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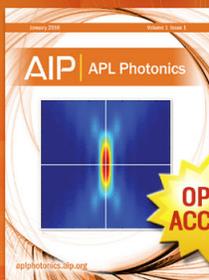
Response functions in the CC3 iterative triple excitation model

Ove Christiansen, Henrik Koch,[a] and Poul Jørgensen

Department of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

The derivation of response functions for coupled cluster models is discussed in a context where approximations can be introduced in the coupled cluster equations. The linear response function is derived for the approximate coupled cluster singles, doubles, and triples model CC3. The linear response functions for the approximate triples models, CCSDT-1a and CCSDT-1b, are obtained as simplifications to the CC3 linear response function. The consequences of these simplifications are discussed for the evaluation of molecular properties, in particular, for excitation energies. Excitation energies obtained from the linear response eigenvalue equation are analyzed in orders of the fluctuation potential. Double replacement dominated excitations are correct through second order in all the triples models mentioned, whereas they are only correct to first order in the coupled cluster singles and doubles model (CCSD). Single replacement dominated excitation energies are correct through third order in CC3, while in CCSDT-1a, CCSDT-1b, and CCSD they are only correct through second order. Calculations of excitation energies are reported for CH^+, N_2, and C_2H_4 to illustrate the accuracy that can be obtained in the various triples models. The CH^+ results are compared to full configuration interaction results, the C_2H_4 results are compared with complete active space second order perturbation theory (CASPT2) and experiment, and the N_2 results are compared to experiment. Double replacement dominated excitations are improved significantly relative to CCSD in all the triples models mentioned, and is of the same quality in CC3 and CCSDT-1a. The single replacement dominated excitation are close to full configuration interaction results for the CC3 model and significantly improved relative to CCSD. The CCSDT-1 results for the single replacement dominated excitations are not improved compared to CCSD. © *1995 American Institute of Physics.*

I. INTRODUCTION

Coupled cluster methods have proven to be accurate and economical tools for describing electron correlation. Until now especially coupled cluster restricted to single and double excitations (CCSD) and CCSD with a noniterative correction for triple excitations CCSD(T) (Ref. 1) has been widely used. A variety of molecular properties have been calculated using these and other coupled cluster models. Frequency independent properties have been obtained as energy derivatives for both iterative[2] and noniterative coupled cluster approaches.[3] Frequency dependent response functions have been derived for iterative cluster models like CCSD.[4−6] The CCSD(T) model, being a two step approach, does not have a well defined frequency dependent response function with one set of correlated poles consistent with the accuracy of the CCSD(T) total energy. Coupled cluster linear response (CCLR) theory has been used to determine frequency dependent polarizabilities,[7] transition moments,[8] and excitation energies.[9] Equation of motion coupled cluster[10] (EOM-CC) gives excitation energies that are identical to the those obtained from coupled cluster linear response theory for usual truncated and nonapproximated coupled cluster models. EOM-CC is based on a biorthogonal approach with no interaction between the reference and the excited states. The EOM-CC approach is therefore not well defined for approximate coupled cluster models where approximations are introduced in the cluster amplitude equations. Transition moments and polarizabilities differ in the coupled cluster response and EOM-CC approaches, the most important difference being that coupled cluster response functions gives properties that scale correct with the size of the system contrary to EOM-CC.[8,9]

Electronic excitation energies from an electronic ground state to excited states dominated by single electron replacements can be determined accurately in a CCSD approach. This was clearly demonstrated in the first CCSD linear response (CCSDLR) calculations of excitation energies[9] and has later been confirmed on numerous occasions. Contrary excitation energies to states dominated by double electron replacements are poorly described in CCSD. Recently, Watts and Bartlett have significantly improved the accuracy of double replacement dominated excitations using approximative coupled cluster singles doubles and triples (CCSDT) approaches.[11,12] In Ref. 11 the CCSDT reference was optimized without approximations but the CCSDT Jacobian matrix elements beyond CCSD was approximated to include only up to two-electron density matrix terms. In Ref. 12 Watts and Bartlett calculated excitation energies in the computational cheaper CCSDT-1a model.[13] The description of double replacement dominated excitations is significantly improved in both models while the description of the single replacement dominated excitations was not improved in either one. We derive in this paper the linear response function for the CC3 model introduced in Ref. 14, and demonstrate that both single and double electron replacement excitations are significantly improved compared to CCSD. The approxi-

[a]Present address: UNI-C, Olof Palmes Allé 38, DK 8200 Aarhus N, Denmark.

mations in the CC3 model relative to CCSDT are solely in the equation for the triples. This equation is approximated according to two principles: (i) We restrict the triples equation to the form entering in second order in fluctuation potential; (ii) the singles are treated as zeroth order parameters. The first criteria alone leads to the CCSDT-1b model.[15] The CCSDT-1a is obtained from CCSDT-1b by further neglecting a term bilinear in single and triple amplitudes in the doubles equation.[15] The second criteria is motivated by the fact that singles are important since they provide an approximate description of orbital relaxation. This is especially important when perturbing the molecular system and when non-Hartree–Fock orbitals are used.

Features of the CC3 wave function is that the energy is correct through fourth order in the fluctuation potential and includes the fifth-order terms that are also included in CCSD(T). The CC3 model scales as N^7, where N is the number of orbitals. This should be compared with the N^8 scaling for CCSDT and the N^6 scaling for CCSD. The CC3 method is thus between CCSD and CCSDT in computational effort, and comparable to CCSD(T). In the CC3 model we iterate all equations and thus need more N^7 processes than in CCSD(T), where only CCSD equations are iterated. In the CC3 model we need not store triples amplitudes as is the case in CCSDT. Since CC3 is a one step iterative approach, it gives one consistent set of poles with an improved accuracy relative to CCSD.

We have carried out an order analysis of the excitation energies of approximate coupled cluster models. In CCSD excitation energies are correct through second and first order for single and double replacement dominated excitations respectively. In CC3 this is improved to third and second order respectively. In the CCSDT-1 models the single replacement dominated excitations are correct through second order only. The CC3 linear response function is fully correct through third order, and only a single term is missing in fourth order. The CCSDT-1a and CCSD-1b linear response functions are not correct through third order.

From an iterative eigenvalue equation one may define noniterative approximate corrections to lower order models as demonstrated by Head-Gordon et al.[16] A noniterative excitation energy model was introduced in Ref. 12 based on the CCSDT-1a excitation energies; it was denoted as EOM-CCSD(T). It is not based on a strict derivation of a CCSD(T) response function or EOM-CCSD(T) approach, but by defining a noniterative triples excitation energy from a CCSDT-1a excitation energy expression. There is thus no strict relationship between the CCSD(T) total energy and the EOM-CCSD(T) excitation energies. It is clear that noniterative corrections can only be introduced from corresponding iterative models. In this paper we restrict ourself to investigate iterative models. The introduction and testing of noniterative models is postponed to later investigations.

In Sec. II we give a short summary of the most important equations for the CC3 model. In Sec. III we discuss time-independent perturbation theory for the CC3 model. In Sec. IV we derive the CC3 frequency dependent linear response response function. The linear response function and equations for determining the excitation energies is also com-

pared in Sec. IV for various triples methods. In Sec. V we present sample calculations of excitation energies for CH^+, N_2, and C_2H_4 in the CC3 and CCSDT-1 models and in Sec. VI we give some concluding remarks.

II. THE CC3 MODEL

In Ref. 14 we introduced the CC3 model as an approximation to the CCSDT model. The CCSDT state is defined as

$$|CCSDT\rangle = \exp(T_1 + T_2 + T_3)|HF\rangle \tag{1}$$

where T_1, T_2, and T_3 are the usual cluster operators

$$T_i = \sum_{\nu_i} t_{\nu_i} \tau_{\nu_i}. \tag{2}$$

The label ν_i refers to an ordering with respect to excitation level i, $i = 1,2,3$ and numbering ν within the excitation class. The excitation operator is denoted as τ_{ν_i} and t_{ν_i} the corresponding amplitude. The cluster amplitudes are determined by projecting the time-independent Schrödinger equation

$$\exp(-T_1 - T_2 - T_3)H|CCSDT\rangle = E|HF\rangle \tag{3}$$

onto the space of single, double, and triple excitations from the Hartree–Fock reference,

$$\langle \mu_i| = \langle HF|\tau^\dagger_{\mu_i}, \tag{4}$$

where $i = 1,2,3$. In order to obtain the CCSDT state we thus solve the complete set of equations

$$\langle \mu_i|\exp(-T_1 - T_2 - T_3)H \exp(T_1 + T_2 + T_3)|HF\rangle = 0 \tag{5}$$

with $i = 1,2,3$. This determines the $|CCSDT\rangle$ state and the energy is in turn obtained by projecting Eq. (3) onto the reference $\langle HF|$

$$E = \langle HF|H \exp(T_1 + T_2)|HF\rangle. \tag{6}$$

We now introduce a partitioning of the Hamilton operator H into a Fock operator F and a fluctuation operator U, describing the difference between the Fock potential V^F and the two-electron repulsion,

$$H = F + U, \tag{7}$$

where

$$F = \sum_{pq} (h_{pq} + V^F_{pq})a^+_p a_q = \sum_p \epsilon_p a^+_p a_p, \tag{8}$$

$$U = \frac{1}{2} \sum_{pqrs} (pq|rs)a^+_p a^+_r a_s a_q - \sum V^F_{pq} a^+_p a_q. \tag{9}$$

In Ref. 14 we presented an alternative derivation of many body perturbation theory using a coupled cluster parametrization of the exact wave function. Based on this and the subsequent analysis we introduced the CC3 model from the requirements that it should provide an energy correct to fourth order in U, and retain the approximate description of orbital relaxation given by the T_1 operators. This leads us to approximate the CCSDT amplitude equations such that the singles and doubles equations of CCSDT are retained without approximation, and the triples equations are approxi-

mated to have the form entering in second order in the fluctuation potential, but with the singles treated as zeroth order or having no order. Determining the triple excitations correct through second order ensures the total energy is correct through fourth order for a set of Hartree–Fock orbitals. For the unperturbed system the singles enter in second order in the fluctuation potential, but this is solely a consequence of using optimized Hartree–Fock orbitals for the reference. Using nonoptimized orbitals this is not the case. The singles respond to external perturbations to zeroth order in U. In molecular property calculations the singles thus provide approximate orbital relaxation in two senses: relaxation to the correlation and relaxation to the external perturbation. The fact that singles respond to external perturbations to zeroth order in U, makes the treatment of singles as zeroth order parameters necessary for obtaining a balanced description of molecular properties. The singles and doubles equation of both CC3 and CCSDT can be written as

$$\langle\mu_1|\hat{H}+[\hat{H},T_2]|\text{HF}\rangle+\langle\mu_1|[\hat{H},T_3]|\text{HF}\rangle=0, \tag{10}$$

$$\langle\mu_2|\hat{H}+[\hat{H},T_2]+\tfrac{1}{2}[[\hat{H},T_2],T_2]|\text{HF}\rangle+\langle\mu_2|[\hat{H},T_3]|\text{HF}\rangle$$
$$=0, \tag{11}$$

where T_1 transformed operators are defined through

$$\hat{O}=\exp(-T_1)\,O\,\exp(T_1). \tag{12}$$

See Ref. 17 for features of T_1 transformed operators and their use in integral direct coupled cluster techniques. Without external perturbations the equations determining the triples are

$$\langle\mu_3|[F,T_3]|\text{HF}\rangle+\langle\mu_3|[\hat{U},T_2]|\text{HF}\rangle=0. \tag{13}$$

Equations (10), (11), and (13) define the CC3 energy in the absence of external perturbations. The practical consequences of the approximations is that the N^8 operation count of the CCSDT triples equation in Eq. (5) is reduced to an N^7 operation count of the CC3 triples equation Eq. (13). The triple terms of the single double equations are N^7. Equation (13) can be solved for an analytical form of the triples amplitudes in terms of single and double amplitudes and two-electron integrals. This expression can be inserted into the triples terms of Eqs. (10) and (11). The CC3 amplitude equations may thus be solved in a computational efficient way involving N^7 processes only and without explicit storage of triple amplitudes (see Ref. 14 for details).

In this paper we consider the case where the system described by $H_0=F+U$ is perturbed by a time-independent one-electron perturbation βV. Here we derive general frequency dependent response functions, and we therefore do not allow the orbitals to relax explicitly. This would lead to Hartree–Fock poles in the response function in addition to the correlated poles, as well as product poles will appear. The presence of noncorrelated poles in a correlated response function is clearly an undesired feature. This additional set of poles as well as their second order nature is inconsistent with the pole structure of the exact response function. Since we do not treat orbital response explicitly, we use a generalized version of Eq. (13) where we generalize the perturbational analysis in Ref. 14 to double perturbation theory in the fluc-

tuation potential U and the external perturbation V. Instead of treating $F+\beta V$ as the zeroth-order problem as in the orbital relaxed case we let F be the zeroth-order problem perturbed by the two independent perturbations U and V. This gives a viable alternative to explicit orbital relaxation due to the special treatment of the singles in the reference state calculation. The crucial importance of the singles for calculating accurate properties is clearly exposed in the double perturbation analysis since the singles are zeroth order in U, and first order in the one-electron perturbation V. No approximations in the singles can thus be justified if one considers the perturbed system and do not explicitly allow the orbitals to relax. Approximating to second order in U and keeping all terms in V, the equations determining the triples in the presence of external perturbations can be written as

$$\langle\mu_3|[F+\beta\hat{V},T_3]|\text{HF}\rangle+\langle\mu_3|[\hat{U},T_2]|\text{HF}\rangle$$
$$+\tfrac{1}{2}\langle\mu_3|[[\beta\hat{V},T_2],T_2]|\text{HF}\rangle=0. \tag{14}$$

Equation (14) corresponds to the orbital relaxed form, where orbital relaxation is not introduced explicitly. For one-electron perturbations the singles are the only parameters responding in zeroth order in U. For two-electron perturbations the situation is more complicated and the analysis above is not fully adequate. Equation (14) is specialized to one-electron perturbations. This is not a severe limitation since most frequency dependent properties and transition moments refer to one-electron operators. The perturbed form of the singles and doubles equations in the CC3 model are obtained from Eqs. (10) and (11) where H is substituted with $H_0+\beta V$. Equations (10), (11) and (14) defines the CC3 model in the presence of an external perturbation and these are used in the following sections to derive the CC3 linear response function.

The CCSDT-1a and CCSDT-1b models are obtained making further approximations in the CCSDT equations, where the criteria that T_1 should be treated as zeroth order parameters is not imposed. The T_1 transformed operator in Eq. (13) is thus not considered in CCSDT-1a and CCSDT-1b, but is replaced with the usual Born–Oppenheimer Hamiltonian. The only difference between CCSDT-1a and CCSDT-1b is that the T_1 transformed operator in the last term of the doubles equation [Eq. (11)] is also replaced by the untransformed operator in CCSDT-1a. Based on a perturbation theory analysis these approximations are reasonable for calculation of the total energy, but as described earlier, the singles are of crucial importance for calculations of molecular properties.

III. TIME-INDEPENDENT PERTURBATION THEORY

The CC response theory developed in Ref. 6 is based on the introduction of a dual type vector $\langle\Lambda|$ to the $|\text{CC}\rangle$ reference function. In this section we investigate the consequences of making approximations in the cluster equations. Consider a nonapproximated CC theory, that is a theory where no approximations are made in the equations obtained by projection of the coupled cluster Schrödinger equation in Eq. (3).   In the time-independent case we have a well defined energy and we may combine Eqs. (5) and (6) to write the total energy as

$$E = \langle \Lambda | H | CC \rangle, \tag{15}$$

where the dual type vector is defined as

$$\langle \Lambda | = \langle HF | + \sum_{\mu_i} \bar{t}_{\mu_i} \langle \mu_i | \exp(-T). \tag{16}$$

The $\bar{t}$ parameters are so far arbitrary but may be fixed by requiring the $\langle \Lambda |$ state to be a left solution of the Schrödinger equation

$$\langle \Lambda | H = E \langle \Lambda |. \tag{17}$$

The dual type vector $\langle \Lambda |$ satisfy the normalization

$$\langle \Lambda | CC \rangle = 1 \tag{18}$$

and from the above we may derive a generalized Hellmann–Feynman theorem

$$\frac{d}{d\beta} \langle \Lambda(\beta) | H_0 + \beta V | CC(\beta) \rangle = \langle \Lambda | V | CC \rangle. \tag{19}$$

The energy in Eq. (15) may alternatively be viewed as an energy Lagrangian[18] with $\bar{t}$ parameters as Lagrangian parameters. Both t and $\bar{t}$ parameters are then determined using the variational principle. Variation with respect to the Lagrangian parameters gives Eq. (5) and variation with respect to the cluster parameters give the equation determining the $\bar{t}$ parameters. This equation is identical to the one obtained from Eq. (17) by projection. If orbital relaxation is treated explicitly the Lagrangian needs to be modified to allow for this and becomes

$$L_{CC} = \langle HF | \exp(-\kappa) H \exp(\kappa) \exp(T) | HF \rangle + \sum_{\mu_i} \bar{t}_{\mu_i} \langle \mu_i |$$

$$\times \exp(-T) \exp(-\kappa) H \exp(\kappa) \exp(T) | HF \rangle$$

$$+ \sum_{m > n} \bar{\kappa}_{mn} \langle HF | \exp(-\kappa) [E_{mn}, H] \exp(\kappa) | HF \rangle. \tag{20}$$

The orbital rotation generator,

$$\kappa = \sum_{mn} \kappa_{mn} E_{mn}, \tag{21}$$

contain nonredundant orbital parameters and $\bar{\kappa}$ is the Lagrangian parameters corresponding to the nonredundant orbital rotations. In our derivation of time-dependent response functions, orbital relaxation is not treated explicitly as discussed previously. In some cases for example when describing geometrical derivatives one may wish to use the orbital relaxed energy function and the Lagrangian in Eq. (20) then must be used.[2]

The expectation value of Eq. (19) combined with equations for the time dependence of the t and $\bar{t}$ parameters obtained by requiring the $|CC\rangle$ and $\langle \Lambda |$ states to satisfy the time-dependent Schrödinger equation, can be used to derive frequency dependent response functions for nonapproximated CC methods. In this paper we consider the CC3 model where approximations are introduced in the triples equations and the triples equations are therefore not obtained by projection. The CC3 total energy may be expressed as

$$E = \langle \Lambda_{SD} | H_0 + \beta V | CC3 \rangle + \sum_{\mu_3} \bar{t}_{\mu_3} \bigg(\langle \mu_3 | [F + \beta V, T_3]$$

$$+ [\hat{U}, T_2] + \frac{\beta}{2} [[V, T_2], T_2] | HF \rangle \bigg), \tag{22}$$

where

$$\langle \Lambda_{SD} | = \langle HF | + \sum_{\substack{\mu_i \\ i=1,2}} \bar{t}_{\mu_i} \langle \mu_i | \exp(-T_1 - T_2). \tag{23}$$

The CC3 energy in Eq. (22) is not a simple transition matrix element between a CC3 state and a dual vector. Generally the dual state concept can only be used when the energy and all constraints are obtained by projection onto the same equation. In approximate coupled cluster models we introduce approximations in the cluster equations and the dual state approach can not be used in general. However, the energy in Eq. (22) may be viewed as an energy Lagrangian where the t and $\bar{t}$ parameters are determined from the variational principle. The first derivative of the CC3 energy becomes

$$\frac{dE}{d\beta} = \langle \Lambda_{SD} | V | CC3 \rangle + \sum_{\mu_3} \bar{t}_{\mu_3} (\langle \mu_3 | [\hat{V}, T_3] | HF \rangle$$

$$+ \tfrac{1}{2} \langle \mu_3 | [[\hat{V}, T_2], T_2] | HF \rangle). \tag{24}$$

We thus do not have a generalized Hellmann–Feynmann expressed in terms of an average value between two states as in Eq. (19). This again is a consequence of the fact that the triples equation in the CC3 model is not determined directly from the Schrödinger equation by projection. In CC3 the singles and doubles equations are identical to the ones obtained from projection, but the equations determining the triples are approximated as described in Sec. II. It is clear that the aforementioned discussion applies to other approximative coupled cluster models, e.g., the CCSDT-1a and CCSDT-1b models.

The dual state approach is based on a generalized Hellmann–Feynman theorem, and the fact that the time dependence of the parameters can be determined directly from the time-dependent Schrödinger equation for the two states $|CC\rangle$ and $\langle \Lambda |$. It is clear that these assumptions are not fulfilled for approximate coupled cluster models. However, molecular properties can be defined from the CC3 energy in Eq. (22) using the variational Lagrangian approach, since this approach is applicable for both approximated [Eq. (22)] and nonapproximated coupled cluster models [Eqs. (15) and (20)]. In Sec. VI we use the Lagrangian concept to derive the frequency dependent response functions for coupled cluster models.

IV. TIME-DEPENDENT PERTURBATION THEORY

A. General theory of response functions

The expectation value derivation of response functions is not possible for approximated coupled cluster models, while an energy-based approach could straightforwardly be applied using the Lagrangian technique. In the time-dependent case an energy as such is not well defined. Sasagane, Aiga, and Itoh[19] have circumvented this problem by expressing the re-

sponse functions as derivatives of a so-called quasienergy. This approach is applicable to both variational and nonvariational wave functions, and in the time-independent limit finite field results are obtained for molecular properties.

We now outline the essential ideas in order to establish the connection between exact and approximate theory. We may write the exact wave function as

$$|\bar{\psi}\rangle = e^{-iF}|\tilde{\psi}\rangle, \tag{25}$$

where the phase F is a function of time. Projecting the time-dependent Schrödinger for $|\bar{\psi}\rangle$ against $\langle\tilde{\psi}|$, we obtain an equation for this phase factor

$$\dot{F} = \langle\tilde{\psi}|\left(H - i\frac{\partial}{\partial t}\right)|\tilde{\psi}\rangle. \tag{26}$$

Equation (26) gives a recipy for determining the phase-factor when we have determined $|\tilde{\psi}\rangle$. It is therefore advantageous to separate the phasefactor from the equations determining $|\tilde{\psi}\rangle$. Various principles can be used to determine the time dependence of $|\tilde{\psi}\rangle$ see, for example, Olsen and Jørgensen[20] for a review. The time derivative of the phase as it occurs in Eq. (26) is referred to as a quasienergy and appears in the time-dependent Hellmann–Feynman theorem

$$\frac{d\langle\tilde{\psi}|[H - i(\partial/\partial t)]|\tilde{\psi}\rangle}{d\lambda} = \left\langle\tilde{\psi}\left|\frac{\partial H}{\partial\lambda}\right|\tilde{\psi}\right\rangle - i\frac{\partial}{\partial t}\left\langle\tilde{\psi}\left|\frac{\partial\tilde{\psi}}{\partial\lambda}\right.\right\rangle. \tag{27}$$

The time-dependent Hellmann–Feynman theorem is valid for all variational wave functions. We consider an external perturbation written as

$$V^t = \sum_{i=-n}^{n}\sum_{x} H^x\epsilon_x(\omega_i)\exp(-i\omega_i t), \tag{28}$$

and we occasionally use the short hand notation $H^A = A$. Different approaches can be taken to determine response functions for the operators in Eq. (28). The response functions may be defined in terms of an expansion of the time-dependent expectation value

$$\mu_A(t) = \langle\bar{\psi}|A|\bar{\psi}\rangle = \langle\tilde{\psi}|A|\tilde{\psi}\rangle. \tag{29}$$

Introducing the time-dependent Hellmann–Feynman theorem it is seen that response functions may alternatively be determined from an expansion of the derivative of the quasienergy with respect to an arbitrary Fourier component

$$\mu_A(t) = \left(\frac{d\langle\tilde{\psi}|[H - i(\partial/\partial t)]|\tilde{\psi}\rangle}{d\epsilon_A(\omega)}\right.$$
$$\left. + i\frac{\partial}{\partial t}\left\langle\tilde{\psi}\left|\frac{\partial\tilde{\psi}}{\partial\epsilon_A(\omega)}\right.\right\rangle\right)\exp(i\omega t). \tag{30}$$

The $\mu_A(t)$ then contain a term involving the quasienergy and a term involving time differentiation of the wave function.

The time-dependent Hellmann–Feynman theorem is valid for all variational wave functions and the above approaches are therefore equivalent for variational wave functions. When Eq. (29) is used the phase is removed from the calculation.[20] For nonvariational wave functions Eq. (29) can only straightforwardly be used if a generalized Hellmann–Feynman theorem can be expressed in terms of an expecta-

tion value. The coupled cluster dual state approach is based on this strategy, where the expectation value is replaced by the generalized Hellmann–Feynman theorem in Eq. (19), and the time dependence of the coupled cluster and the dual state is determined from the time-dependent Schrödinger equation. Equation (30) applies equally well to both variational and nonvariational wave functions and gives in the time-independent limit the energy differentiated results. Sasagane et al.[19] have shown how response functions for nonvariational wave functions may be obtained based on Eq. (30)

An essential idea in the work of Sasagane et al.[19] is that the contributions from the second term on the right hand side of Eq. (28) can be eliminated choosing a particular value for ω

$$\omega = -\omega_\sigma = -\sum_{i=1}^{n}\omega_i \tag{31}$$

for the nth order response functions with associated frequencies ω_i. The n frequencies ω_i are arbitrary (see Ref. 19 for details). Expressions for response properties in terms of the quasienergy become

$$\langle A\rangle = \frac{\partial\dot{F}(t)}{\partial\epsilon_A(0)}, \tag{32}$$

$$\langle\langle A;B\rangle\rangle_{\omega_1} = \left.\frac{\partial^2\dot{F}(t)}{\partial\epsilon_A(-\omega)\partial\epsilon_B(\omega_1)}\right|_0, \tag{33}$$

and so on. The phase factor approach does not require explicit states and expectation values to be given in order to derive response functions. Only the quasienergy need to be defined to derive the response functions. The quasienergy can be formulated in terms of constraints and the Lagrangian technique can therefore be generalized to time-dependent wave functions as well. Using this technique MP2 (Ref. 21) and Brueckner Coupled Cluster (Ref. 22) frequency dependent properties have been derived.

B. Coupled cluster quasienergy approach

We first outline the theory for usual non-approximated coupled cluster theory, since the principles are the same as for approximate coupled cluster models like the CC3 model. The response functions we obtain for nonapproximated coupled cluster models are identical to the ones previously derived in the literature. The time dependence for such a coupled cluster state can be parametrized as

$$|\overline{CC}(t)\rangle = e^{-iF}|\widetilde{CC}(t)\rangle = e^{-iF}\exp[T(t)]|HF\rangle. \tag{34}$$

Projecting the time-dependent Schrödinger equation,

$$\left(H - i\frac{\partial}{\partial t}\right)\left|\overline{CC}(t)\right\rangle = 0, \tag{35}$$

onto the Hartree–Fock reference determines the quasienergy as

$$\dot{F} = \left\langle \mathrm{HF} \left| \left(H - i\,\frac{\partial}{\partial t} \right) \right| \widetilde{\mathrm{CC}}(t) \right\rangle = \langle \mathrm{HF}|H|\widetilde{\mathrm{CC}}(t)\rangle. \tag{36}$$

Monkhorst[4] and Dalgaard and Monkhorst[5] used this to derive coupled cluster linear response functions. (Without using a quasienergy Lagrangian approach.) The time-dependent amplitudes are obtained by projection onto $\langle \mu_i | \exp(-T)$. We may express this in term of a quasienergy Lagrangian

$$L = \langle \mathrm{HF}|H|\widetilde{\mathrm{CC}}(t)\rangle + \sum_{\mu_i} \bar{t}_{\mu_i}(t) \left\langle \mu_i \left| \exp[-T(t)] \right(H \right. \right.$$
$$\left. \left. - i\,\frac{\partial}{\partial t} \right) \right| \widetilde{\mathrm{CC}}(t) \right\rangle. \tag{37}$$

The use of Lagrangians allows the $2n+1$ and $2n+2$ rules[18] to be used. We may at this point also introduce relaxed orbitals in the description similar to what is done in the time-independent case [see Eq. (20)]. The corresponding Lagrangian becomes

$$L_{\mathrm{CC}} = \langle \mathrm{HF}| \exp[-\kappa(t)] \left(H - i\,\frac{\partial}{\partial t} \right) \exp[\kappa(t)] \exp[T(t)] |\mathrm{HF}\rangle + \sum_{\mu_i} \bar{t}_{\mu_i}(t) \left\langle \mu_i \left| \exp[-T(t)] \exp[-\kappa(t)] \left(H - i\,\frac{\partial}{\partial t} \right) \right. \right.$$

$$\times \exp[\kappa(t)] \exp[T(t)] |\mathrm{HF}\rangle + \sum_{mn} \bar{\kappa}_{mn}(t) \langle \mathrm{HF}| \left[E_{mn}, \; \exp[-\kappa(t)] \left(H - i\,\frac{\partial}{\partial t} \right) \exp[\kappa(t)] \right] |\mathrm{HF}\rangle. \tag{38}$$

Time-dependent Hartree–Fock equations must then be solved. However, as mentioned earlier, the orbital relaxation introduces features not consistent with true response functions, and we therefore do not use explicitly relaxed orbitals. As described in Sec. II, the T_1 operator in coupled cluster theory gives an approximate description of the orbital relaxation.

Introducing the time-averaged Lagrangian

$$\{L(t)\}_T = \frac{1}{T} \int_{t_0}^{t_0+T} L(t)\,dt, \tag{39}$$

where the period T is the shortest common multiple period of the periodic perturbations in Eq. (28), we require the Lagrangian to be optimal with respect to variations of $\bar{\mathbf{t}}$ and t parameters

$$\delta\{L(t)\}_T = 0. \tag{40}$$

Based on the V^t in Eq. (28) we can make an expansion of the amplitudes

$$t = t^{(0)} + t^{(1)}(t) + t^{(2)}(t) + \cdots , \tag{41}$$

where the responses are expressed as, for example,

$$t^{(1)}(t) = \sum_i \exp(-i\omega_i t) \sum_x \epsilon_x(\omega_i) t^{(x)}(\omega_1). \tag{42}$$

Expanding the time-development of the $\bar{\mathbf{t}}(t)$ parameters similar to t in Eqs. (41) and (42), we can collect terms in the Lagrangian in orders in the perturbation

$$L(t) = L^{(0)} + L^{(1)}(t) + L^{(2)}(t) + \cdots , \tag{43}$$

where $L^{(0)}$ is the unperturbed energy of the CC model. To order n in the external perturbation V^t we have

$$\{L^{(n)}(t)\}_T = \{\langle \tilde{\Lambda}|H + V^t|\widetilde{\mathrm{CC}}\rangle^{(n)}\}_T$$
$$+ \left\{ \left\langle \tilde{\Lambda} \left| -i\,\frac{\partial}{\partial t} \right| \widetilde{\mathrm{CC}} \right\rangle^{(n)} \right\}_T \tag{44}$$

with a combination of frequencies for the perturbations fulfilling

$$\sum_{i=1}^n \omega_i = 0 \tag{45}$$

and Eq. (40) is used to determine $\bar{t}^{(i)}, t^{(i)}$, $i = 1,n$. The same equations are obtained as in the dual state approach. The Lagrangian $\{L(t)\}_T$ is fully variational, and thus satisfies the $2n+1$ and $2n+2$ rules. Furthermore, the time-differentiation term in Eq. (44) does not contribute to the properties. This can be seen as a consequence of the $2n+2$ and $2n+1$ rules, writing it as

$$\left(\sum_{k=0,n} \sum_\mu \bar{t}_\mu^{(k)} - i\,\frac{dt_\mu^{(n-k)}(t)}{dt} \right)_T. \tag{46}$$

Only $\bar{t}_\mu^{(k)}$ with $n \geq k+2$ contributes according to the $2n+2$ rules. This means that $k \leq (n/2) - 1$ and, thus, $n - k \geq (n/2) + 1$, and according to the $2n+1$ rule for the t parameters, the $t^{(n-k)}$ can be eliminated. We can thus write

$$\frac{\partial}{\partial\epsilon(\omega)} \{L(t)\}_T = \frac{\partial}{\partial\epsilon(\omega)} \left[\left\langle \tilde{\Lambda} \left| \left(H - i\,\frac{\partial}{\partial t} \right) \right| \widetilde{\mathrm{CC}} \right\rangle \right]_T$$
$$= [\langle \tilde{\Lambda}|A|\widetilde{\mathrm{CC}}\rangle \exp(-i\omega t)]_T. \tag{47}$$

From Eq. (47) response functions are obtained as derivatives according to the scheme proposed by Sasagane et al.,[19] and indicated in Eqs. (32) and (33). The response functions are equivalent to the ones obtained in Ref. 6.

The essential results from the derivation of the linear response function are summarized as follows. From the variational requirements we obtain the equation for the cluster amplitudes

$$(\omega \mathbf{I} - \mathbf{A})\mathbf{t}^A = -\xi^A, \tag{48}$$

$$\zeta \mathbf{A} = -\eta, \tag{49}$$

where the CC Jacobian $\mathbf{A}$ is defined as

$$A_{\mu_i \nu_j} = \langle \mu_i | \exp(-T)[H_0, \tau_{\nu_j}] \exp(T) | \text{HF} \rangle \tag{50}$$

and the vectors ξ and η are given as

$$\xi^A_{\mu_i} = \langle \mu_i | \exp(-T) A \, \exp(T) | \text{HF} \rangle, \tag{51}$$

$$\eta_{\nu_j} = \langle \text{HF} | [H_0, \tau_{\nu_j}] \exp(T) | \text{HF} \rangle. \tag{52}$$

From Eq. (44) we may then determine the linear response function as

$$^{\text{CC}}\langle\langle A; B \rangle\rangle_\omega = \frac{\partial^2 \{L\}_T}{\partial \epsilon_A(-\omega) \partial \epsilon_B(\omega)}\bigg|_0$$

$$= \langle \Lambda | [A, T^B(\omega)] | \text{CC} \rangle$$

$$+ \langle \Lambda | [B, T^A(-\omega)] | \text{CC} \rangle$$

$$+ \langle \Lambda | [[H_0, T^A(-\omega)], T^B(\omega)] | \text{CC} \rangle. \tag{53}$$

Excitation energies and transition moments can be obtained from poles and residues of the response functions. The poles

of the response function occur at the poles of the amplitude responses. From Eq. (47) it is seen that the excitation energies become the eigenvalues of the nonsymmetric CC Jacobian.

$$\mathbf{AS} = \omega \mathbf{S}. \tag{54}$$

If $T = T_1 + T_2$, Eqs. (47)–(54) give the CCSD result. Higher-order response functions are easily obtained as well. The advantage of the quasienergy approach is that it may be applied to approximate CC models as well. In the next section we consider application to the CC3 model.

C. The CC3 linear response function

Response functions for approximate coupled cluster models can be derived from a quasienergy Lagrangian, where the approximations are introduced into the time-dependent equations. The quasienergy Lagrangian for the CC3 model is obtained from the CCSDT Lagrangian [see Eq. (39)], where approximations are introduced in accordance with the perturbed CC3 equations, Eq. (14),

$$L_{\text{CC3}} = \langle \text{HF} | H \exp[T_1(t) + T_2(t)] | \text{HF} \rangle + \sum_{\substack{\mu_i \\ i=1,2}} \bar{t}_{\mu_i}(t) \langle \mu_i | \exp[-T_1(t) - T_2(t)] \left(H - i \frac{\partial}{\partial t} \right) \exp[T_1(t) + T_2(t) + T_3(t)] | \text{HF} \rangle$$

$$+ \sum_{\mu_3} \bar{t}_{\mu_3}(t) \langle \mu_3 | \left[F + \hat{V}^t - i \frac{\partial}{\partial t}, T_3(t) \right] + [\hat{U}, T_2(t)] + \tfrac{1}{2}[[\hat{V}^t, T_2(t)], T_2(t)] | \text{HF} \rangle. \tag{55}$$

Equations equivalent to Eqs. (47)–(54) are obtained where the Jacobian now is the CC3 Jacobian,

$$\left\{ \begin{array}{ccc} \langle \mu_1 | [\hat{H}_0 + [\hat{H}_0, T_2], \tau_{\nu_1}] | \text{HF} \rangle & \langle \mu_1 | [\hat{H}_0, \tau_{\nu_2}] | \text{HF} \rangle & \langle \mu_1 | [H_0, \tau_{\nu_3}] | \text{HF} \rangle \\ \langle \mu_2 | [\hat{H}_0 + [\hat{H}_0, T_2 + T_3], \tau_{\nu_1}] | \text{HF} \rangle & \langle \mu_2 | [\hat{H}_0 + [\hat{H}_0, T_2], \tau_{\nu_2}] | \text{HF} \rangle & \langle \mu_2 | [\hat{H}_0, \tau_{\nu_3}] | \text{HF} \rangle \\ \langle \mu_3 | [[\hat{H}_0, T_2], \tau_{\nu_1}] | \text{HF} \rangle & \langle \mu_3 | [\hat{H}_0, \tau_{\nu_2}] | \text{HF} \rangle & \delta_{\mu\nu} \omega_{\mu_3} \end{array} \right\}, \tag{56}$$

and the ξ vector becomes

$$\xi^A = \begin{pmatrix} \langle \mu_1 | \hat{A} + [\hat{A}, T_2] | \text{HF} \rangle \\ \langle \mu_2 | [\hat{A}, T_2 + T_3] | \text{HF} \rangle \\ \langle \mu_3 | [\hat{A}, T_3] + \tfrac{1}{2}[[\hat{A}, T_2], T_2] | \text{HF} \rangle \end{pmatrix}. \tag{57}$$

The η vector is unchanged since the triple contributions vanish. The CC3 response function can be expressed as one term having the same structure as the CCSD linear response function and additional contributions from triples that we give as explicit:

$$^{\text{CC3}}\langle\langle A; B \rangle\rangle_\omega = {}^{\text{CCSD}}\langle\langle A; B \rangle\rangle_\omega + \{1 + P[A(-\omega), B(\omega)]\} \left(\sum_{\mu_2} \bar{t}^{(0)}_{\mu_2} \langle \mu_2 | [A, T^B_3(\omega)] + [[H_0, T^A_1(-\omega)], T^B_3(\omega)] | \text{HF} \rangle + \sum_{\mu_3} \bar{t}^{(0)}_{\mu_3} \right.$$

$$\times \langle \mu_3 | [\hat{A}, T^B_3(\omega)] + [[A, T^B_1(\omega)], T^{(0)}_3] + [[\hat{U}, T^A_1(-\omega)], T^B_2(\omega)] + [[[\hat{U}, T^A_1(-\omega)], T^B_1(\omega)], T^{(0)}_2]$$

$$\left. + [[A, T^B_2(\omega)], T^{(0)}_2] | \text{HF} \rangle \right). \tag{58}$$

Equation (58) is the CC3 linear response function for one-electron frequency dependent perturbations. Excitation energies are obtained as eigenvalues of the CC3 Jacobian in Eq. (56) and transition moments are obtained as residues of Eq. (58).

Simplifications in the aforementioned derivation lead to CCSDT-1a and CCSD-1b linear response functions. As described in Sec. II these approximations are somewhat unbalanced as they do not include the singles in the triples equations. In addition CCSDT-1a lacks the singles–triples contributions in the doubles equation. Both CCSDT-1a and CCSDT-1b have a zero triples–singles block in the Jacobian in contrast to the CC3 model. As we discuss later, this triples singles block is important in order to describe single replacement dominated excitation correct through third order. The triples–doubles block does not have a T_1 transformed Hamiltonian in both CCSDT-1a and CCSDT-1b. For CCSDT-1a the doubles–triples block does not have a T_1 transformed Hamiltonian, and there is no triples contributions in the doubles–singles block. Similar approximations occur in the ξ vector. The changes in the Jacobian and the ξ vector in CCSDT-1a and CCSDT-1b compared to CC3 has as a consequence that the triple responses are not correct to second order. The third-order term missing in the CCSD response function [the first term in the parenthesis in Eq. (58)] are thus only partially included, and CCSDT-1a and CCSDT-1b linear response functions are not fully correct through third order.

In CC3 the triples response is correct through second order, and the form of all singles, doubles, and triples third-and fourth-order terms in the response function are retained. The CC3 linear response function is thus fully correct to third order. The third-order term in the doubles space with triples responses (first term in the parenthesis in Eq. (58)) will, however, also include a fourth-order term through the triples responses in third order in the fluctuation potential. Since the triple responses are only correct to second order, the CC3 lacks this fourth-order term in the singles doubles and triples space. Quadruples enter the response function in fourth order. Thus CCSDT based models can not provide frequency dependent response functions correct through fourth order.

D. Order analysis of excitation energies

In this section we carry out an order analysis of the excitation energies in various coupled cluster models. The exact excitation energies are obtained if no truncations is introduced in the excitation manifold and all equations are solved non-approximated. Excitation energies in coupled cluster theory are obtained from the eigenvalues of the CC Jacobian

$$\mathbf{A}\mathbf{S} = \omega\mathbf{S}. \tag{59}$$

Recognizing that T_2 enter in first order and T_1 and T_3 in second order, etc., we may expand the matrix elements of the Jacobian as

$$A_{\mu_i \nu_j} = \langle \mu_i | [F, \tau_{\nu_j}] | \mathrm{HF} \rangle + \langle \mu_i | [U, \tau_{\nu_j}] | \mathrm{HF} \rangle + \langle \mu_i | [[U, \tau_{\nu_j}], T_2] | \mathrm{HF} \rangle$$

$$+ \langle \mu_i | \tfrac{1}{2}[[U, \tau_{\nu_j}], T_2], T_2] + [[U, \tau_{\nu_j}], T_1 + T_3] | \mathrm{HF} \rangle + \mathrm{O}(4), \tag{60}$$

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

$$\left\{ \begin{array}{cccccc} & S & D & T & Q & P \\ S & d(0)+\mathrm{O}(1) & \mathrm{O}(1) & \mathrm{O}(1) & 0 & 0 \\ D & \mathrm{O}(1) & d(0)+\mathrm{O}(1) & \mathrm{O}(1) & \mathrm{O}(1) & 0 \\ T & \mathrm{O}(2) & \mathrm{O}(1) & d(0)+\mathrm{O}(1) & \mathrm{O}(1) & \mathrm{O}(1) \\ Q & \mathrm{O}(3) & \mathrm{O}(2) & \mathrm{O}(1) & d(0)+\mathrm{O}(1) & \mathrm{O}(1) \\ P & \mathrm{O}(4) & \mathrm{O}(3) & \mathrm{O}(2) & \mathrm{O}(1) & d(0)+\mathrm{O}(1) \end{array} \right\}, \tag{61}$$

where $d(0)$ denote the zeroth-order diagonal elements consisting of Hartree–Fock orbital differences and $\mathrm{O}(n)$ denote the lowest nonvanishing order of the Jacobian matrix elements. For example the ST block enter in first order since the second term in Eq. (60) contribute, whereas the TS block enter in second order since the first and second term in Eq. (60) is zero and the third term contribute.

We now consider excitations that are dominated by single and double replacements relative to the reference configuration in more detail, and accordingly write Eq. (59) as

$$\begin{pmatrix} \mathbf{A}^{SD} & \mathbf{B} \\ \mathbf{C} & \mathbf{D} \end{pmatrix} \begin{pmatrix} \mathbf{S}_\mathrm{I} \\ \mathbf{S}_\mathrm{II} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{S}_\mathrm{I} \\ \mathbf{S}_\mathrm{II} \end{pmatrix}, \tag{62}$$

where A^{SD} refer to the singles and doubles block of the Jacobian. The definition of $\mathbf{B}$, $\mathbf{C}$ and $\mathbf{D}$ is clear from the context. All zero and first order contributions to the single and double replacement dominated excitations are contained in $\mathbf{A}^{SD}$. The effect of triples and higher excitation manifolds on the single and double replacement dominated excitations can be analyzed using partitioning techniques giving an effective eigenvalue equation in the singles and doubles space [assuming that $(\mathbf{D} - \omega \mathbf{1})^{-1}$ exist],

$$[\mathbf{A}^{SD} - \mathbf{B}(\mathbf{D} - \omega \mathbf{1})^{-1}\mathbf{C}]\mathbf{S}_\mathrm{I} = \omega \mathbf{S}_\mathrm{I}. \tag{63}$$

The accuracy of the single and double replacement domi-

nated excitations is obtained examining the orders of the matrices $\mathbf{A}^{SD}$, $\mathbf{B}$, $\mathbf{C}$, and $\mathbf{D}$. We write the lowest order of $\mathbf{B}$, $\mathbf{C}$ and $\mathbf{D}$ matrices needed in the subsequent analysis

$$B^{(0)}_{\mu_i \nu_j} = C^{(0)}_{\mu_i \nu_j} = 0, \tag{64}$$

$$D^{(0)}_{\mu_i \nu_j} = \omega_{\mu_i} \delta_{\mu\nu} \delta_{ij}, \tag{65}$$

$$B^{(1)}_{\mu_i \nu_j} = \langle \mu_i | [U, \tau_{\nu_j}] | \mathrm{HF} \rangle [\delta_{i1}\delta_{j3} + \delta_{i2}(\delta_{j3} + \delta_{j4})], \tag{66}$$

$$C^{(1)}_{\mu_i \nu_j} = \langle \mu_i | [U, \tau_{\nu_j}] | \mathrm{HF} \rangle \delta_{i3}\delta_{j2}, \tag{67}$$

$$C^{(2)}_{\mu_3 \nu_1} = \langle \mu_3 | [[U, \tau_{\nu_1}], T_2] | \mathrm{HF} \rangle. \tag{68}$$

We note that the TD ($B^{(1)}_{\mu_2 \nu_3}$) and DT ($C^{(1)}_{\mu_3 \nu_2}$) blocks of the Jacobian enter in first order. Since $\mathbf{D}$ contains zeroth-order contributions, the effective eigenvalue equation, Eq. (63), shows that these matrices gives a second-order contribution. This contribution is the only second-order contributions from higher excitation manifolds and gives only direct contributions to the doubles spectrum.

In CCSD the singles and doubles amplitudes are correct to second order, and the full $\mathbf{A}^{SD}$ is, therefore, correct through second order. The single replacement dominated excitations are therefore correct through second order, whereas the double replacement dominated excitations are correct through first order only missing the second order triples contribution described earlier.

In CC3 the singles and doubles amplitudes are correct through third order and the triples amplitudes through second. $\mathbf{A}^{SD}$ is therefore correct through third order. The second-order triples contribution lacking in CCSD is included in CC3, and the double replacement dominated excitations are therefore correct through second order. The same second-order contribution is also included in the CCSDT-1 models and similar accuracy may therefore be expected in CC3 and CCSDT-1 for the double replacement dominated excitations, the differences being higher order terms. Note that the contribution in $\mathbf{B}^{(1)}$ from the quadruples vanishes in second order because the corresponding term in $\mathbf{C}$ is of second order. To obtain higher than second-order accuracy in the doubles spectrum, the quadruple manifold needs to be taken into account.

We now investigate the single replacement dominated excitations. Recall that $\mathbf{A}^{SD}$ is correct through third order in CC3. From the structure of the Jacobian in Eq. (61) it is seen that for the single replacement dominated excitations the only additional third-order contributions arise from the coupling between the second-order TS block in $\mathbf{C}^{(2)}$ [Eq. (68)] and the first-order ST block [Eq. (66)]. The inclusion of the TS block of the Jacobian is thus necessary in order to obtain single replacement excitations correct through third order. This contribution is retained in CC3 due to the special treatment of the singles amplitudes. In CCSDT-1a and CCSDT-1b the coupling between the triples and singles manifold is neglected. In fact, it is also neglected in the approximate EOM-CCSDT study of Watts and Bartlett[11] this being the reason why their single replacement excitation energies are of second order quality only. CC3 thus gives double replacement excitation energies correct through sec-

ond order, and single replacement excitation energies correct through third order. This property is unique to CC3 compared to the other triples corrected excitation energy models published so far and a consequence of treating the singles as zeroth order parameters in U. This treatment of singles ensures that the coupling between the single spectrum and higher excitations manifolds is described correct through lowest order, which is important in a balanced description of response properties as well as the total energy.

We mention that the CCSDT-3 and CCSDT-4 models of Urban et al.[15] include this coupling. The CCSDT-4 model is a N^8 model and comparable to the full CCSDT model in computational requirement. Calculations of total energies indicate that the CCSDT-3 model is not better than CCSDT-1a and CCSDT-1b.[23,24] The CCSDT-3 model is somewhat unbalanced since third-order terms from the doubles are included in the cluster equations but the triples third-order term excluded. These models have only been used for total energies and no excitation energies have been published using these models. The linear response function for CCSDT-3 is correct through third order.

E. Partitioning of CC3 equations

One of the major problems in triple excitation models is the storing of triples amplitudes. In actual CC3 calculations the triples amplitudes are therefore eliminated. In Ref. 14 we demonstrated how this could be done in the optimization of the reference CC3 state. In this section we discuss a similar approach for evaluation of the linear response function. Since the CC3 Jacobian in Eq. (56) has a simple diagonal TT block equations (48) and (49) may be solved explicitly for triples parameters in terms of singles and doubles parameters and matrix elements. We obtain for the triples amplitude responses

$$(\omega_j - \omega_{\mu_3}) t^A_{\mu_3}(\omega_j) = \xi_{\mu_3} + \sum_{\substack{\nu_i \\ i=1,2}} A_{\mu_3 \nu_i} t^A_{\nu_i}(\omega_j), \tag{69}$$

and for the triples $\bar{t}$ parameters,

$$\omega_{\nu_3} \bar{t}^{(0)}_{\nu_3} = - \sum_{\substack{\mu_i \\ i=1,2}} \bar{t}^{(0)}_{\mu_i} A_{\mu_i \nu_3}. \tag{70}$$

Inserting this into the singles and doubles equations we obtain equations for the singles and doubles parameters expressed solely in the singles and doubles space. The triples parameters can always be obtained from Eqs. (69) and (70) if they are needed explicit. The partitioned form of the CC3 frequency dependent Jacobian in the singles and doubles space is

$$^P A_{\mu_i \nu_j}(\omega) = \langle \mu_i | [\hat{H}_0 + [\hat{H}_0, T_2], \tau_{\nu_j}] | \mathrm{HF} \rangle + \sum_{\nu_3} \frac{A_{\mu_i \nu_3} A_{\nu_3 \nu_j}}{\omega - \omega_{\nu_3}}. \tag{71}$$

Introducing the effective triple excitation operator $b^3_{\nu_j}(\omega)$ as

$$b^3_{\nu_j}(\omega) = \delta_{j2} \sum_{\mu_3} \frac{\langle \mu_3 | [\hat{U}, \tau_{\nu_2}] | \text{HF} \rangle}{\omega - \omega_\mu} \tau_{\mu_3}$$

$$+ \delta_{j1} \sum_{\mu_3} \frac{\langle \mu_3 | [[\hat{U}, \tau_{\nu_j}], T_2] | \text{HF} \rangle}{\omega - \omega_\mu} \tau_{\mu_3}, \tag{72}$$

we can write this as

$$^P A_{\mu_i \nu_j}(\omega) = {}^{\text{CCSD}} A_{\mu_i \nu_j} + \langle \mu_i | [\hat{H}_0, b^3_{\nu_j}(\omega)] | \text{HF} \rangle$$

$$+ \delta_{i2} \delta_{j1} \langle \mu_2 | [[\hat{H}_0, T_3], \tau_{\nu_1}] | \text{HF} \rangle. \tag{73}$$

The first term has the same structure as the CCSD Jacobian, the second term arises from the partitioning and the third from the approximate triples operator. The second term gives the lowest order triples contributions as described in the previous section. Using this Jacobian the partioned equations for the CC3 singles and doubles response parameters become

$$[\omega_j \mathbf{1} - {}^P\mathbf{A}(\omega_j)] \mathbf{t}^x(\omega_j) = {}^P\boldsymbol{\xi}^x(\omega_j), \tag{74}$$

$$\overline{\mathbf{t}}^{(0)P}\mathbf{A}(0) = -\boldsymbol{\eta}^{(0)}. \tag{75}$$

The frequency dependent ξ vector is

$$^P \xi^A_{\mu_i}(\omega_j) = \xi^A_{\mu_i} + \sum_{\nu_3} A_{\mu_i \nu_3} \xi^A_{\nu_3}$$

$$= {}^{\text{CCSD}} \xi^A_{\mu_i} + \langle \mu_i | [\hat{A}, T_3] | \text{HF} \rangle$$

$$+ \left\langle \mu_i \left| \left(\hat{H}_0, \sum_{\mu_3} \frac{\xi_{\mu_3}}{\omega_j - \omega_{\mu_3}} \tau_{\mu_3} \right) \right| \text{HF} \right\rangle. \tag{76}$$

Similarly, we may partition the eigenvalue equation in Eq. (60). The triples C vector can be written as

$$(\omega - \omega_{\nu_3}) C_{\nu_3} = \sum_{\substack{\mu_j \\ j=1,2}} A_{\nu_3 \mu_j} C_{\mu_j} \tag{77}$$

and the eigenvalue equation can be written as an equation in ω in the single and double space;

$$^P\mathbf{A}(\omega)\mathbf{C} = \omega\mathbf{C}. \tag{78}$$

We may use this equation to determine the singles and doubles spectrum of the full CC3 eigenvalue equation. Additional zeroth-order triples poles exist in Eq. (78) but these zeroth order poles will for most purposes not introduce any problem in determining the single and double excitation spectrum. In practical applications we thus solve an "eigenvalue" equation in the single and double space self consistent in ω.

In solving the eigenvalue equation or sets of linear equations we need to carry out linear transformation with the Jacobian on trial vectors

$$\rho_{\mu_i} = \sum_{\nu_j} \mathbf{A}_{\mu_i \nu_j} \mathbf{C}_{\nu_j}. \tag{79}$$

We can write the linear transformations in the CC3 model as

$$^{\text{CC3}}\rho(\omega)_{\mu_1} = {}^{\text{CCSD}}\rho_{\mu_1} + \langle \mu_1 | [H_0, B_3(C_1, C_2, \omega)] | \text{HF} \rangle, \tag{80}$$

$$^{\text{CC3}}\rho(\omega)_{\mu_2} = {}^{\text{CCSD}}\rho_{\mu_2}$$

$$+ \langle \mu_2 | [[H_0, C_1], B_3(0, t_2^{(0)}, 0)] | \text{HF} \rangle$$

$$+ \langle \mu_2 | [\hat{H}_0, B_3(C_1, C_2, \omega)] | \text{HF} \rangle, \tag{81}$$

where we have introduced the effective triples operator

$$B_3(C_1, C_2, \omega) = \sum_{\nu_i} C_{\nu_i} b^3_{\nu_i}(\omega)$$

$$= \sum_{\mu_3} \frac{\langle \mu_3 | [\hat{U}, C_2] | \text{HF} \rangle}{\omega - \omega_\mu} \tau_{\mu_3}$$

$$+ \sum_{\mu_3} \frac{\langle \mu_3 | [[\hat{U}, C_1], T_2^{(0)}] | \text{HF} \rangle}{\omega - \omega_\mu} \tau_{\mu_3}. \tag{82}$$

The triples contribution to the equations for optimization of the reference can be written as

$$\langle \mu_i | [\hat{H}_0, B_3(0, T_2, 0)] | \text{HF} \rangle, \quad i = 1, 2. \tag{83}$$

It is thus seen that relative to CCSD, essentially the same kinds of terms are involved for the wave function optimization and in the transformations that are necessary for solving eigenvalue equations. For the terms involving C_2 only a generalized triples diagonal needs to be taken into account. The rest involve C_1 and originate from the singles in $\hat{H}$. These terms can be calculated using the same strategy as before but with a one index transformed Hamiltonian

$$\tilde{H} = [\hat{H}, C_1]. \tag{84}$$

Building on the capability of doing CC3 wave function optimization and CCSD excitation energies, the amount of extra programming is fairly small. The CCSDT-1a and CCSDT-1b models are easily obtained by neglecting some of the terms as described in Sec. IV C. The CCSDT-1b are obtained by neglecting T_1 and C_1 contributions in B_3 and CCSDT-1a is obtained by further neglecting T_1 and C_1 in the second and third term in Eq. (81).

The construction of the right hand sides and the final contraction for calculating other properties than excitation energies is more involved. We postpone further discussion of these matters to later work. We have demonstrated here that we may solve CC3 linear equations and eigenvalue equations in the single and double space without storing triples trial and transformed vectors with an N^7 operation count similar to what is required to optimize the reference wave function.[14]

V. CALCULATIONS

Calculations are presented for excitation energies of CH^+, N_2, and C_2H_4. For CH^+ we compare CC3 results to FCI, CCSD, CCSDT-1a, CCSDT-1b, approximative EOM-CCSDT results from Ref. 11, and noniterative CCSDT-1a results reported in Ref. 12. For N_2 and C_2H_4 we compare CC3 excitation energies with CCSDT-1a and experiment as well as CCS, CC2, CCSD results obtained in the hierarchy of coupled cluster models described in Ref. 25. For C_2H_4 we

TABLE I. CH$^+$ excitation energies in eV and ground state energies in a.u.

Excitation	CISD[a]	CCSD[a]	Noniter CCSDT-1a[b]	CCSDT-1a[b]	CCSDT-1b	Approx. EOM CCSDT[c]	CC3	FCI[d]	% t_1 in CCSD
$X\,^1\Sigma^+\to\,^1\Sigma^+$	9.917	9.109	8.783	8.781	8.779	8.624	8.779	8.549	1
	14.941	13.581	13.559	13.583	13.584	13.576	13.541	13.525	93
	18.651	17.316	17.269	17.285	17.285	17.265	17.243	17.217	84
$^1\Pi$	4.457	3.261	3.246	3.271	3.274	3.279	3.242	3.230	97
	15.572	14.454	14.395	14.339	14.401	14.266	14.346	14.127	72
$^1\Delta$	8.438	7.888	7.299	7.287	7.284	7.029	7.282	6.964	0
	18.488	17.689	17.177	17.097	17.095	16.798	17.094	16.833	24
Ground state energy ($^1\Sigma^+$)	−38.014 201	−38.017 670		−38.019 131	−38.019 131	−38.019 516	−38.019 131	−38.109 638	

[a]CISD and CCSD result from Ref. 9.
[b]CCSDT-1a and noniterative CCSDT-1a (results from Ref. 12).
[c]Approximate EOM-CCSDT result from Ref. 11.
[d]FCI numbers from Ref. 27.

further compare with CASPT2 (Ref. 26) (second order perturbation theory building on a complete active space reference) results.

A. CH$^+$

The CH$^+$ calculations were carried out at the internuclear distance 2.13713 a.u., using the $14\sigma5\pi1\delta$ basis of Ref. 27. CH$^+$ has a ground state electronic configuration $1\sigma^2 2\sigma^2 3\sigma^2$ with a large nondynamical correlation contribution from $1\sigma^2 2\sigma^2 1\pi^2$. CH$^+$ has a $^1\Pi$ valence state dominated by $1\sigma^2 2\sigma^2 3\sigma^1 1\pi^1$, that is single replacement dominated relative to the ground state. Furthermore, CH$^+$ has one valence excited state of $^1\Sigma^+$ symmetry and one of $^1\Delta$ symmetry that originate from the $1\sigma^2 2\sigma^2 1\pi^2$ electronic configuration and are predominantly double replacements relative to the ground state. In Table I, we report ground state energies and excitation energies from the $X\,^1\Sigma^+$ ground state to the valence excited states and to some higher states for the various approaches.

The CC3 ground state energy in Table I is within 0.5 milliHartree of the CCSDT energy and the FCI energy. The CCSDT-1a and CCSDT-1b energies are almost identical to the CC3 energy. The reference is thus described at similar accuracy in CC3 and the CCSDT-1 models.

The CCSDT-1a and CCSDT-1b excitation energies are almost identical for all excitations. The excitation energies of double excitation character is significantly improved relative to CCSD for all approximative triples method. The error in

CCSD is of order 0.5–1.0 eV. In the triples models this is improved to be less than 0.3 eV relative to FCI, whereas the differences between CC3 and CCSDT-1 is less that 0.05 eV. For the double replacement excitations the differences between the CC3 and CCSDT-1a approaches are thus minor. The approximative EOM-CCSDT includes some triples–doubles and triples–triples interaction and transitions with large double excitation contributions are closer to FCI in this model than for the other triples models. The errors in this approximative EOM-CCSDT model is 0.1 eV. The description of single replacement dominated excitations is improved significantly in CC3 compared to CCSD while CCSDT-1 does not improve the CCSD energies for single replacement dominated excitations. The approximative EOM-CCSDT model does not either improve the single replacement dominated excitations significantly. The CCSDT-1 models and the approximative EOM-CCSDT model exclude the third order triples corrections to the single excitation energies, and therefore give no improvement relative to CCSD. For double replacement dominated excitations the noniterative CCSDT-1a model, denoted EOM-CCSD(T) in Ref. 12, is very close to CCSDT-1a. For single replacement dominated excitations closer agreement with FCI is obtained than in CCSDT-1a. The authors of Ref. 12 noted that this may be accidental.

For the single replacement dominated excitations the CCSDT-1a corrections to CCSD does not include the third-

TABLE II. N$_2$ excitation energies in eV and ground state energies in a.u. Basis set from Ref. 29. Basis set is [$11s7p2d/6s5p2d$]. R_{NN}=2.067 a.u.

	CCS[a]	CC2[a]	CCSD[a]	CC3	CCSDT-1a	Expt.[b]	% T_1
$^1\Pi_u$	15.63	14.11	13.74	13.48	13.73	13.4	86
$^1\Sigma_u^+$	16.67	14.39	14.63	14.39	14.76	14.4	95
$^1\Delta_u$	9.14	11.08	10.68	10.53	10.92	10.3	97
$^1\Sigma_u^-$	8.58	10.54	10.27	10.16	10.61	9.9	98
$^1\Pi_g$	10.10	9.65	9.62	9.55	9.89		94
$^1\Sigma_u^+$	15.31	15.65	15.70	15.14	15.88		96
Gs. E.	−108.985 177	−109.402 101	−109.394 480	−109.413 431	−109.413 364		

[a]CCS, CC2, and CCSD results from Ref. 25.
[b]Experimental results from Ref. 30.

TABLE III. C_2H_4 singlet excitation energies in eV. Ground state energies in a.u. Basis set and geometry as in Ref. 31. Basis set is an atomic natural orbital type (ANO) where $(14s9p4d/8s4p)$ is contracted to $[4s3p2d/3s2p]$ and where a set of diffuse $(2s2p1d)$ is added on carbon. The geometry is $r_{CC}=1.339$ Å, $r_{CH}=1.086$ Å, and $<HCH=117.6$.

	RPA[a]	CCS[a]	CC2[a]	CCSD[a]	CC3	CCSDT-1a	CASPT2[b]	Expt.[c]
$^1B_{3u}$	7.07	7.09	7.14	7.29	7.23	7.45	7.17	7.11
$^1B_{1g}$	7.66	7.67	7.78	7.95	7.90	8.12	7.85	7.80
$^1B_{2g}$	7.82	7.83	7.82	7.99	7.94	8.16	7.95	7.90
$^1B_{1u}$	7.33	7.67	7.86	7.98	7.87	8.19	8.40	8.01
^1A_g	8.14	8.16	8.23	8.46	8.42	8.64	8.40	8.29
$^1B_{3u}$	8.54	8.55	8.58	8.79	8.75	8.97	8.66	8.62
^1A_u	8.74	8.74	8.77	9.02	8.99	9.21	8.94	
$^1B_{3u}$	8.79	8.79	8.84	9.08	9.04	9.26	9.03	8.90
$^1B_{2u}$	8.96	8.97	9.07	9.27	9.22	9.44	9.18	9.05
$^1B_{1u}$	8.94	8.97	9.03	9.31	9.27	9.50	9.31	9.33
E_{tot}	−78.064 796	−78.064 796	−78.388 064	−78.411 268	−78.425 041	−78.424 996		

[a]RPA, CCS, CC2, and CCSD results from Ref. 25.
[b]CASPT2 results from Ref. 31.
[c]Experimental data from the compilation in Ref. 31.

order contributions from the TS-ST blocks. These third order contributions are in the opposite direction of the other corrections. The CC3 model includes all contributions and is therefore significantly closer to FCI than any of the other triples models. The superior performance of CC3 have been observed in benchmark calculations on other systems.[28]

B. N_2

In Ref. 25 we performed CCS, CC2, and CCSD calculations on N_2 with the geometry and basis set of Ref. 29, see Table II. We performed CC3 and CCSDT-1a calculations of the same excitation energies; the results are given in Table II. Further basis set studies are needed to estimate the basis set error but it appears that the current basis set is sufficiently large to describe the major features of the spectrum. All excitations are single replacement dominated as indicated by the percent t_1 contributions. Significant differences are observed between the results of the various coupled cluster models. The CCSDT-1a and CC3 differ by up to 0.6 eV, with CCSDT-1a generally going in the opposite direction of CC3 relative to CCSD. This indicates that large third-order contributions exist in N_2. Like in CH^+, the third-order contributions that couple to the triples space are in opposite direction of the other contributions. As a consequence of the more balanced treatment, the CC3 results are closer to the experimental results than are the CCSDT-1a results.

C. C_2H_4

In Ref. 31 CASPT2 calculations on ethylene are reported. We have carried out CCSDT-1a and CC3 calculations using the same basis set and geometry, see Table III. The results are given in Table III together with CCS, CC2, and CCSD results from Ref. 25. All excitations are single replacement dominated with a single replacement contribution between 94–97% t_1. The difference between CCSD and CC3 is of order 0.04 eV. From the convergence in the hierarchy of CCS, CC2, CCSD, CC3 excitation energies and from the experience of other benchmark calculations, the CC3 excitation energies are expected to be accurate with the

difference between CCSD and CC3 as a conservative estimate of the error bound. The CCSDT-1 model give changes of about 0.2 eV relative to CCSD, and in the opposite direction of the changes in CC3. Thus CCSDT-1a seems to give an unbalanced treatment of single replacement excitations energies which may leads to significant errors, and in fact spoils the accuracy obtained at the CCSD level.

CASPT2 results are also given in Table III. The approaches for obtaining excitation energies in the CASPT2 and in coupled cluster linear response are completely different. In CASPT2 the total energies of the individual states are found in a complete active space multiconfigurational self-consistent field (CAS MCSCF) calculation followed by a second-order perturbation energy correction. In the coupled cluster linear response approach the ground state function is calculated explicitly and the excitation spectrum is found solving the linear response eigenvalue equation. Recent benchmark calculations indicate that the energy in CASPT2 is of approximately MP2 quality but robust towards larger static correlation effects.[32] For many systems CASPT2 has provided excitation energies within 0.3 eV of the experimental results. This accuracy is thus obtained due to cancellation of errors between the ground state and excited state energy and is thus sensitive to a balanced treatment of the ground and excited state.

The CASPT2 results are within 0.1 eV of the CC3 results for all excitations except the $^1B_{1u}$ state, and also within 0.2 eV from experiment. For most of the CASPT2 results the calculations thus seem to be balanced and give a remarkable accuracy. However the accuracy of the mixed valence-Rydberg state is not consistent with the accuracy of the other excited states. In the coupled cluster linear response calculation no special problems are encountered treating mixed valence Rydberg states. In order to provide a final comparison with experiment, basis set and geometry effects needs to be considered in more detail.

VI. CONCLUDING REMARKS

We have outlined a general approach for deriving response functions for approximated coupled cluster models.

The linear response function for the iterative approximate triples coupled cluster model CC3 was derived, and from simplifications of the CC3 response function, response functions for CCSDT-1a and CCSDT-1b are obtained.

We have carried out an order analysis of CC3 linear response properties in particular excitation energies. The CC3 linear response function is correct through third order in contrast to the CCSDT-1 models where the linear response functions are correct through second order. In CC3 excitation energies of single replacement character are correct through third order, and the double replacement excitation energies are correct through second order. The latter also holds in CCSDT-1 whereas the single excitation dominated excitations are correct to second order and not improved in CCSDT-1 relative to CCSD. The same applies for the approximative EOM-CCSDT excitation energies of Ref. 11. The aforementioned features of the CC3 model are all consequences of the fact that the singles are treated as zeroth-order parameters. The special treatment of the singles is easily justified by a double perturbation theory expansion of the cluster equations. Keeping all terms in the external perturbation but approximating to second order in the fluctuation potential in the triples cluster equations, the CC3 triples equations are obtained. This approach assures that the important coupling to the singles is accounted for, and a balanced description of one-electron response properties, excitation energies, and the ground-state energy is therefore obtained. In Ref. 25 the CC3 model is included in a hierarchy of coupled cluster models. Through the series CCS, CC2, CCSD, CC3, etc. properties are improved at each step in this hierarchy. One-electron response properties are improved from being correct through second order in CCSD (with full inclusion of all singles and doubles term) to being correct through third order in CC3. The same holds for single replacement dominated excitations. For double replacement excitations CCSD is correct through first order and CC3 improves this to second order.

We have demonstrated how excitation energies and other properties in CC3 can be calculated using N^7 operation counts and without explicit storage of triples trial and result vectors. The strength of the CC3 approach is demonstrated through calculations of excitation energies of CH^+, N_2, and C_2H_4. Benchmark calculations on CH^+ convey significant improvements of both single and double replacements in CC3 relative to CCSD. Benchmark calculations on other systems show the same trends.[28] Significant contributions to all excitations have thus been obtained in CC3, and the importance of treating the triples contribution in a balanced way is clearly exposed by all the calculations.

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