω_x is the corresponding excitation energy. The Jacobian reads [cf. Eq. (129)]

$$\mathcal{J}_{\mu_i, \nu_j} = \langle \mu_i | [e^{\bar{Z}} e^{-Z} H_0^{*T} e^Z e^{-\bar{Z}} | \nu_j \rangle \langle \text{HF} |] | \text{HF} \rangle, \quad i, j = 1, 2, 3, \quad (174)$$

or, in the expanded form,

$$\begin{aligned} \mathcal{J}_{\mu_i, \nu_j} &= \langle \mu_i | e^{\bar{Z}} e^{-Z} H_0^{*T} e^Z e^{-\bar{Z}} | \nu_j \rangle - \delta_{\mu_i, \nu_j} \langle \text{HF} | e^{\bar{Z}} e^{-Z} H_0^{*T} e^Z e^{-\bar{Z}} | \text{HF} \rangle \\ &= \langle \mu_i | H_0^{*T} | \nu_j \rangle - z_{\mu_i} \langle \text{HF} | H_0^{*T} | \nu_j \rangle - \langle \mu_i | e^{-Z} H_0^{*T} e^Z | \text{HF} \rangle \bar{z}_{\nu_j} \\ &\quad - \delta_{\mu_i, \nu_j} \left(\langle \text{HF} | H_0^{*T} | \text{HF} \rangle + \sum_{r=1}^3 \sum_{\lambda_r} \langle \text{HF} | H_0^{*T} | \lambda_r \rangle z_{\lambda_r} \right. \\ &\quad \left. + \sum_{r=1}^3 \sum_{\lambda_r} \bar{z}_{\lambda_r} \langle \lambda_r | e^{-Z} H_0^{*T} e^Z | \text{HF} \rangle \right), \quad i, j = 1, 2, 3. \end{aligned} \quad (175)$$

Using Eqs. (96) and (33) together with Eq. (38), we obtain from Eq. (175)

$$\begin{aligned} \mathcal{J}_{\mu_i, \nu_j} &= A_{\mu_i, \nu_j} - z_{\mu_i} \langle \text{HF} | \Phi^{*T} | \nu_j \rangle (\delta_{j1} + \delta_{j2}) - \delta_{\mu_i, \nu_j} \sum_{r=1}^2 \sum_{\lambda_r} \langle \text{HF} | \Phi^{*T} | \lambda_r \rangle z_{\lambda_r}, \\ &\quad i, j = 1, 2, 3. \end{aligned} \quad (176)$$

To obtain Eq. (176), we have further used that the last term in Eq. (38) vanishes when the auxiliary space is restricted to contain only one excitation level [see Sec. III C], following from Eq. (49). The amplitudes z_{μ_i} in Eq. (176) satisfy [cf. Eq. (52)]

$$\begin{aligned} \sum_{j=1}^3 \sum_{\nu_j} A_{\mu_i, \nu_j} z_{\nu_j} + \langle \mu_i | \Phi^{*T} | \text{HF} \rangle \delta_{i3} - z_{\mu_i} \left(\sum_{j=1}^2 \sum_{\nu_j} \langle \text{HF} | \Phi^{*T} | \nu_j \rangle z_{\nu_j} \right) &= 0, \\ i = 1, 2, 3. \end{aligned} \quad (177)$$

Both Eqs. (176) and (177) contain the extended parent-state Jacobian in Eq. (37). To determine molecular property perturbation corrections, including excitation energy corrections, we use in CP theory the parent-state Jacobian partitioning of Eqs. (56) and (57) for the extended parent-state Jacobian. Substituting Eqs. (56) and (57) into Eqs. (176) and (177), we obtain

$$\begin{aligned} \mathcal{J}_{\mu_i, \nu_j} &= A_{\mu_i, \nu_j}^{(0)} + A_{\mu_i, \nu_j}^{(1)} - z_{\mu_i} \langle \text{HF} | \Phi^{*T} | \nu_j \rangle (\delta_{j1} + \delta_{j2}) \\ &\quad - \delta_{\mu_i, \nu_j} \sum_{r=1}^2 \sum_{\lambda_r} \langle \text{HF} | \Phi^{*T} | \lambda_r \rangle z_{\lambda_r}, \quad i, j = 1, 2, 3, \end{aligned} \quad (178)$$

$$\begin{aligned} \sum_{j=1}^3 \sum_{\nu_j} A_{\mu_i, \nu_j}^{(0)} z_{\nu_j} + \sum_{j=1}^3 \sum_{\nu_j} A_{\mu_i, \nu_j}^{(1)} z_{\nu_j} + \langle \mu_i | \Phi^{*T} | \text{HF} \rangle \delta_{i3} \\ - z_{\mu_i} \left(\sum_{j=1}^2 \sum_{\nu_j} \langle \text{HF} | \Phi^{*T} | \nu_j \rangle z_{\nu_j} \right) &= 0, \quad i = 1, 2, 3. \end{aligned} \quad (179)$$

In the following, we will determine a series of corrections to the CCSD excitation energies that target CPSD(LT) excitation energies, by expanding the Jacobian in Eq. (178) in orders of the parent-state similarity-transformed fluctuation potential

$$\mathcal{J} = \mathcal{J}^{(0)} + \mathcal{J}^{(1)} + \mathcal{J}^{(2)} + \mathcal{J}^{(3)} + \dots, \quad (180)$$

where the zeroth-order eigenvalue equation satisfies

$$\mathcal{J}^{(0)} \mathcal{R}_x^{(0)} = \omega_x^{(0)} \mathcal{R}_x^{(0)}, \quad (181a)$$

$$\mathcal{L}_x^{(0)} \mathcal{J}^{(0)} = \mathcal{L}_x^{(0)} \omega_x^{(0)}, \quad (181b)$$

$$\mathcal{L}_x^{(0)} \mathcal{R}_x^{(0)} = 1, \quad (181c)$$

$$\omega_x^{(0)} = \omega_x^{\text{CCSD}}, \quad (182)$$

where ω_x^{CCSD} is a CCSD Jacobian eigenvalue, and then solving the response eigenvalue equation order by order in the parent-state similarity-transformed fluctuation potential.

All terms in the Jacobian expansion in Eq. (178) contain the parent-state similarity-transformed fluctuation potential and are thus of at least first order, except $\mathbf{A}^{(0)}$, for which fluctuation potential terms are regarded as having zeroth order. $\mathbf{A}^{(0)}$ contains Fock operator terms in addition to the fluctuation potential terms in the parent space sub-block. Assigning $\mathcal{J}^{(0)}$ to be equal to $\mathbf{A}^{(0)}$ of Eq. (57a), $\mathcal{J}^{(0)}$ can in the two-component form be written as [cf. Eq. (59)]

$$\mathcal{J}^{(0)} = \mathbf{A}^{(0)} = \begin{pmatrix} \mathbf{J}^{\text{CCSD}} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\varepsilon}_T \end{pmatrix}. \quad (183)$$

The singles-and-doubles component of the matrix $\mathcal{J}^{(0)}$ satisfies the zeroth-order response eigenvalue equation in Eqs. (181) and (182)

$$\begin{pmatrix} \mathbf{J}^{\text{CCSD}} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\varepsilon}_T \end{pmatrix} \begin{pmatrix} \mathbf{R}_x^{\text{CCSD}} \\ \mathbf{0} \end{pmatrix} = \omega_x^{\text{CCSD}} \begin{pmatrix} \mathbf{R}_x^{\text{CCSD}} \\ \mathbf{0} \end{pmatrix}, \quad (184)$$

implying that

$$\mathbf{R}_x^{(0)} = \begin{pmatrix} \mathbf{R}_x^{\text{CCSD}} \\ \mathbf{0} \end{pmatrix}, \quad (185)$$

$$\mathcal{L}_x^{(0)} = (\mathbf{L}_x^{\text{CCSD}} \mathbf{0}). \quad (186)$$

The amplitudes z_{μ_i} entering in the Jacobian of Eq. (178) are determined solving Eq. (179) order by order in Φ^{*T} . Explicit expressions for the lowest-order amplitude corrections are given in Eqs. (66)–(68). Substituting these lowest-order corrections in Eq. (178), we obtain the lowest-order Jacobian corrections as

$$\begin{aligned} \mathcal{J}_{\mu_i \nu_j}^{(0)} = A_{\mu_i \nu_j}^{(0)} = & \langle \mu_i | [H_0^{*T}, \theta_{\nu_j}] | \text{HF} \rangle (\delta_{i1} \delta_{j1} + \delta_{i1} \delta_{j2} + \delta_{i2} \delta_{j1} + \delta_{i2} \delta_{j2}) \\ & + \varepsilon_{\nu_j} \delta_{\mu_i \nu_j} \delta_{i3} \delta_{j3}, \quad i, j = 1, 2, 3, \end{aligned} \quad (187)$$

$$\begin{aligned} \mathcal{J}_{\mu_i \nu_j}^{(1)} = A_{\mu_i \nu_j}^{(1)} = & \langle \mu_i | [\Phi^{*T}, \theta_{\nu_j}] | \text{HF} \rangle (\delta_{i1} \delta_{j3} + \delta_{i2} \delta_{j3} + \delta_{i3} \delta_{j1} \\ & + \delta_{i3} \delta_{j2} + \delta_{i3} \delta_{j3}), \quad i, j = 1, 2, 3, \end{aligned} \quad (188)$$

$$\begin{aligned} \mathcal{J}_{\mu_i \nu_j}^{(2)} = & -z_{\mu_i}^{(1)} \langle \text{HF} | \Phi^{*T} | \nu_j \rangle (\delta_{j1} + \delta_{j2}) - \delta_{\mu_i \nu_j} \sum_{r=1}^2 \sum_{\lambda_r} \langle \text{HF} | \Phi^{*T} | \lambda_r \rangle z_{\lambda_r}^{(1)} \\ = & -z_{\mu_i}^{(1)} \langle \text{HF} | \Phi^{*T} | \nu_j \rangle (\delta_{i3} \delta_{j1} + \delta_{i3} \delta_{j2}), \quad i, j = 1, 2, 3, \end{aligned} \quad (189)$$

$$\begin{aligned} \mathcal{J}_{\mu_i \nu_j}^{(3)} = & -z_{\mu_i}^{(2)} \langle \text{HF} | \Phi^{*T} | \nu_j \rangle (\delta_{j1} + \delta_{j2}) - \delta_{\mu_i \nu_j} \sum_{r=1}^2 \sum_{\lambda_r} \langle \text{HF} | \Phi^{*T} | \lambda_r \rangle z_{\lambda_r}^{(2)}, \\ & i, j = 1, 2, 3. \end{aligned} \quad (190)$$

To obtain Eqs. (187) and (188), we have used Eqs. (57). To obtain the second equality in Eq. (189), we have used Eq. (66a).

B. Arbitrary-order corrections for excitation energies

To determine a series of excitation energy corrections in orders of the parent-state similarity-transformed fluctuation potential, we introduce an order expansion of the excitation energies and the left and right eigenvectors of Eq. (173)

$$\mathbf{R}_x = \mathbf{R}_x^{(0)} + \mathbf{R}_x^{(1)} + \mathbf{R}_x^{(2)} + \mathbf{R}_x^{(3)} + \dots, \quad (191)$$

$$\mathcal{L}_x = \mathcal{L}_x^{(0)} + \mathcal{L}_x^{(1)} + \mathcal{L}_x^{(2)} + \mathcal{L}_x^{(3)} + \dots, \quad (192)$$

$$\omega_x = \omega_x^{(0)} + \omega_x^{(1)} + \omega_x^{(2)} + \omega_x^{(3)} + \dots, \quad (193)$$

and substitute Eqs. (191)–(193), together with the Jacobian expansion in Eq. (180), into the response eigenvalue equation of Eq. (173). Collecting terms of order k , we obtain the k th-order eigenvalue equation

$$\sum_{p=0}^k \mathcal{J}^{(p)} \mathbf{R}_x^{(k-p)} = \sum_{p=0}^k \omega_x^{(p)} \mathbf{R}_x^{(k-p)}, \quad (194)$$

which can be rearranged as

$$(\mathcal{J}^{(0)} - \omega_x^{(0)} \mathbf{I}) \mathbf{R}_x^{(k)} = \sum_{p=1}^k \omega_x^{(p)} \mathbf{R}_x^{(k-p)} - \sum_{p=1}^k \mathcal{J}^{(p)} \mathbf{R}_x^{(k-p)}, \quad (195)$$

where the zeroth-order Jacobian, $\mathcal{J}^{(0)}$ of Eq. (183), has a block-diagonal structure. Projecting Eq. (195) against the zeroth-order left eigenvector, $\mathcal{L}_x^{(0)}$, we obtain the k -order correction to the CCSD excitation energy

$$\omega_x^{(k)} = \sum_{p=1}^k \mathcal{L}_x^{(0)} \mathcal{J}^{(p)} \mathbf{R}_x^{(k-p)}, \quad (196)$$

where we have used Eq. (181b) and

$$\mathcal{L}_x^{(0)} \mathbf{R}_x^{(k)} = 0, \quad k > 0. \quad (197)$$

Note that the right-hand side of Eq. (196) depends only on the right eigenvectors through order $(k-1)$.

When excitation energy corrections have been determined through order k , they can be substituted into Eq. (195) to determine the k th-order correction to the right eigenvector. The k th-order right eigenvalue equation can in the two-component form be written as

$$\begin{aligned} (\mathbf{J}^{\text{CCSD}} - \omega_x^{(0)} \mathbf{I}) \mathbf{R}_{xSD}^{(k)} = & \sum_{p=1}^k \omega_x^{(p)} \mathbf{R}_{xSD}^{(k-p)} - \sum_{p=2}^k \mathcal{J}_{SD,SD}^{(p)} \mathbf{R}_{xSD}^{(k-p)} \\ & - \sum_{p=1}^{k-1} \mathcal{J}_{SD,T}^{(p)} \mathbf{R}_{xT}^{(k-p)}, \end{aligned} \quad (198a)$$

$$\begin{aligned} \mathbf{R}_{xT}^{(k)} = & (\boldsymbol{\varepsilon}_T - \omega_x^{(0)} \mathbf{I})^{-1} \left(\sum_{p=1}^{k-1} \omega_x^{(p)} \mathbf{R}_{xT}^{(k-p)} \right. \\ & \left. - \sum_{p=1}^k \mathcal{J}_{T,SD}^{(p)} \mathbf{R}_{xSD}^{(k-p)} - \sum_{p=1}^{k-1} \mathcal{J}_{T,T}^{(p)} \mathbf{R}_{xT}^{(k-p)} \right), \end{aligned} \quad (198b)$$

where SD denotes the singles-and-doubles subspace and T denotes the triples subspace. To obtain Eqs. (198), we used the first-order Jacobian which has a vanishing $SD-SD$ sub-block [see Eq. (188)]

and the triples component of the zeroth-order right eigenvector vanishes [see Eq. (185)]. In the following, we use Eqs. (196) and (198) to determine lowest-order corrections to excitation energies.

1. First-order excitation energies

Using Eqs. (196) and (198), we obtain first-order corrections to the excitation energy and to the right eigenvector

$$\omega_x^{(1)} = \mathcal{L}_x^{(0)} \mathcal{J}^{(1)} \mathcal{R}_x^{(0)} = (\mathbf{L}_x^{\text{CCSD}} \mathbf{0}) \begin{pmatrix} \mathbf{0} & \mathcal{J}_{SD,T}^{(1)} \\ \mathcal{J}_{T,SD}^{(1)} & \mathcal{J}_{T,T}^{(1)} \end{pmatrix} \begin{pmatrix} \mathbf{R}_x^{\text{CCSD}} \\ \mathbf{0} \end{pmatrix} = 0, \quad (199)$$

$$(\mathbf{J}^{\text{CCSD}} - \omega_x^{\text{CCSD}} \mathbf{I}) \mathcal{R}_{xSD}^{(1)} = \omega_x^{(1)} \mathbf{R}_x^{\text{CCSD}} = \mathbf{0}, \quad (200a)$$

$$\mathcal{R}_{xT}^{(1)} = -(\boldsymbol{\varepsilon}_T - \omega_x^{\text{CCSD}} \mathbf{I})^{-1} \mathcal{J}_{T,SD}^{(1)} \mathbf{R}_x^{\text{CCSD}}. \quad (200b)$$

The first-order singles-and-doubles component vanishes

$$\mathcal{R}_{x\mu_i}^{(1)} = 0, \quad i = 1, 2, \quad (201)$$

and the triples component becomes

$$\mathcal{R}_{x\mu_3}^{(1)} = -(\varepsilon_{\mu_3} - \omega_x^{\text{CCSD}})^{-1} \langle \mu_3 | [\Phi^{*T}, R_x^{\text{CCSD}}] | \text{HF} \rangle, \quad (202)$$

where

$$\mathbf{R}_x^{\text{CCSD}} = \sum_{i=1}^2 \sum_{\mu_i} R_{x\mu_i}^{\text{CCSD}} \theta_{\mu_i}. \quad (203)$$

To obtain Eqs. (199)–(202), we have used Eqs. (185)–(188).

2. Second-order excitation energies

The second-order correction to the excitation energy becomes

$$\begin{aligned} \omega_x^{(2)} &= \mathcal{L}_x^{(0)} \mathcal{J}^{(2)} \mathcal{R}_x^{(0)} + \mathcal{L}_x^{(0)} \mathcal{J}^{(1)} \mathcal{R}_x^{(1)} \\ &= \mathbf{L}_x^{\text{CCSD}} \mathcal{J}_{SD,SD}^{(2)} \mathbf{R}_x^{\text{CCSD}} + \mathbf{L}_x^{\text{CCSD}} \mathcal{J}_{SD,T}^{(1)} \mathcal{R}_{xT}^{(1)} \\ &= \mathbf{L}_x^{\text{CCSD}} \mathcal{J}_{SD,T}^{(1)} \mathcal{R}_{xT}^{(1)}, \end{aligned} \quad (204)$$

where to obtain the second equality we have used Eqs. (185)–(188) and to obtain the last equality we have used that $\mathcal{J}_{SD,SD}^{(2)} = \mathbf{0}$ [see Eq. (189)]. The second-order corrections to the right eigenvector read

$$(\mathbf{J}^{\text{CCSD}} - \omega_x^{\text{CCSD}} \mathbf{I}) \mathcal{R}_{xSD}^{(2)} = \omega_x^{(2)} \mathbf{R}_x^{\text{CCSD}} - \mathcal{J}_{SD,T}^{(1)} \mathcal{R}_{xT}^{(1)}, \quad (205a)$$

$$\mathcal{R}_{xT}^{(2)} = -(\boldsymbol{\varepsilon}_T - \omega_x^{\text{CCSD}} \mathbf{I})^{-1} \left(\mathcal{J}_{T,SD}^{(2)} \mathbf{R}_x^{\text{CCSD}} + \mathcal{J}_{T,T}^{(1)} \mathcal{R}_{xT}^{(1)} \right). \quad (205b)$$

In the commutator form, Eqs. (204) and (205) become

$$\omega_x^{(2)} = \langle L_x^{\text{CCSD}} | [\Phi^{*T}, \mathcal{R}_{x3}^{(1)}] | \text{HF} \rangle, \quad (206)$$

$$\sum_{j=1}^2 \sum_{v_j} (J_{\mu_i v_j}^{\text{CCSD}} - \omega_x^{\text{CCSD}} \delta_{\mu_i v_j}) \mathcal{R}_{xv_j}^{(2)} = \omega_x^{(2)} R_{x\mu_i}^{\text{CCSD}} - \langle \mu_i | [\Phi^{*T}, \mathcal{R}_{x3}^{(1)}] | \text{HF} \rangle, \quad (207a)$$

$$i = 1, 2,$$

$$\begin{aligned} \mathcal{R}_{x\mu_3}^{(2)} &= -(\varepsilon_{\mu_3} - \omega_x^{\text{CCSD}})^{-1} \left(-z_{\mu_3}^{(1)} \langle \text{HF} | \Phi^{*T} | R_x^{\text{CCSD}} \rangle \right. \\ &\quad \left. + \langle \mu_3 | [\Phi^{*T}, \mathcal{R}_{x3}^{(1)}] | \text{HF} \rangle \right), \end{aligned} \quad (207b)$$

where we have introduced the notation

$$\mathcal{R}_{x3}^{(k)} = \sum_{\mu_3} \mathcal{R}_{x\mu_3}^{(k)} \theta_{\mu_3}. \quad (208)$$

3. Third-order excitation energies

The third-order correction to the CCSD excitation energy is given by

$$\begin{aligned} \omega_x^{(3)} &= \mathcal{L}_x^{(0)} \mathcal{J}^{(1)} \mathcal{R}_x^{(2)} + \mathcal{L}_x^{(0)} \mathcal{J}^{(2)} \mathcal{R}_x^{(1)} + \mathcal{L}_x^{(0)} \mathcal{J}^{(3)} \mathcal{R}_x^{(0)} \\ &= \mathbf{L}_x^{\text{CCSD}} \mathcal{J}_{SD,T}^{(1)} \mathcal{R}_{xT}^{(2)} + \mathbf{L}_x^{\text{CCSD}} \mathcal{J}_{SD,T}^{(2)} \mathcal{R}_{xT}^{(1)} + \mathbf{L}_x^{\text{CCSD}} \mathcal{J}_{SD,SD}^{(3)} \mathbf{R}_x^{\text{CCSD}} \\ &= \mathbf{L}_x^{\text{CCSD}} \mathcal{J}_{SD,T}^{(1)} \mathcal{R}_{xT}^{(2)} + \mathbf{L}_x^{\text{CCSD}} \mathcal{J}_{SD,SD}^{(3)} \mathbf{R}_x^{\text{CCSD}}, \end{aligned} \quad (209)$$

where to obtain the second equality we have used Eqs. (188) and (201) and to obtain the last equality we have used Eq. (189). Using Eqs. (188) and (190), the commutator form of Eq. (209) becomes

$$\begin{aligned} \omega_x^{(3)} &= \langle L_x^{\text{CCSD}} | [\Phi^{*T}, \mathcal{R}_{x3}^{(2)}] | \text{HF} \rangle - \left(\sum_{i=1}^2 \sum_{\mu_i} L_{x\mu_i}^{\text{CCSD}} z_{\mu_i}^{(2)} \right) \\ &\quad \times \langle \text{HF} | \Phi^{*T} | R_x^{\text{CCSD}} \rangle - \left(\sum_{i=1}^2 \sum_{\mu_i} L_{x\mu_i}^{\text{CCSD}} R_{x\mu_i}^{\text{CCSD}} \right) \\ &\quad \times \left(\sum_{j=1}^2 \sum_{v_j} \langle \text{HF} | \Phi^{*T} | v_j \rangle z_{v_j}^{(2)} \right). \end{aligned} \quad (210)$$

4. Weak size-extensivity of excitation energies

We will now compare the lowest-order excitation energy corrections in the CPSD(LT) model with the ones we have obtained in Paper II⁷ for the CPSD(T) model. Initially, we recognize that the first-order right eigenvector $R_{x\mu_i}^{(1)}$, $i = 1, 2, 3$, in Eqs. (97) of Paper II⁷ is equal to the first-order eigenvector $\mathcal{R}_{x\mu_i}^{(1)}$, $i = 1, 2, 3$ in Eqs. (201) and (202). For the second-order right eigenvector, the sum of the first and third term of the right-hand side of the singles-and-doubles component $R_{x\mu_i}^{(2)}$, $i = 1, 2$, of Eq. (99a) in Paper II⁷ gives $\mathcal{R}_{x\mu_i}^{(2)}$, $i = 1, 2$, of Eq. (207a); the second term of the right-hand side of Eq. (99a) in Paper II⁷ is a connected contribution involving $\delta T_3^{(1)}$ that has no counterpart in Eq. (207a). The second-order triples component $R_{x\mu_3}^{(2)}$ in Eq. (99b) of Paper II⁷ has the last term on the right-hand side in common with $\mathcal{R}_{x\mu_3}^{(2)}$ of Eq. (207b), while the first term, describing a connected commutator contribution which involves the first-order triples amplitudes and the CCSD right excitation amplitudes, is replaced by a non-size-extensive contribution in Eq. (207b) involving the same quantities. The first-order excitation energy corrections vanish in both models. For the CPSD(T) model, the second-order excitation energy correction in Eq. (98) of Paper II⁷ contains two terms. The first term is a connected contribution involving the first-order triples amplitude corrections and the CCSD right eigenvector, while the second term involves the first-order right triples eigenvector. This last term is the only contribution in $\omega_x^{(2)}$ of the CPSD(LT) model in Eq. (206). For the CPSD(LT) model, $\omega_x^{(3)}$ in Eq. (210) contains three terms, the first term is structurally equal to the last term in $\omega_x^{(3)}$ in Eq. (100) of Paper II,⁷ while the last two terms in Eq. (210) show a quadratic dependence on the

system size, and $\omega_x^{(3)}$ therefore is not size-extensive. However, the excitation energies in the CPSD(LT) model are weakly size-extensive because the zeroth-order CCSD excitation energy contribution and the first non-vanishing correction (i.e., second-order contribution) in Eq. (206) are size-extensive, and non-size-extensive contributions first start to enter in third order in the series of excitation energy corrections.

C. Lowest-order corrections for linear response function

In this subsection, we will determine the zeroth- and first-order corrections to the linear response function of Eq. (164). Since the parent state for the CPSD(LT) model is a CCSD state and since the time evolution of the |CL> state is linearly parametrized, the zeroth-order linear response function will become the EOM-CCSD linear response function.^{19,31,32} The linear response function in Eq. (164) can be written as

$$\langle\langle X; Y \rangle\rangle_{\omega_Y} = \frac{1}{2} C^{\pm\omega} P_{\omega_X \omega_Y}^{XY} \mathbf{y}^X \mathbf{c}^Y(\omega_Y), \quad \omega_X + \omega_Y = 0, \quad (211)$$

where \mathbf{c}^X contains the response amplitudes of Eq. (162)

$$\left(\mathcal{J} - \omega_X \mathbf{I} \right) \mathbf{c}^X(\omega_X) = -\mathbf{\Omega}^X, \quad (212)$$

and $\mathbf{\Omega}^X$ and \mathbf{y}^X are given in Eqs. (170) and (171), respectively. The amplitude and multiplier corrections in orders of Φ^{*T} are given in Eqs. (65)–(71). We initially consider the zeroth- and first-order contributions to the vectors $\mathbf{\Omega}^X$ and \mathbf{y}^X . An element of the $\mathbf{\Omega}^X$ vector of Eq. (170) can be written as

$$\begin{aligned} \Omega_{\mu_i}^X &= \langle \mu_i | e^{-Z} X^{*T} e^Z | \text{HF} \rangle = \langle \mu_i | X^{*T} | \text{HF} \rangle + \langle \mu_i | [X^{*T}, Z] | \text{HF} \rangle \\ &\quad + \frac{1}{2} \langle \mu_i | [[X^{*T}, Z], Z] | \text{HF} \rangle, \quad i = 1, 2, 3, \end{aligned} \quad (213)$$

where to obtain the first equality we have used Eq. (92) and to obtain the second equality we have applied the BCH expansion and used that $Z^2 = 0$. As the property operator X has no order in Φ^{*T} and since the zeroth-order amplitudes vanish, the zeroth- and first-order contributions to the $\mathbf{\Omega}^X$ vector become

$$\mathbf{\Omega}_{\mu_i}^{X(0)} = \langle \mu_i | X^{*T} | \text{HF} \rangle, \quad i = 1, 2, 3, \quad (214)$$

$$\begin{aligned} \mathbf{\Omega}_{\mu_i}^{X(1)} &= \langle \mu_i | [X^{*T}, Z^{(1)}] | \text{HF} \rangle = \sum_{v_3} \langle \mu_i | [X^{*T}, |v_3\rangle \langle \text{HF}|] | \text{HF} \rangle z_{v_3}^{(1)} \\ &= \sum_{v_3} A_{\mu_i v_3}^X z_{v_3}^{(1)}, \quad i = 1, 2, 3, \end{aligned} \quad (215)$$

where in the last equality of Eq. (215) we have introduced the CCSD extended parent-state property Jacobian for a linear parametrization

$$A_{\mu_i v_j}^X = \langle \mu_i | [X^{*T}, |v_j\rangle \langle \text{HF}|] | \text{HF} \rangle, \quad i, j = 1, 2, 3. \quad (216)$$

We now rewrite the CCSD extended parent-state property Jacobian for a linear parametrization to become the CCSD extended

parent-state property Jacobian for an exponential parametrization and therefore write Eq. (216) in the form

$$\begin{aligned} A_{\mu_i v_j}^X &= \langle \mu_i | [X^{*T}, \theta_{v_j}] | \text{HF} \rangle + \langle \mu_i | \theta_{v_j} X^{*T} | \text{HF} \rangle - \delta_{\mu_i v_j} \langle \text{HF} | X^{*T} | \text{HF} \rangle, \\ &\quad i, j = 1, 2, 3, \end{aligned} \quad (217)$$

where $\langle \mu_i | [X^{*T}, \theta_{v_j}] | \text{HF} \rangle$ is the CCSD extended parent-state property Jacobian for an exponential parametrization. Substituting the resolution of the identity in the complete orthonormal basis $|\mathcal{B}\rangle$ of Eq. (5) into the second term of Eq. (217) gives

$$\begin{aligned} \langle \mu_i | \theta_{v_j} X^{*T} | \text{HF} \rangle &= \langle \mu_i | \theta_{v_j} | \text{HF} \rangle \langle \text{HF} | X^{*T} | \text{HF} \rangle + \sum_{r=1}^2 \sum_{\lambda_r} \langle \mu_i | \theta_{v_j} | \lambda_r \rangle \\ &\quad \times \langle \lambda_r | X^{*T} | \text{HF} \rangle + \sum_{r=3}^{\infty} \sum_{\lambda_r} \langle \mu_i | \theta_{v_j} | \lambda_r \rangle \langle \lambda_r | X^{*T} | \text{HF} \rangle \\ &= \delta_{\mu_i v_j} \langle \text{HF} | X^{*T} | \text{HF} \rangle + \sum_{r=1}^2 \sum_{\lambda_r} \langle \mu_i | \theta_{v_j} | \lambda_r \rangle \langle \lambda_r | X^{*T} | \text{HF} \rangle, \\ &\quad i, j = 1, 2, 3, \end{aligned} \quad (218)$$

where to obtain the last equality we have used that $\sum_{r=3}^{\infty} \sum_{\lambda_r} \langle \mu_i | \theta_{v_j} | \lambda_r \rangle = 0$ for $i, j = 1, 2, 3$. Substituting Eq. (218) into Eq. (217), gives

$$\begin{aligned} A_{\mu_i v_j}^X &= \langle \mu_i | [X^{*T}, \theta_{v_j}] | \text{HF} \rangle + \sum_{r=1}^2 \sum_{\lambda_r} \langle \mu_i | \theta_{v_j} | \lambda_r \rangle \langle \lambda_r | X^{*T} | \text{HF} \rangle, \\ &\quad i, j = 1, 2, 3. \end{aligned} \quad (219)$$

We now consider the \mathbf{y}^X vector of Eq. (171). In order to identify the EOM-CCSD linear response function as the zeroth-order term in the CPSD(LT) linear response function series, we include the first-order multipliers in the zeroth-order \mathbf{y}^X vector, giving

$$\mathbf{y}_{v_j}^{X(0)} = \langle \text{HF} | e^{\bar{Z}^{(1)}} X^{*T} e^{-\bar{Z}^{(1)}} | v_j \rangle (\delta_{j1} + \delta_{j2}), \quad j = 1, 2, 3, \quad (220)$$

where we have used that the zeroth-order amplitudes and multipliers vanish and that the vector $\langle \text{HF} | e^{\bar{Z}^{(1)}} X^{*T} e^{-\bar{Z}^{(1)}} | v_j \rangle$ has contributions only in the singles-and-doubles space since the vector $\langle \text{HF} | X^{*T} | v_j \rangle$ and the first-order multipliers of Eq. (69) have non-vanishing contributions only in the singles-and-doubles space. To avoid double counting, we express a k th-order correction to the \mathbf{y}^X vector as

$$\begin{aligned} \mathbf{y}_{v_j}^{X(k)} &= \left\{ \langle \text{HF} | e^{\bar{Z}^{(1)}} e^{-Z} X^{*T} e^Z e^{-\bar{Z}^{(1)}} | v_j \rangle - \langle \text{HF} | e^{\bar{Z}^{(1)}} X^{*T} e^{-\bar{Z}^{(1)}} | v_j \rangle \right. \\ &\quad \left. \times (\delta_{j1} + \delta_{j2}) \right\}^{\{k\}}, \quad j = 1, 2, 3, \quad k > 0, \end{aligned} \quad (221)$$

where the $\{ \cdot \}^{\{k\}}$ notation has been defined after Eq. (65). Using Eq. (221), the first-order contribution to the \mathbf{y}^X vector becomes

$$\mathbf{y}_{v_j}^{X(1)} = \langle \text{HF} | [X^{*T}, Z^{(1)}] | v_j \rangle = 0, \quad j = 1, 2, 3, \quad (222)$$

where to obtain the last equality we have used Eq. (17).

We are now in a position to determine the zeroth- and first-order corrections to the response amplitudes of Eq. (212) and to

the linear response function of Eq. (211). To obtain the response amplitude corrections, we use Eqs. (214), (215), and (56)

$$\sum_{j=1}^2 \sum_{v_j} \left(J_{\mu_i v_j}^{\text{CCSD}} - \omega_X \delta_{\mu_i v_j} \right) c_{v_j}^{X(0)}(\omega_X) = -\langle \mu_i | X^{*T} | \text{HF} \rangle, \quad i = 1, 2, \quad (223a)$$

$$\left(\varepsilon_{\mu_3} - \omega_X \right) c_{\mu_3}^{X(0)}(\omega_X) = -\langle \mu_3 | X^{*T} | \text{HF} \rangle, \quad (223b)$$

$$\sum_{j=1}^2 \sum_{v_j} \left(J_{\mu_i v_j}^{\text{CCSD}} - \omega_X \delta_{\mu_i v_j} \right) c_{v_j}^{X(1)}(\omega_X) = -\sum_{v_3} A_{\mu_i v_3}^X z_{v_3}^{(1)} - \sum_{v_3} J_{\mu_i v_3}^{(1)} c_{v_3}^{X(0)}(\omega_X), \quad i = 1, 2, \quad (224a)$$

$$\left(\varepsilon_{\mu_3} - \omega_X \right) c_{\mu_3}^{X(1)}(\omega_X) = -\sum_{v_3} A_{\mu_3 v_3}^X z_{v_3}^{(1)} - \sum_{j=1}^3 J_{\mu_3 v_j}^{(1)} c_{v_j}^{X(0)}(\omega_X). \quad (224b)$$

Using Eqs. (220) and (222), the zeroth- and first-order corrections to the linear response function of Eq. (211) become

$$\langle \langle X; Y \rangle \rangle_{\omega_Y}^{(0)} = \frac{1}{2} C^{\pm\omega} P_{\omega_X \omega_Y}^{XY} \sum_{j=1}^2 \sum_{v_j} \langle \text{HF} | e^{\bar{Z}^{(1)}} X^{*T} e^{-\bar{Z}^{(1)}} | v_j \rangle c_{v_j}^{Y(0)}(\omega_Y), \quad \omega_X + \omega_Y = 0, \quad (225)$$

$$\langle \langle X; Y \rangle \rangle_{\omega_Y}^{(1)} = \frac{1}{2} C^{\pm\omega} P_{\omega_X \omega_Y}^{XY} \left(\gamma^{X(1)} c^{Y(0)}(\omega_Y) + \gamma^{X(0)} c^{Y(1)}(\omega_Y) \right) = \frac{1}{2} C^{\pm\omega} P_{\omega_X \omega_Y}^{XY} \sum_{j=1}^2 \sum_{v_j} \langle \text{HF} | e^{\bar{Z}^{(1)}} X^{*T} e^{-\bar{Z}^{(1)}} | v_j \rangle c_{v_j}^{Y(1)}(\omega_Y), \quad \omega_X + \omega_Y = 0. \quad (226)$$

The singles-and-doubles space component of the zeroth-order response amplitudes in Eq. (223a) is identical to the CCSD response amplitudes $t_{v_j}^{Y\text{-CCSD}}(\omega_Y)$ [see, e.g., Eq. (381) in Ref. 11], and the first-order multipliers in Eq. (69) have only a singles-and-doubles component that is identical to the CCSD multipliers $t_{\mu_i}^{\text{CCSD}}$ [see, e.g., Eqs. (327)–(329) in Ref. 11]. This means that the zeroth-order linear response function in Eq. (225) can be written as

$$\langle \langle X; Y \rangle \rangle_{\omega_Y}^{(0)} = \frac{1}{2} C^{\pm\omega_Y} P_{\omega_X \omega_Y}^{XY} \sum_{j=1}^2 \sum_{v_j} \langle \text{HF} | e^{\bar{T}^{\text{CCSD}}} X^T e^{-\bar{T}^{\text{CCSD}}} | v_j \rangle t_{v_j}^{Y\text{-CCSD}}(\omega_Y), \quad \omega_X + \omega_Y = 0, \quad (227)$$

where

$$\bar{T}^{\text{CCSD}} = \sum_{i=1}^2 \sum_{\mu_i} t_{\mu_i}^{\text{CCSD}} | \text{HF} \rangle \langle \mu_i |. \quad (228)$$

Equation (227) shows that the zeroth-order linear response function in the CPSD(LT) model is identical to the EOM-CCSD linear response function [cf. Eq. (407) in Ref. 11]

$$\langle \langle X; Y \rangle \rangle_{\omega_Y}^{(0)} = \langle \langle X; Y \rangle \rangle_{\omega_Y}^{\text{EOM-CCSD}}. \quad (229)$$

The EOM-CCSD linear response function is weakly size-extensive (see Paper IX³³). The first-order linear response function correction $\langle \langle X; Y \rangle \rangle_{\omega_Y}^{(1)}$ has non-size-extensive contributions, for example,

via the $-\sum_{v_3} A_{\mu_i v_3}^X z_{v_3}^{(1)}$ term in first-order amplitude equation in Eq. (224a), where the second term in $A_{\mu_i v_j}^X$ of Eq. (219) will introduce a non-size-extensive contribution. Since $\langle \langle X; Y \rangle \rangle_{\omega_Y}^{(1)}$ can be viewed as a correction to the EOM-CCSD series of linear response function corrections as obtained from the CPSD(LT) model, the linear response functions obtained from the series $\langle \langle X; Y \rangle \rangle_{\omega_Y}^{(i)}$, $i = 1, 2, \dots$, can be viewed as additional corrections and the linear response functions obtained from Eq. (211) therefore become weakly size-extensive.

VII. SUMMARY AND CONCLUSIONS

In this paper, we extend CP theory to use a CL state as a target state. In this way, CP theory is extended to comprehend a wave-function model, in which the strengths of CC theory (size-extensivity of energies and molecular properties), Møller-Plesset perturbation theory (simple description of energies and molecular properties without the need of solving amplitude and response equations iteratively), and CI theory (linear parametrization and simple structure of amplitude equations and molecular property expressions) are combined to obtain a simpler and more efficient description of the energy and molecular properties of a molecular system than can be obtained using a standard CC state.

In CP theory with a CL target state, we determine, as for CP theory with a CC target state, a series of energy or molecular property corrections in orders of the CC parent-state similarity-transformed fluctuation potential, where the zeroth-order term is the energy or molecular property of the CC parent state and where the series formally converges to the energy or molecular property of the target state. Since the CL target state is linearly parametrized, the energy and molecular property expressions are simpler for the CL target state than for a CC target state. The amplitude equations are thus quadratic for a CL state, while quartic for a CC state, and molecular property expressions for a CL state have the simple structure characteristic for a linearly parametrized CI state. Since the CL state is linearly parametrized, the energy and molecular properties are not size-extensive, but only weakly size-extensive. For the energy, weak size-extensivity means that non-size-extensive contributions start to enter in sixth order in CP theory, and for molecular properties, weak size-extensivity means that non-size-extensive contributions start to enter in second order. The fact that energies and molecular properties are weakly size-extensive therefore means that the non-size-extensive contributions will have little effect on calculated energies and molecular properties.

These theoretical observations are supported by calculations of the ground-state energies through sixth order, using a CCSD parent state and a target state including triple excitations. Calculations are performed for the HF molecule at three inter-nuclear distances and the N₂ and CH₂ molecules at their equilibrium geometries. It is found that the fifth-order energy is size-extensive for both the CPSD(LT) and CPSD(T) models and is nearly independent of whether an exponential or a linear expansion is used to define the wave function beyond the parent state. For both models, the fifth-order energies are all within 0.0001 Hartree of the CCSDT energies and thus provide a highly accurate approximation. The sixth-order energy corrections do not in general improve the fifth-order results,

irrespective of whether a linear or exponential parametrization is used.

CL states have not previously been considered for describing the electronic structure of a molecular system. Due to its traits summarized earlier in this section, CL theory may constitute an attractive alternative to CC theory even outside the CP framework (i.e., even without considering perturbative approximations to CL states). For that reason, we have in this paper developed the general theory for determining the energy and molecular properties for a CL state. The theoretical development is carried out following an outline similar to the one that is used for determining the energy and molecular properties for a CC state. For determining response functions, and thus molecular properties, it has been imperative to use the development in response function theory described in Ref. 11. However, when this is done and CL states are used as target states in CP theory, a very efficient and compact description is obtained for the energy and molecular properties of a molecular system with a single-configuration dominated ground state. For high accuracy calculations, where the effect of triples and higher excitation levels needs to be considered, CP theory with a CL target state becomes the most efficient way of describing the electronic structure of single-configuration dominated molecular systems. In this way, lower excitation levels are treated at a CC level of theory through the CC parent state, while the effect of higher excitation levels, for which disconnected contributions in the wave function are of little importance, is described using a linear parametrization, which in turn leads to structurally and computationally much simpler expressions for the energy and, in particular, for molecular properties than can be obtained using conventional CC theory.

ACKNOWLEDGMENTS

F.P. and P.J. acknowledge support from the European Research Council under the European Union's (EU) Seventh Framework Programme (FP/2007-2013)/ERC Grant Agreement No. 291371. F.P. acknowledges qLEAP Center for Theoretical Chemistry, Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark, where he was formerly employed and where research leading to this article was carried out. J.O. acknowledges support from the Danish Research Council (Grant No. DFF 4181-00537).

APPENDIX A: THE LOWEST-ORDER ENERGY CORRECTIONS FOR THE CPSD(T) MODEL

$$E_0^{(0)} = {}^*E_0 = \langle \text{HF} | H_0^* T | \text{HF} \rangle, \quad (\text{A1})$$

$$E_0^{(1)} = 0, \quad (\text{A2})$$

$$E_0^{(2)} = 0, \quad (\text{A3})$$

$$E_0^{(3)} = \langle {}^* \hat{t}^{\text{CCSD}} | [\Phi^* T, \delta T^{(1)}] | \text{HF} \rangle, \quad (\text{A4})$$

$$E_0^{(4)} = \langle {}^* \hat{t}^{\text{CCSD}} | [\Phi^* T, \delta T_3^{(2)}] | \text{HF} \rangle, \quad (\text{A5})$$

$$E_0^{(5)} = \langle {}^* \hat{t}^{\text{CCSD}} | [\Phi^* T, \delta T_3^{(3)}] | \text{HF} \rangle + \langle {}^* \hat{t}^{\text{CCSD}} | [[\Phi^* T, \delta T_1^{(2)}], \delta T_3^{(1)}] | \text{HF} \rangle + \frac{1}{2} \langle \text{HF} | [[\Phi^* T, \delta T_1^{(2)}], \delta T_1^{(2)}] | \text{HF} \rangle, \quad (\text{A6})$$

$$E_0^{(6)} = \langle {}^* \hat{t}^{\text{CCSD}} | [\Phi^* T, \delta T_3^{(4)}] | \text{HF} \rangle + \frac{1}{2} \langle {}^* \hat{t}^{\text{CCSD}} | [[\Phi^* T, \delta T_1^{(2)}], \delta T_1^{(2)}] | \text{HF} \rangle + \langle {}^* \hat{t}^{\text{CCSD}} | [[\Phi^* T, \delta T^{(3)}], \delta T^{(1)}] | \text{HF} \rangle + \langle \text{HF} | [[\Phi^* T, \delta T_1^{(2)}], \delta T_1^{(3)}] | \text{HF} \rangle. \quad (\text{A7})$$

APPENDIX B: THE LOWEST-ORDER AMPLITUDE EQUATIONS FOR THE CPSD(T) MODEL

$$\delta t_{\mu_i}^{(1)} = 0, \quad i = 1, 2, \quad (\text{B1a})$$

$$\epsilon_{\mu_3} \delta t_{\mu_3}^{(1)} = -\langle \mu_3 | \Phi^* T | \text{HF} \rangle, \quad (\text{B1b})$$

$$\sum_{j=1}^2 \sum_{\nu_j} J_{\mu_i \nu_j}^{\text{CCSD}} \delta t_{\nu_j}^{(2)} = -\langle \mu_i | [\Phi^* T, \delta T_3^{(1)}] | \text{HF} \rangle, \quad i = 1, 2, \quad (\text{B2a})$$

$$\epsilon_{\mu_3} \delta t_{\mu_3}^{(2)} = -\langle \mu_3 | [\Phi^* T, \delta T_3^{(1)}] | \text{HF} \rangle, \quad (\text{B2b})$$

$$\sum_{j=1}^2 \sum_{\nu_j} J_{\mu_i \nu_j}^{\text{CCSD}} \delta t_{\nu_j}^{(3)} = -\langle \mu_i | [\Phi^* T, \delta T_3^{(2)}] | \text{HF} \rangle, \quad i = 1, 2, \quad (\text{B3a})$$

$$\epsilon_{\mu_3} \delta t_{\mu_3}^{(3)} = -\sum_{j=1}^3 \langle \mu_3 | [\Phi^* T, \delta T_j^{(2)}] | \text{HF} \rangle, \quad (\text{B3b})$$

$$\sum_{j=1}^2 \sum_{\nu_j} J_{\mu_i \nu_j}^{\text{CCSD}} \delta t_{\nu_j}^{(4)} = -\langle \mu_i | [\Phi^* T, \delta T_3^{(3)}] | \text{HF} \rangle - \langle \mu_i | [[\Phi^* T, \delta T_1^{(2)}], \delta T_3^{(1)}] | \text{HF} \rangle \delta_{i2}, \quad i = 1, 2, \quad (\text{B4a})$$

$$\epsilon_{\mu_3} \delta t_{\mu_3}^{(4)} = -\sum_{j=1}^3 \langle \mu_3 | [\Phi^* T, \delta T_j^{(3)}] | \text{HF} \rangle - \langle \mu_3 | [[\Phi^* T, \delta T^{(2)}], \delta T^{(1)}] | \text{HF} \rangle. \quad (\text{B4b})$$

$$\sum_{j=1}^2 \sum_{\nu_j} J_{\mu_i \nu_j}^{\text{CCSD}} \delta t_{\nu_j}^{(5)} = -\langle \mu_i | [\Phi^* T, \delta T_3^{(4)}] | \text{HF} \rangle - \frac{1}{2} \langle \mu_i | [[\Phi^* T, \delta T^{(2)}], \delta T^{(2)}] | \text{HF} \rangle - \langle \mu_i | [[\Phi^* T, \delta T^{(3)}], \delta T^{(1)}] | \text{HF} \rangle, \quad i = 1, 2. \quad (\text{B5})$$

REFERENCES

1. F. Pawłowski, J. Olsen, and P. Jørgensen, "Cluster perturbation theory. I. Theoretical foundation for a coupled cluster target state and ground-state energies," *J. Chem. Phys.* **150**, 134108 (2019).
2. C. Møller and M. S. Plesset, *Phys. Rev.* **46**, 618 (1934).

- ³D. Cremer, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **1**, 509 (2011).
- ⁴J. J. Eriksen, K. Kristensen, T. Kjærgaard, P. Jørgensen, and J. Gauss, *J. Chem. Phys.* **140**, 064108 (2014).
- ⁵J. J. Eriksen, P. Jørgensen, and J. Gauss, *J. Chem. Phys.* **142**, 014102 (2015).
- ⁶K. Kristensen, J. J. Eriksen, D. A. Matthews, J. Olsen, and P. Jørgensen, *J. Chem. Phys.* **144**, 064103 (2016).
- ⁷F. Pawłowski, J. Olsen, and P. Jørgensen, "Cluster perturbation theory. II. Excitation energies for a coupled cluster target state," *J. Chem. Phys.* **150**, 134109 (2019).
- ⁸P. Baudin, F. Pawłowski, D. Bykov, D. Liakh, K. Kristensen, J. Olsen, and P. Jørgensen, "Cluster perturbation theory. III. Perturbation series for coupled cluster singles and doubles excitation energies," *J. Chem. Phys.* **150**, 134110 (2019).
- ⁹M. Head-Gordon, R. J. Rico, M. Oumi, and T. J. Lee, *Chem. Phys. Lett.* **219**, 21 (1994).
- ¹⁰J. J. Goings, M. Caricato, M. J. Frisch, and X. Li, *J. Chem. Phys.* **141**, 164116 (2014).
- ¹¹F. Pawłowski, J. Olsen, and P. Jørgensen, *J. Chem. Phys.* **142**, 114109 (2015).
- ¹²T. Helgaker, P. Jørgensen, and J. Olsen, *Molecular Electronic-Structure Theory* (Wiley, Chichester, 2000).
- ¹³I. Shavitt and R. J. Bartlett, *Many-Body Methods in Chemistry and Physics: MBPT and Coupled-Cluster Theory* (Cambridge University Press, 2009).
- ¹⁴H. Koch and P. Jørgensen, *J. Chem. Phys.* **93**, 3333 (1990).
- ¹⁵T. Helgaker, S. Coriani, P. Jørgensen, K. Kristensen, J. Olsen, and K. Ruud, *Chem. Rev.* **112**, 543 (2012).
- ¹⁶O. Christiansen, P. Jørgensen, and C. Hättig, *Int. J. Quantum Chem.* **68**, 1 (1998).
- ¹⁷S. Coriani, F. Pawłowski, J. Olsen, and P. Jørgensen, *J. Chem. Phys.* **144**, 024102 (2016).
- ¹⁸J. F. Stanton and R. J. Bartlett, *J. Chem. Phys.* **98**, 7029 (1993).
- ¹⁹R. Kobayashi, H. Koch, and P. Jørgensen, *Chem. Phys. Lett.* **219**, 30 (1994).
- ²⁰T. Helgaker and P. Jørgensen, *Theor. Chem. Acc.* **75**, 111 (1989).
- ²¹T. Helgaker and P. Jørgensen, in *Methods in Computational Molecular Physics*, edited by S. Wilson and G. H. F. Diercksen (Plenum Press, New York, 1992), Vol. 293, pp. 353–421.
- ²²K. Kristensen, P. Jørgensen, A. J. Thorvaldsen, and T. Helgaker, *J. Chem. Phys.* **129**, 214103 (2008).
- ²³J. J. Eriksen, K. Kristensen, D. A. Matthews, P. Jørgensen, and J. Olsen, *J. Chem. Phys.* **145**, 224104 (2016).
- ²⁴J. Olsen, *J. Chem. Phys.* **113**, 7140 (2000).
- ²⁵LUCIA: A program for correlation calculations on atoms and molecules written by J. Olsen with contributions from A. Köhn and S. Kähler.
- ²⁶We use the term "physical perturbation operator" to distinguish $V(t, \epsilon)$ from the parent-state similarity-transformed fluctuation potential perturbation operator, Φ^{*T} of Eq. (28).
- ²⁷H. Sambe, *Phys. Rev. A* **7**, 2203 (1973).
- ²⁸To derive molecular property expressions, we count orders in the physical perturbation strengths, $\epsilon_x, (\omega_x)$ of Eq. (103).
- ²⁹D. C. Comeau and R. J. Bartlett, *Chem. Phys. Lett.* **207**, 414 (1993).
- ³⁰H. Koch, R. Kobayashi, A. Sánchez de Merás, and P. Jørgensen, *J. Chem. Phys.* **100**, 4393 (1994).
- ³¹J. F. Stanton and R. J. Bartlett, *J. Chem. Phys.* **99**, 5178 (1993).
- ³²P. B. Rozyczko, S. A. Perera, M. Nooijen, and R. J. Bartlett, *J. Chem. Phys.* **107**, 6736 (1997).
- ³³F. Pawłowski, D. Bykov, D. Liakh, and P. Jørgensen, "Cluster perturbation theory. IX. Equation of motion coupled cluster singles and doubles linear response function and transition strengths" (unpublished).