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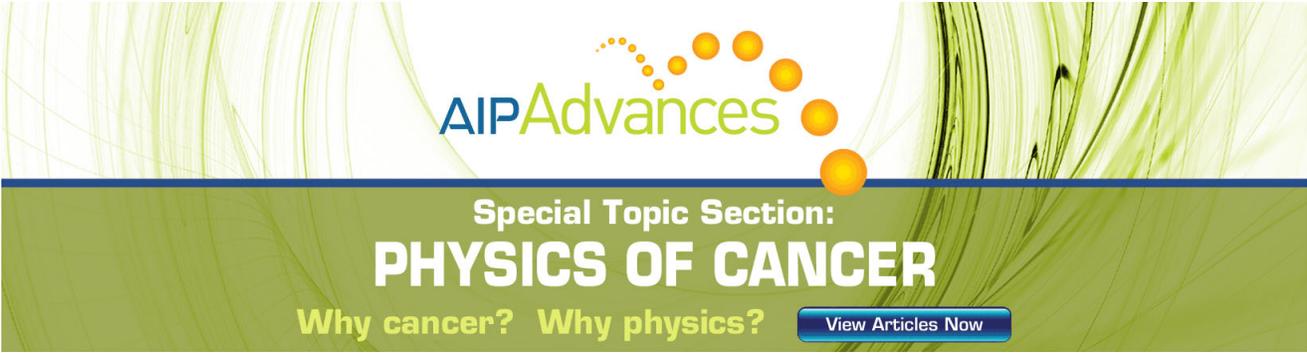
Coupled cluster response functions

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The linear and quadratic response functions have been determined for a coupled cluster reference state. From the response functions, computationally tractable expressions have been derived for excitation energies, first- and second-order matrix transition elements, transition matrix elements between excited states, and second- and third-order frequency-dependent molecular properties.

I. INTRODUCTION

During the last decade, the coupled cluster approach[1] has evolved to become one of the most promising methods in *ab initio* quantum chemistry.[2] The development of efficient methods for the calculation of analytic coupled cluster energy derivatives and static molecular properties has stressed the potential of the method.[3,4] Applications of the coupled cluster approach to excited states have been limited, due to the difficulties in converging the coupled cluster equations for excited states.[5] Multireference coupled cluster approaches (MRCC)[6] have also been used to determine excited states, but these methods are at the moment far from competitive compared to more conventional methods. Some fundamental problems arise when coupled cluster (CC) calculations on individual states are used to calculate excitation energies. The CC states are nonorthogonal and interacting, and it is difficult to make them orthogonal and noninteracting. The calculation of transition matrix elements are hampered for the same reason.

Molecular properties, excitation energies, and transition moments may alternatively be calculated from coupled cluster response functions. This has been investigated by Monkhorst[7] and Dalgaard and Monkhorst[7] who derived expressions for the coupled cluster linear response function by analyzing the time development of the phase factor.[7] In the phase factor approach to the linear response function, the first- and second-order correction to the cluster amplitudes enter the derivation and the second-order correction is eliminated afterwards using tedious algebra. Similar and even more tedious eliminations have to be performed if the phase factor approach is extended to higher response functions.

In this paper, we present a formalism that determines CC response functions based on analyzing the time evolution of a transition expectation value. The derivation constitutes a generalization of the Lagrangian technique introduced by Helgaker and Jørgensen[8] for determining response functions for a static perturbation. When the Lagrangian technique is used for CC wave functions, the Hellmann Feynmann theorem is generalized to a transition expectation value with respect to the CC state and a dual type state. The time evolution of this transition expectation value defines the response functions for a time-dependent perturbation. We derive expressions for the linear and quadratic response functions for a coupled cluster state and

show that no elimination is required of higher-order cluster amplitude responses. The linear response function contains the first-order response of the cluster amplitudes and the first-order response of the dual type state. The quadratic response function contains, in addition, the second-order responses. From the linear response function, second-order molecular properties may be calculated, e.g., the frequency dependent polarizability. The poles of the linear response function determines the excitation energies, and the residues determine the transition matrix elements, e.g., the one-photon absorption matrix element between the reference state and an excited state. The quadratic response function determines third-order molecular properties, e.g., the first hyperpolarizability. The residues of the quadratic response function determine the second-order transition matrix elements between the reference state and an excited state (e.g., the two-photon absorption matrix element) and the transition matrix elements between two excited states. Expressions are derived for the above-mentioned molecular properties for a coupled cluster wave function. In the limit of a time-independent perturbation, the response functions become identical to the ones that are determined using the Lagrangian technique.[4,8] The linear response function for the extended coupled cluster method has been derived by Arponen *et al.*[9] In Ref. 10 more details can be found about the determination of molecular properties from the linear and quadratic response functions for various external as well as internal fields. It should be noted that the states entering response function calculations are orthogonal and noninteracting.

In the following paper,[11] we have shown that accurate excitation energies can be determined from the linear response eigenvalue equation for a coupled cluster single and double reference state. The excitation energies are shown to be size intensive.[11]

In the next section, we briefly discuss the development of response function theory for an exact state. Section III summarizes the development of response theory for a coupled cluster state when the perturbation is time independent. The time evolution of a coupled cluster state is discussed for a time-dependent perturbation in Sec. IV, and in Sec. V the responses of the coupled cluster state is determined. The linear and quadratic response functions derived in Secs. VI and VII contain some concluding remarks.

II. RESPONSE THEORY FOR EXACT STATES

In this section, we briefly summarize a few of the results from response theory for exact states, which become important for identifying the response functions for a CC reference wave function. For details, the reader is referred to the work by Olsen and Jørgensen.[10] Consider a molecular system described by the time-independent Hamiltonian H_0, and apply the interaction operator V^t to the molecular system. Assume V^t vanishes at $t = -\infty$. The interaction operator is expressed in terms of its Fourier transform,

$$V^t = \int_{-\infty}^{\infty} d\omega \, V^\omega \exp(-i\omega + \alpha)t, \tag{1}$$

where α is a real positive infinitesimal. The representation of the interaction operator in Eq. (1) is often called an adiabatically switched on perturbation. Assume the eigenvalues and eigenstates for H_0 are known, and the system is in the state $|O\rangle$ at $t = -\infty$,

$$H_0|O\rangle = E_0|O\rangle. \tag{2}$$

The orthogonal complement to $|O\rangle$ is denoted $\{|n\rangle\}$ and

$$H_0|n\rangle = E_n|n\rangle. \tag{3}$$

We now determine the time evolution of $|O\rangle$ and use the notation $|\bar{O}\rangle$ for the time-dependent state. The time evolution of the system is governed by the time-dependent Schrödinger equation

$$i\frac{d}{dt}|\bar{O}\rangle = (H_0 + V^t)|\bar{O}\rangle. \tag{4}$$

Following Ref. 8, we write

$$|\bar{O}\rangle = |\tilde{O}\rangle \exp(i2P_o^R), \tag{5}$$

where $\exp(i2P_o^R)$ is the phase factor in Eq. (2.11) of Ref. 10. The phase factor does not enter the calculation of the response functions and will not be discussed further. The state $|\tilde{O}\rangle$ may be expanded in orders of the perturbation V^t,

$$|\tilde{O}\rangle = |O\rangle + |O^{(1)}\rangle + |O^{(2)}\rangle + \cdots, \tag{6}$$

and $|O^{(n)}\rangle$ can be determined using Ehrenfest's theorem. The response functions are defined by the expansion coefficients of the expectation value of the time-independent operator A,

$$A_{AV}(t) = \langle \bar{O}|A|\bar{O}\rangle = \langle O|A|O\rangle + \int_{-\infty}^{\infty} d\omega_1 \langle\langle A; V^{\omega_1}\rangle\rangle_{\omega_1 + i\alpha} \exp(-i\omega_1 + \alpha)t$$

$$+ \frac{1}{2}\int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \langle\langle A; V^{\omega_1}; V^{\omega_2}\rangle\rangle_{\omega_1 + i\alpha, \omega_2 + i\alpha} \exp(-i\omega_1 - i\omega_2 + 2\alpha)t + \cdots. \tag{7}$$

The explicit expression for the response functions up to the cubic response function are given in Ref. 10. We limit our discussion to the linear

$$\langle\langle A; V^{\omega_1}\rangle\rangle_{\omega_1 + i\alpha} = \sum_k \left\{ \frac{\langle O|A|k\rangle \langle k|V^{\omega_1}|O\rangle}{\omega_1 - \omega_k + i\alpha} - \frac{\langle O|V^{\omega_1}|k\rangle \langle k|A|O\rangle}{\omega_1 + \omega_k + i\alpha} \right\} \tag{8}$$

and quadratic response function

$$\langle\langle A; V^{\omega_1}; V^{\omega_2}\rangle\rangle_{\omega_1 + i\alpha, \omega_2 + i\alpha} = P(1,2)\left\{ \sum_{kn} \frac{\langle O|A|k\rangle(\langle k|V^{\omega_1}|n\rangle - \delta_{kn}\langle O|V^{\omega_1}|O\rangle)\langle n|V^{\omega_2}|O\rangle}{(\omega_1 + \omega_2 - \omega_k + 2i\alpha)(\omega_2 - \omega_n + i\alpha)} \right.$$

$$+ \sum_{kn} \frac{\langle O|V^{\omega_2}|n\rangle(\langle n|V^{\omega_1}|k\rangle - \delta_{kn}\langle O|V^{\omega_1}|O\rangle)\langle k|A|O\rangle}{(\omega_1 + \omega_2 + \omega_k + 2i\alpha)(\omega_2 + \omega_n + i\alpha)}$$

$$\left. - \sum_{kn} \frac{\langle O|V^{\omega_1}|k\rangle(\langle k|A|n\rangle - \delta_{kn}\langle O|A|O\rangle)\langle n|V^{\omega_2}|O\rangle}{(\omega_1 + \omega_k + i\alpha)(\omega_2 - \omega_n + i\alpha)} \right\}. \tag{9}$$

The properties of the residues and poles of the linear and quadratic response functions have been discussed several places. We summarize the results needed for the analysis of the coupled cluster response functions. The first-order poles $\{\pm\omega_k\}$ of the linear response functions in Eq. (8) occur at the excitation and deexcitation energies of the unperturbed system. The corresponding transition matrix elements are obtained from the residues at $\{\pm\omega_k\}$, which are given by

$$\lim_{\omega_1 \to \omega_k} (\omega_1 - \omega_k)\langle\langle A; V^{\omega_1}\rangle\rangle_{\omega_1}$$

$$= \langle O|A|k\rangle \langle k|V^{\omega_k}|O\rangle = \Gamma^A_{o\to k}\Gamma^{V^{\omega_k}}_{k\to o}, \tag{10}$$

$$\lim_{\omega_1 \to -\omega_k} (\omega_1 + \omega_k)\langle\langle A; V^{\omega_1}\rangle\rangle_{\omega_1}$$

$$= -\langle O|V^{-\omega_k}|k\rangle \langle k|A|O\rangle = -\Gamma^{V^{-\omega_k}}_{o\to k}\Gamma^A_{k\to o}. \tag{11}$$

The second-order transition matrix elements between $|O\rangle$ and $|m\rangle$ are determined from the residues of the quadratic response function,

$$\lim_{\omega_2 \to \omega_m} (\omega_2 - \omega_m) \langle\langle A; V^{\omega_1}; V^{\omega_2} \rangle\rangle_{-\omega_1, \omega_2}$$

$$= \sum_k \left\{ \frac{\langle O|A|k\rangle (\langle k|V^{-\omega_1}|m\rangle - \delta_{km}\langle O|V^{-\omega_1}|O\rangle)}{-\omega_1 + \omega_m - \omega_k} \right.$$

$$\left. - \frac{\langle O|V^{-\omega_1}|k\rangle (\langle k|A|m\rangle - \delta_{km}\langle O|A|O\rangle)}{-\omega_1 + \omega_k} \right\}$$

$$\times \langle m|V^{\omega_m}|O\rangle = \Gamma_{0 \to m}^{AV^{-\omega_1}}(\omega_1) \Gamma_{m \to o}^{V^{\omega_m}}. \tag{12}$$

The complex conjugate of the second-order transition matrix elements is determined from the residue,

$$- \lim_{\omega_2 \to -\omega_m} (\omega_2 + \omega_m) \langle\langle A; V^{\omega_1}; V^{\omega_2} \rangle\rangle_{\omega_1, \omega_2}$$

$$= \sum_k \left\{ \frac{(\langle m|V^{\omega_1}|k\rangle - \delta_{km}\langle O|V^{\omega_1}|O\rangle)\langle k|A|O\rangle}{-\omega_1 + \omega_m - \omega_k} \right.$$

$$\left. - \frac{(\langle m|A|k\rangle - \delta_{km}\langle O|A|O\rangle)\langle k|V^{\omega_1}|O\rangle}{-\omega_1 + \omega_k} \right\}$$

$$\times \langle O|V^{-\omega_m}|m\rangle = \Gamma_{m \to o}^{AV^{\omega_1}}(\omega_1) \Gamma_{o \to m}^{V^{-\omega_m}}. \tag{13}$$

The transition matrix element between excited states $|m\rangle$ and $|k\rangle$ may be calculated from the residue,

$$\lim_{\omega_1 \to -\omega_k} (\omega_1 + \omega_k) \{ \lim_{\omega_2 \to \omega_m} (\omega_2 - \omega_m) \langle\langle A; V^{\omega_1}; V^{\omega_2} \rangle\rangle_{\omega_1, \omega_2} \}$$

$$= - \langle O|V^{-\omega_k}|k\rangle \langle k|(A - \langle O|A|O\rangle)|m\rangle$$

$$\times \langle m|V^{\omega_m}|O\rangle, \tag{14}$$

when the transition matrix element between the reference state and excited states $|m\rangle$ and $|k\rangle$ have been identified. The complex conjugate of the transition amplitude is obtained from the expression in Eq. (14) by making the substitution $k \leftrightarrow m$.

III. THE COUPLED CLUSTER ANSATZ IN THE TIME-INDEPENDENT CASE

The coupled cluster ansatz for the closed shell wave function is

$$|CC\rangle = \exp(T)|HF\rangle, \tag{15}$$

where the cluster operator T for an N-electron system is

$$T = T_1 + T_2 + \cdots + T_N, \tag{16}$$

and

$$T_1 = \sum_{ai} \sum_{\sigma\sigma'} t_{i\sigma'}^{a\sigma} a_{a\sigma}^+ a_{i\sigma'}, \tag{17}$$

$$T_2 = \sum_{aibj} \sum_{\substack{\sigma\sigma' \\ \sigma''\sigma'''}} t_{i\sigma'j\sigma'''}^{a\sigma b\sigma''} a_{a\sigma}^+ a_{i\sigma'} a_{b\sigma''}^+ a_{j\sigma'''} \tag{18}$$

are the one- and two-electron operators. The indices $ijkl$ and $abcd$ refer to occupied and unoccupied orbitals in the reference state $|HF\rangle$, and $pqrs$ are general orbital indices. Using a shorthand notation, the cluster operator is

$$T = t\tau = \sum_\mu t_\mu \tau_\mu, \tag{19}$$

where t denotes the cluster amplitudes and τ the corresponding excitation operators, and $\mu\nu\gamma\delta$ denote single, double, and higher-order electron replacement operators. The following properties of the cluster operators τ,

$$\tau_\mu^+ |HF\rangle = 0, \tag{20}$$

$$\langle HF|\tau_\nu^+ \tau_\mu|HF\rangle = \delta_{\nu\mu}, \tag{21}$$

$$[\tau_\nu, \tau_\mu] = 0, \tag{22}$$

will be used throughout this paper. The Hartree–Fock state $|HF\rangle$ in Eq. (15) is determined from the Brillouin condition

$$\langle HF|[E_{ai}^-, H_o]|HF\rangle = 0, \tag{23}$$

where

$$E_{ai}^- = E_{ai} - E_{ia}, \quad E_{ai} = \sum_\sigma a_{a\sigma}^+ a_{i\sigma} \tag{24}$$

and H_o is the Born–Oppenheimer Hamiltonian.

The coupled cluster state satisfies the time-independent Schrödinger equation

$$\exp(-T)H_o|CC\rangle = E_o \exp(-T)|CC\rangle, \tag{25}$$

where the total energy is determined from projecting Eq. (25) from the left with $\langle HF|$,

$$E_o = \langle HF|H_o|CC\rangle, \tag{26}$$

and the cluster amplitudes are determined from the projection

$$\langle \mu|\exp(-T)H_o|CC\rangle = 0, \tag{27}$$

where

$$\langle \mu| = \langle HF|\tau_\mu^+. \tag{28}$$

Using Eq. (27), the CC total energy in Eq. (26) may be written as

$$E_o = \langle \Lambda|H_o|CC\rangle, \tag{29}$$

where

$$\langle \Lambda| = \langle HF| + \sum_\mu \zeta_\mu \langle \mu|\exp(-T). \tag{30}$$

The parameters $\{\zeta_\mu\}$ are so far arbitrary and may be determined requiring $\langle \Lambda|$ satisfy the time independent Schrödinger equation

$$\langle \Lambda | H_o \exp(T) = \langle \Lambda | \exp(T) E_o. \qquad (31)$$

Right projecting this equation onto the subspace $\{ | \mathrm{HF} \rangle, | v \rangle \}$ gives the equation for the energy in (29) and

$$\sum_\mu \zeta_\mu A_{\mu v} = - \langle \mathrm{HF} | [H_o, \tau_v] | \mathrm{CC} \rangle, \qquad (32)$$

where

$$A_{\mu v} = \langle \mu | \exp(-T) [H_o, \tau_v] | \mathrm{CC} \rangle, \qquad (33)$$

which determines the $\{\zeta_\mu\}$ parameters. In deriving Eq. (32), we have used Eqs. (26), (27), and (30). Equation (32) may also be derived from the equations for the cluster amplitudes by viewing $\{\zeta_\mu\}$ as Lagrange multipliers; this derivation is described in detail by Koch et al.[4] The A matrix in Eq. (33) is the coupled cluster Jacobian and is the first derivative of the coupled cluster equations with respect to the cluster amplitudes.

From the above analysis, it is seen that $\langle \Lambda |$ is a dual type vector to $| \mathrm{CC} \rangle$ that satisfies the time-independent Schrödinger equation and the normalization

$$\langle \Lambda | \mathrm{CC} \rangle = 1. \qquad (34)$$

When a perturbation described by the operator βV (β is a strength parameter) is added to the molecular system, we obtain, using Eqs. (27), (30), and (32),

$$\frac{d}{d\beta} \langle \Lambda(\beta) | H_o + \beta V | \mathrm{CC}(\beta) \rangle |_{\beta=0}$$

$$= \sum_v \frac{\partial \zeta_v}{\partial \beta} \Big|_{\beta=0} \langle v | \exp(-T) H_o | \mathrm{CC} \rangle$$

$$- \sum_{v\mu} \zeta_v \langle v | \exp(-T) \tau_\mu \frac{\partial t_\mu}{\partial \beta} \Big|_{\beta=0} H_o | \mathrm{CC} \rangle$$

$$+ \langle \Lambda | V | \mathrm{CC} \rangle + \sum_\mu \langle \Lambda | H_o \tau_\mu \frac{\partial t_\mu}{\partial \beta} \Big|_{\beta=0} | \mathrm{CC} \rangle$$

$$= \langle \Lambda | V | \mathrm{CC} \rangle. \qquad (35)$$

The Hellmann–Feynmann theorem can thus be generalized to a transition expectation value with respect to $| \mathrm{CC} \rangle$ and $\langle \Lambda |$. Without truncation in the cluster operator, $| \mathrm{CC} \rangle$ and $\langle \Lambda |$ become the exact state with the normalization in Eq. (34). For a truncated cluster operator, $\langle \Lambda |$ is not the adjoint of $| \mathrm{CC} \rangle$. The generalized Hellmann–Feynmann theorem in Eq. (35) is still satisfied, and response functions may be identified from the time evolution of the transition expectation value $\langle \Lambda | V | \mathrm{CC} \rangle$. In the limit of a time-independent perturbation, the response functions become equal to the ones previously obtained for a time-independent perturbation (for example, using the Lagrangian technique[4,8] or using the relaxed density formalism of Refs. 12 and 13).

IV. THE TIME EVOLUTION OF THE COUPLED CLUSTER STATE

We now consider a time-dependent perturbation (1) and parametrize the time evolution of the coupled cluster state as

$$| \mathrm{CC}(t) \rangle = \exp(T(t)) | \mathrm{HF} \rangle \exp(i\epsilon(t)), \qquad (36)$$

where $\exp(i\epsilon(t))$ is a time-dependent phase factor and the cluster operator

$$T(t) = t(t)\tau \qquad (37)$$

contains time-dependent amplitudes. The Hartree–Fock state is determined from Eq. (23) and is not allowed to relax to the applied perturbation. An approximate description of the orbital relaxation is obtained from T_1. The time evolution of $| \mathrm{CC}(t) \rangle$ is determined from the coupled cluster time-dependent Schrödinger equation

$$\exp(-T(t)) i \frac{d}{dt} | \mathrm{CC}(t) \rangle$$

$$= \exp(-T(t))(H_o + V^t) | \mathrm{CC}(t) \rangle \qquad (38)$$

by projection onto the space $\{\langle \mathrm{HF} |, \langle \mu | \}$. The projection on $\langle \mathrm{HF} |$ determines the time evolution of the phase factor

$$\frac{d\epsilon(t)}{dt} = - \langle \mathrm{HF} | (H_o + V^t) \exp(T(t)) | \mathrm{HF} \rangle, \qquad (39)$$

and the projection on $\langle \mu |$ determines the time evolution of the cluster amplitudes

$$\frac{dt_\mu(t)}{dt} = - i \langle \mu | \exp(-T(t))(H_o$$

$$+ V^t) \exp(T(t)) | \mathrm{HF} \rangle. \qquad (40)$$

The time evolution of the state $\langle \Lambda(t) |$ is parametrized as

$$\langle \Lambda(t) | = \Big[\langle \mathrm{HF} | + \sum_\mu \zeta_\mu(t) \langle \mu | \exp(-T(t)) \Big]$$

$$\times \exp(-i\epsilon(t)), \qquad (41)$$

where the phase factor $\epsilon(t)$, the cluster amplitudes $t(t)$, and the $\zeta(t)$ parameters depend on time. The time dependence of the cluster amplitudes $t(t)$ is determined from Eq. (40) and the time dependence of $\zeta(t)$ and $\epsilon(t)$ is determined from the time-dependent Schrödinger equation for the $\langle \Lambda(t) |$ state

$$\Big(\frac{d}{dt} \langle \Lambda(t) | \Big) \exp(0(t) = i \langle \Lambda(t) | (H_o + V^t) \exp(T(t)).$$

$$(42)$$

Multiplying Eq. (42) by $\exp(i\epsilon(t))$ gives

$$-i\frac{d\epsilon(t)}{dt}\left(\langle HF| + \sum_\mu \zeta_\mu(t)\langle\mu|\right) + \sum_\mu \frac{d\zeta_\mu(t)}{dt}\langle\mu|$$

$$-\sum_\mu \zeta_\mu(t)\langle\mu|\frac{d}{dt}T(t)$$

$$=i<\widetilde{\Lambda}(t)|(H_o+V^t)\exp(T(t)), \qquad (43)$$

where

$$\langle\widetilde{\Lambda}(t)| = \langle HF| + \sum_\mu \zeta_\mu(t)\langle\mu|\exp(-T(t)). \qquad (44)$$

Using Eqs. (21) and (40), the projection of Eq. (43) onto $|HF\rangle$ is seen to give the equation for the phase factor in Eq. (39). Projection of Eq. (43) onto $\{|\nu\rangle\}$ gives

$$-i\frac{d\epsilon(t)}{dt}\zeta_\nu(t) + \frac{d}{dt}\zeta_\nu(t) - \sum_\mu \zeta_\mu(t)\langle\mu|\frac{d}{dt}T(t)|\nu\rangle$$

$$=i\langle\widetilde{\Lambda}(t)|(H_o+V^t)\tau_\nu|\widetilde{CC}(t)\rangle, \qquad (45)$$

where

$$|\widetilde{CC}(t)\rangle = \exp(T(t))|HF\rangle. \qquad (46)$$

Using Eqs. (39) and (40), we may then write Eq. (45) as

$$\frac{d}{dt}\zeta_\nu(t) = i\langle\widetilde{\Lambda}(t)|[H_o+V^t,\tau_\nu]|\widetilde{CC}(t)\rangle - i\langle HF|(H_o+V^t)|\widetilde{CC}(t)\rangle\zeta_\nu(t) - i\sum_{\mu\eta}\zeta_\mu(t)$$

$$\times\langle\mu|\tau_\eta|\nu\rangle\langle\eta|\exp(-T(t))(H_o+V^t)|\widetilde{CC}(t)\rangle + i\sum_\mu \zeta_\mu(t)\langle\mu|\tau_\nu\exp(-T(t))(H_o+V^t)|\widetilde{CC}(t)\rangle. \qquad (47)$$

Inserting a complete set of states,

$$1 = |HF\rangle\langle HF| + \sum_\nu \tau_\nu|HF\rangle\langle HF|\tau_\nu^+, \qquad (48)$$

in the last term in Eq. (47) shows that the last three terms cancel and the time evolution of $\zeta(t)$ is determined from the equation

$$\frac{d\zeta_\nu(t)}{dt} = i\langle\widetilde{\Lambda}(t)|[H_o+V^t,\tau_\nu]|\widetilde{CC}(t)\rangle. \qquad (49)$$

The states $|CC(t)\rangle$ and $\langle\Lambda(t)|$ satisfy the normalization condition

$$\langle\Lambda(t)|CC(t)\rangle = \langle\widetilde{\Lambda}(t)|\widetilde{CC}(t)\rangle = 1. \qquad (50)$$

The time evolution of $t(t)$, $\epsilon(t)$, and $\zeta(t)$ is thus determined from left and right projections onto the space $\{|HF\rangle,|\mu\rangle\}$ of the time-dependent Schrödinger equations for the states $|CC(t)\rangle$ and $\langle\Lambda(t)|$. Initially, the $t(t)$ amplitudes are determined from the time dependent Schrödinger equation for $|CC(t)\rangle$ and the $\zeta(t)$ parameters are subsequently determined from the time-dependent Schrödinger equation for $\langle\Lambda(t)|$. The $|CC(t)\rangle$ and $\langle\Lambda(t)|$ time-dependent Schrödinger equations give both the equation for the phase factor $\epsilon(t)$ when projected against the Hartree–Fock state.

V. RESPONSE EQUATIONS

In order to derive expressions for coupled cluster response functions, we need to solve Eq. (40) for the cluster amplitudes and Eq. (49) for the ζ parameters for each order in the perturbation. In this section, we derive the response equations necessary to obtain the linear and quadratic response function.

A. The t amplitude response

We consider initially the equation for the cluster amplitudes in (40) and expand the cluster amplitudes

$$t_\mu(t) = t_\mu^{(0)} + t_\mu^{(1)} + t_\mu^{(2)} + \cdots \qquad (51)$$

in orders of the perturbation. In Eq. (51) we have suppressed the time dependence of $t_\mu^{(1)}$ and $t_\mu^{(2)}$. The response equations are obtained by inserting Eq. (51) into Eq. (40),

$$i\frac{dt_\mu^{(0)}}{dt} = \langle\overline{\mu}|H_o|CC\rangle = 0, \qquad (52)$$

$$i\frac{dt_\mu^{(1)}}{dt} = \langle\overline{\mu}|V^t|CC\rangle + \langle\overline{\mu}|[H_o,T^{(1)}]|CC\rangle, \qquad (53)$$

$$i\frac{dt_\mu^{(2)}}{dt} = \langle\overline{\mu}|[V^t,T^{(1)}]|CC\rangle$$

$$+ \frac{1}{2}\langle\overline{\mu}|[[H_o,T^{(1)}],T^{(1)}]|CC\rangle$$

$$+ \langle\overline{\mu}|[H_o,T^{(2)}]|CC\rangle, \qquad (54)$$

where we have used the shorthand notation

$$\langle\overline{\mu}| = \langle\mu|\exp(-T^{(0)}). \qquad (55)$$

Introducing the Fourier transform of $t_\mu^{(1)}$ and $t_\mu^{(2)}$,

$$t_\mu^{(1)} = \int_{-\infty}^{\infty} d\omega_1 X_\mu^{(1)}(\omega_1+i\alpha)\exp(-i\omega_1+\alpha)t \qquad (56)$$

$$t_\mu^{(2)} = \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 X_\mu^{(2)}(\omega_1+i\alpha,\omega_2+i\alpha)$$

$$\times\exp(-i\omega_1-i\omega_2+2\alpha)t \qquad (57)$$

into Eqs. (52) and (53) determines the expressions for $X_\mu^{(1)}(\omega_1)$ and $X_\mu^{(2)}(\omega_1,\omega_2)$

$$X_\mu^{(1)}(\omega_1 + i\alpha) = \sum_\nu \ (-\mathbf{A} + (\omega_1 + i\alpha)\mathbf{I})_{\mu\nu}^{-1} \xi_\nu^{(1)}(\omega_1),$$

(58)

$$X_\mu^{(2)}(\omega_1 + i\alpha, \omega_2 + i\alpha)$$

$$= \sum_\nu \ (-\mathbf{A} + (\omega_1 + \omega_2 + 2i\alpha)\mathbf{I})_{\mu\nu}^{-1}$$

$$\times \xi_\nu^{(2)}(\omega_1 + i\alpha, \omega_2 + i\alpha),$$

(59)

where we have used the notation

$$\xi_\nu^{(1)}(\omega_1) = \langle \bar{\nu} | V^{\omega_1} | \mathrm{CC} \rangle,$$

(60)

$$\xi_\nu^{(2)}(\omega_1 + i\alpha, \omega_2 + i\alpha)$$

$$= \tfrac{1}{2} P(1,2)\{ \langle \bar{\nu} | [V^{\omega_1}, T^{(1)}(\omega_2 + i\alpha)] | \mathrm{CC} \rangle$$

$$+ \tfrac{1}{2} \langle \bar{\nu} | [[H_o, T^{(1)}(\omega_1 + i\alpha)],$$

$$T^{(1)}(\omega_2 + i\alpha)] | \mathrm{CC} \rangle \},$$

(61)

$$T^{(1)}(\omega_1 + i\alpha) = \sum_\nu \tau_\nu X_\nu^{(1)}(\omega_1 + i\alpha),$$

and the definition of the **A** matrix in Eq. (33). We note that the last term in Eq. (61) is symmetric in interchanging indexes 1 and 2 and may be taken outside the $P(1,2)$ permutation operator.

In order to proceed, we assume that the nonsymmetric **A** matrix may be diagonalized

$$\Omega_{nm} = (\mathbf{S}^{-1}\mathbf{AS})_{nm} = \delta_{nm}\omega_n,$$

(62)

where ω_n will be interpreted as the excitation energy from the reference state to the excited state. Inserting Eq. (62) into Eq. (58) gives

$$X_n^{(1)}(\omega_1) = \sum_\nu S_{n\nu}^{-1} X_\nu^{(1)} = \frac{V_n^{\omega_1}}{\omega_1 - \omega_n + i\alpha},$$

(63)

where $V_n^{\omega_1}$ is the element of the vector $\xi_n^{(1)}(\omega_1)$ [Eq. (60)] in the diagonal basis

$$V_n^{\omega_1} = \sum_\nu S_{n\nu}^{-1} \xi_\nu(\omega_1).$$

(64)

Similarly, we may express $X_\mu^{(2)}(\omega_1 + i\alpha, \omega_2 + i\alpha)$ in the diagonal basis as

$$X_n^{(2)}(\omega_1 + i\alpha, \omega_2 + i\alpha) = \frac{1}{2} P(1,2) \left\{ \sum_m \frac{\langle \bar{n} | [V^{\omega_1}, \tau_m] | \mathrm{CC} \rangle V_m^{\omega_2}}{(\omega_1 + \omega_2 - \omega_n + 2i\alpha)(\omega_2 - \omega_m + i\alpha)} \right.$$

$$\left. + \frac{1}{2} \sum_{mk} \frac{\langle \bar{n} | [[H_o, \tau_m], \tau_k] | \mathrm{CC} \rangle V_m^{\omega_1} V_k^{\omega_2}}{(\omega_1 + \omega_2 - \omega_n + 2i\alpha)(\omega_1 - \omega_m + i\alpha)(\omega_2 - \omega_k + i\alpha)} \right\},$$

(65)

where

$$\langle \bar{n} | = \sum_\nu S_{n\nu}^{-1} \langle \bar{\nu} |,$$

(66)

$$\tau_m = \sum_\mu \tau_\mu S_{\mu m}.$$

(67)

B. The ζ amplitude response

The $\{\zeta_\mu\}$ parameters are expanded in orders of the perturbation:

$$\zeta_\mu = \zeta_\mu^{(0)} + \zeta_\mu^{(1)} + \zeta_\mu^{(2)} + \cdots$$

(68)

and response equations for these parameters are obtained by inserting Eq. (68) into Eq. (49). The zeroth equation,

$$\frac{d\zeta_\nu^{(0)}}{dt} = i\langle \mathrm{HF} | [H_o, \tau_\nu] | \mathrm{CC} \rangle + i \sum_\mu \zeta_\mu^{(0)} A_{\mu\nu} = 0, \quad (69)$$

is identical to the equation for the ζ parameters in Eq. (32). The first-order equation reads

$$\frac{d\zeta_\nu^{(1)}}{dt} = i\langle \Lambda | ([[H_o, \tau_\nu], T^{(1)}] + [V^t, \tau_\nu]) | \mathrm{CC} \rangle$$

$$+ i \sum_\mu \zeta_\mu^{(1)} A_{\mu\nu}$$

(70)

and the second-order equation becomes

$$\frac{d\zeta_\nu^{(2)}}{dt} = i\langle \Lambda | ([[H_o, \tau_\nu], T^{(2)}] + [[V^t, \tau_\nu], T^{(1)}]$$

$$+ \tfrac{1}{2} [[[H_o, \tau_\nu], T^{(1)}], T^{(1)}]) | \mathrm{CC} \rangle$$

$$+ i\langle \Lambda^{(1)} | ([V^t, \tau_\nu] + [[H_o, \tau_\nu], T^{(1)}]) | \mathrm{CC} \rangle$$

$$+ i \sum_\mu \zeta_\mu^{(2)} A_{\mu\nu},$$

(71)

where

$$\langle \Lambda^{(1)} | = \sum_\mu \zeta_\mu^{(1)} \langle \mu | \exp(-T^{(0)}).$$

(72)

Introducing the Fourier transform of $\zeta_\mu^{(1)}$ and $\zeta_\mu^{(2)}$,

$$\zeta_\mu^{(1)} = \int_{-\infty}^\infty d\omega_1 \ Y_\mu^{(1)}(\omega_1 + i\alpha) \exp(-i\omega_1 + \alpha)t,$$

(73)

$$\zeta_\mu^{(2)} = \int_{-\infty}^\infty d\omega_1 \int_{-\infty}^\infty d\omega_2 \ Y_\mu^{(2)}(\omega_1 + i\alpha, \omega_2 + i\alpha)$$

$$\times \exp(-i\omega_1 - i\omega_2 + 2\alpha)t,$$

(74)

into Eqs. (70) and (71) determines the expressions for $Y_\mu^{(1)}(\omega_1)$ and $Y_\mu^{(2)}(\omega_1, \omega_2)$. We obtain

$$Y_\mu^{(1)}(\omega_1 + i\alpha) = - \sum_\nu \left(\eta_\nu^{(1)}(\omega_1) \right.$$

$$\left. + \sum_\gamma F_{\nu\gamma} X_\gamma^{(1)}(\omega_1 + i\alpha) \right)$$

$$\times (\mathbf{A} + (\omega_1 + i\alpha)\mathbf{I})_{\nu\mu}^{-1}, \quad (75)$$

where

$$\eta_\nu^{(1)}(\omega_1) = \langle \Lambda | [V^{\omega_1}, \tau_\nu] | CC \rangle, \quad (76)$$

$$F_{\nu\gamma} = \langle \Lambda | [[H_o, \tau_\nu], \tau_\gamma] | CC \rangle. \quad (77)$$

In a similar way, we obtain

$$Y_\mu^{(2)}(\omega_1 + i\alpha, \omega_2 + i\alpha) = - \sum_\nu \left[\eta_\nu^{(2)}(\omega_1 + i\alpha, \omega_2 + i\alpha) + \sum_\gamma F_{\nu\gamma} X_\gamma^{(2)}(\omega_1 + i\alpha, \omega_2 + i\alpha) \right]$$

$$\times (\mathbf{A} + (\omega_1 + \omega_2 + 2i\alpha)\mathbf{I})_{\nu\mu}^{-1}, \quad (78)$$

where

$$\eta_\nu^{(2)}(\omega_1 + i\alpha, \omega_2 + i\alpha) = \frac{1}{2} P(1,2) \left[\sum_\gamma \langle \Lambda | [[V^{\omega_1}, \tau_\nu], \tau_\gamma] | CC \rangle X_\gamma^{(1)}(\omega_2 + i\alpha) + \frac{1}{2} \sum_{\gamma\rho} \langle \Lambda | [[[H_o, \tau_\nu], \tau_\gamma], \tau_\rho] | CC \rangle \right.$$

$$\times X_\gamma^{(1)}(\omega_1 + i\alpha) X_\rho^{(1)}(\omega_2 + i\alpha) + \sum_{\gamma\rho} Y_\gamma^{(1)}(\omega_1 + i\alpha) \langle \bar{\gamma} | [[H_o, \tau_\nu], \tau_\rho] | CC \rangle X_\rho^{(1)}(\omega_2 + i\alpha)$$

$$\left. + \sum_\gamma Y_\gamma^{(1)}(\omega_1 + i\alpha) \langle \bar{\gamma} | [V^{\omega_2}, \tau_\nu] | CC \rangle \right]. \quad (79)$$

The Fourier transform in Eqs. (75) and (78) may now be written in the diagonal basis; we obtain for $Y_n^{(1)}(\omega_1 + i\alpha)$,

$$Y_n^{(1)}(\omega_1 + i\alpha) = \sum_\mu Y_\mu^{(1)}(\omega_1 + i\alpha) S_{\mu n}^{-1}$$

$$= - \frac{\eta_n^{(1)}(\omega_1)}{\omega_1 + \omega_n + i\alpha}$$

$$- \sum_k \frac{F_{nk} V_k^{\omega_1}}{(\omega_1 + \omega_n + i\alpha)(\omega_1 - \omega_k + i\alpha)}, \quad (80)$$

where

$$\eta_n^{(1)}(\omega_1) = \sum_\nu \eta_\nu^{(1)}(\omega_1) S_{\nu n} \quad (81)$$

$$F_{nm} = \sum_{\nu\gamma} F_{\nu\gamma} S_{\nu n} S_{\gamma m}. \quad (82)$$

In a similar way, we get

$$Y_n^{(2)}(\omega_1 + i\alpha, \omega_2 + i\alpha) = - \frac{\eta_n^{(2)}(\omega_1 + i\alpha, \omega_2 + i\alpha)}{\omega_1 + \omega_2 + \omega_n + 2i\alpha}$$

$$- \sum_m \frac{F_{nm} X_m^{(2)}(\omega_1 + i\alpha, \omega_2 + i\alpha)}{\omega_1 + \omega_2 + \omega_n + 2i\alpha} \quad (83)$$

VI. RESPONSE FUNCTIONS

The identification of the coupled cluster response functions is obtained by analyzing the transition expectation value of the time-independent operator A,

$$A_{AV}(t) = \langle \Lambda(t) | A | CC(t) \rangle$$

$$= \langle \tilde{\Lambda}(t) | A | \widetilde{CC}(t) \rangle. \quad (84)$$

We expand this expectation value in orders of the perturbation,

$$A_{AV}(t) = \langle \Lambda | A | CC \rangle + \sum_\mu \zeta_\mu^{(1)} \langle \bar{\mu} | A | CC \rangle + \langle \Lambda | [A, T^{(1)}] | CC \rangle + \sum_\mu \zeta_\mu^{(2)} \langle \bar{\mu} | A | CC \rangle + \langle \Lambda | [A, T^{(2)}] | CC \rangle$$

$$+ \sum_\mu \zeta_\mu^{(1)} \langle \bar{\mu} | [A, T^{(1)}] | CC \rangle + \frac{1}{2} \langle \Lambda | [[A, T^{(1)}], T^{(1)}] | CC \rangle, \quad (85)$$

where we have used Eqs. (51) and (68). Comparing this expression with the expression from exact theory in Eq. (7), we determine the coupled cluster expectation value,

$$\langle O | A | O \rangle \equiv \langle \Lambda | A | CC \rangle, \quad (86)$$

the coupled cluster linear response function,

$$\int_{-\infty}^{\infty} d\omega_1 \langle\langle A;V^{\omega_1}\rangle\rangle_{\omega_1+i\alpha} \exp(-i\omega_1+\alpha)t \equiv \sum_{\mu} \zeta_{\mu}^{(1)}\langle\bar{\mu}|A|\text{CC}\rangle + \langle\Lambda|[A,T^{(1)}]|\text{CC}\rangle, \tag{87}$$

and the coupled cluster quadratic response function,

$$\frac{1}{2}\int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \langle\langle A;V^{\omega_1};V^{\omega_2}\rangle\rangle_{\omega_1+i\alpha,\omega_2+i\alpha} \exp(-i\omega_1-i\omega_2+2\alpha)t$$

$$= \sum_{\mu} \zeta_{\mu}^{(2)}\langle\bar{\mu}|A|\text{CC}\rangle + \langle\Lambda|[A,T^{(2)}]|\text{CC}\rangle + \sum_{\mu} \zeta_{\mu}^{(1)}\langle\bar{\mu}|[A,T^{(1)}]|\text{CC}\rangle + \frac{1}{2}\langle\Lambda|[[A,T^{(1)}],T^{(1)}]|\text{CC}\rangle. \tag{88}$$

Inserting the Fourier transform from Sec. V, Eqs. (56), (57), (73), and (74), the linear response function becomes

$$\langle\langle A;V^{\omega_1}\rangle\rangle_{\omega_1+i\alpha} = \sum_{\mu} Y_{\mu}^{(1)}(\omega_1+i\alpha)\langle\bar{\mu}|A|\text{CC}\rangle + \sum_{\mu} X_{\mu}^{(1)}(\omega_1+i\alpha)\langle\Lambda|[A,\tau_{\mu}]|\text{CC}\rangle. \tag{89}$$

The quadratic response function is defined to be symmetric in the integration variables, giving

$$\langle\langle A;V^{\omega_1};V^{\omega_2}\rangle\rangle_{\omega_1+i\alpha,\omega_2+i\alpha} = 2\sum_{\mu} Y_{\mu}^{(2)}(\omega_1+i\alpha,\omega_2+i\alpha)\langle\bar{\mu}|A|\text{CC}\rangle + 2\sum_{\mu} X_{\mu}^{(2)}(\omega_1+i\alpha,\omega_2+i\alpha)\langle\Lambda|[A,\tau_{\mu}]|\text{CC}\rangle$$

$$+ P(1,2)\left\{\sum_{\mu\nu} Y_{\mu}^{(1)}(\omega_1+i\alpha)\langle\bar{\mu}|[A,\tau_{\nu}]|\text{CC}\rangle X_{\nu}^{(1)}(\omega_2+i\alpha) + \frac{1}{2}\sum_{\mu\nu} X_{\mu}^{(1)}(\omega_1+i\alpha)\right.$$

$$\left.\times F_{\mu\nu}^A X_{\nu}^{(1)}(\omega_2+i\alpha)\right\}, \tag{90}$$

where we have introduced the symmetric matrix

$$F_{\mu\nu}^A = \langle\Lambda|[[A,\tau_{\mu}],\tau_{\nu}]|\text{CC}\rangle. \tag{91}$$

The linear response function in Eq. (89) becomes in the diagonal representation

$$\langle\langle A;V^{\omega_1}\rangle\rangle_{\omega_1+i\alpha} = \sum_{n} Y_n^{(1)}(\omega_1+i\alpha)\langle\bar{n}|A|\text{CC}\rangle + \sum_{n} X_n^{(1)}(\omega_1+i\alpha)\langle\Lambda|[A,\tau_n]|\text{CC}\rangle. \tag{92}$$

In the diagonal representation, the quadratic response function reads

$$\langle\langle A;V^{\omega_1};V^{\omega_2}\rangle\rangle_{\omega_1+i\alpha,\omega_2+i\alpha} = 2\sum_{n} Y_n^{(2)}(\omega_1+i\alpha,\omega_2+i\alpha)\langle\bar{n}|A|\text{CC}\rangle$$

$$+ 2\sum_{n} X_n^{(2)}(\omega_1+i\alpha,\omega_2+i\alpha)\langle\Lambda|[A,\tau_n]|\text{CC}\rangle + \sum_{nm} X_n^{(1)}(\omega_1+i\alpha)F_{nm}^A X_m^{(1)}(\omega_2+i\alpha)$$

$$+ P(1,2)\sum_{nm} Y_n^{(1)}(\omega_1+i\alpha)\langle\bar{n}|[A,\tau_m]|\text{CC}\rangle X_m^{(1)}(\omega_2+i\alpha). \tag{93}$$

In the following two sections, we carry out a pole and residue analysis of the linear and quadratic response functions in order to determine the expressions for the molecular properties described in Sec. II.

A. Linear response function

1. Evaluation of the linear response function

In order to determine the coupled cluster linear response function (CCLR) $\langle\langle A;B\rangle\rangle_{\omega_1}$, we need to calculate the first-order response of the amplitudes. This is conveniently done in the elementary basis where the linear response function may be written as

$$\langle\langle A;B\rangle\rangle_{\omega_1} = \sum_{\mu} Y_{\mu}^B(\omega_1)\langle\mu|A|\text{CC}\rangle + \sum_{\mu} \langle\Lambda|[A,\tau_{\mu}]|\text{CC}\rangle X_{\mu}^B(\omega_1)$$

$$= \sum_{\mu} \langle\Lambda|[A,\tau_{\mu}]|\text{CC}\rangle X_{\mu}^B(\omega_1) + \sum_{\mu} \left\{\langle\Lambda|[B,\tau_{\mu}]|\text{CC}\rangle + \sum_{\gamma} F_{\mu\gamma}X_{\gamma}^B(\omega_1)\right\} X_{\mu}^A(-\omega_1), \tag{94}$$

where

$$X_\mu^B(\omega_1) = \sum_\nu (-\mathbf{A} + \omega_1 \mathbf{I})_{\mu\nu}^{-1} B_\nu \qquad (95)$$

and

$$B_\nu = \langle \bar\nu | B | CC \rangle. \qquad (96)$$

The evaluation of the linear response function at frequency ω_1 thus requires that we solve two sets of linear equations to obtain $X_\mu^A(-\omega_1)$ and $X_\mu^B(\omega_1)$. We note that for real operators and truncated excitation operator manifolds,

$$\langle\langle A;B \rangle\rangle_{\omega_1} \neq \langle\langle B;A \rangle\rangle_{\omega_1}. \qquad (97)$$

For exact and variational wave functions the inequality is replaced by an equality. Equation (97) is a result of the projection used to determine the cluster amplitudes.

2. Excitation energies

The simple poles of the coupled cluster linear response function occur at the eigenvalues of the nonsymmetric coupled cluster Jacobian

$$(\mathbf{A} - \omega_1 \mathbf{I})\mathbf{X} = 0. \qquad (98)$$

In the subsequent paper, we have calculated the excitation energies using Eq. (98) for a CCSD reference wave function. The excitation energies are size intensive, i.e., the excitation energies of noninteracting subsystems are the excitation energies of the combined system.

3. Transition matrix elements

The transition matrix elements may be identified from the residue in Eqs. (10) and (11) of the linear response function. Using

$$\lim_{\omega_1 \to \omega_k} (\omega_1 - \omega_k)X_n^A(\omega_1) = \delta_{nk}A_k, \qquad (99)$$

$$\lim_{\omega_1 \to -\omega_k} (\omega_1 + \omega_k)X_n^A(\omega_1) = 0, \qquad (100)$$

we write the residue of Eq. (92) as

$$\langle O|A|k \rangle \langle k|B|O \rangle$$

$$= \lim_{\omega_1 \to \omega_k} (\omega_1 - \omega_k)\langle\langle A;B \rangle\rangle_{\omega_1}$$

$$= \left[\langle \Lambda | [A,\tau_n] | CC \rangle - \sum_n \langle \bar{n} | A | CC \rangle \right.$$

$$\left. \times (\omega_n + \omega_k)^{-1}F_{nk} \right] B_k. \qquad (101)$$

The transition matrix elements may thus be identified as

$$\Gamma_{o\to k}^A = \langle O|A|k \rangle$$

$$= \langle \Lambda | [A,\tau_k] | CC \rangle$$

$$- \sum_n A_n(\omega_n + \omega_k)^{-1}F_{nk} \qquad (102)$$

and

$$\Gamma_{k\to o}^B = \langle k|B|O \rangle = B_k, \qquad (103)$$

except for an overall sign. The transition matrix element $\Gamma_{o\to k}^A$ differs from $\Gamma_{k\to o}^A$ for a real operator A. This is so because a right or left projection of the time-dependent Schrödinger equation has been carried out in order to determine the response parameters. The residue in Eq. (11),

$$\lim_{\omega_1 \to -\omega_k} (\omega_1 + \omega_k)\langle\langle A;B \rangle\rangle_{\omega_1}$$

$$= -\left[\langle \Lambda | [B,\tau_n] | CC \rangle - \sum_n \langle \bar{n} | B | CC \rangle \right.$$

$$\left. \times (\omega_n + \omega_k)^{-1}F_{nk} \right] A_k, \qquad (104)$$

leads to the same identification of the transition matrix elements as the residue in Eq. (10). When evaluating the transition matrix element, the last term in Eq. (102) is calculated in the elementary basis

$$\sum_n A_n(\omega_n + \omega_k)^{-1}F_{nk} = -\sum_\nu X_\nu^A(-\omega_k)F_{\nu k}. \qquad (105)$$

The evaluation of

$$\langle O|A|k \rangle \langle k|B|O \rangle$$

$$= \left[\langle \Lambda | [A,\tau_k] | CC \rangle + \sum_n X_\nu^A(-\omega_k)F_{\nu k} \right] B_k \qquad (106)$$

thus requires that we solve one set of linear equations determining the response vector $X_\nu^A(-\omega_k)$ and determine the eigenvector representing the excitation operator τ_k.

B. Quadratic response function

1. Evaluation of the quadratic response function

The coupled cluster quadratic response function (CCQR) in the diagonal basis is obtained using Eqs. (93), (78), (79), and (65):

$\langle\langle A;B:C\rangle\rangle_{\omega_1,\omega_2}$

$$= \sum_{nm} Y_n^B(\omega_1)\langle\bar{n}\,|\,[A,\tau_m]\,|\,CC\rangle X_m^C(\omega_2) + \sum_{nm} Y_n^C(\omega_2)\langle\bar{n}\,|\,[A,\tau_m]\,|\,CC\rangle X_m^B(\omega_1)$$

$$+ \sum_{nm} Y_n^A(-\omega_1-\omega_2)\langle\bar{n}\,|\,[B,\tau_m]\,|\,CC\rangle X_m^C(\omega_2) + \sum_{nm} Y_n^A(-\omega_1-\omega_2)\langle\bar{n}\,|\,[C,\tau_m]\,|\,CC\rangle X_m^B(\omega_1)$$

$$+ \sum_{nmk} Y_n^A(-\omega_1-\omega_2)\langle\bar{n}\,|\,[[H_o,\tau_m],\tau_k]\,|\,CC\rangle X_m^B(\omega_1)X_k^C(\omega_2)$$

$$+ \sum_{nm} X_n^B(\omega_1)F_{nm}^A X_m^C(\omega_2) + 2\sum_n \eta_n^{BC}(\omega_1,\omega2)X_n^A(-\omega_1-\omega_2), \tag{107}$$

where

$$\eta_n^{BC}(\omega_1,\omega_2) = \frac{1}{2}\Bigg[\sum_k \langle\Lambda\,|\,[[B,\tau_n],\tau_k]\,|\,CC\rangle X_k^C(\omega_2) + \sum_k \langle\Lambda\,|\,[[C,\tau_n],\tau_k]\,|\,CC\rangle X_k^B(\omega_1)$$

$$+ \sum_{mk} Y_m^B(\omega_1)\langle\bar{m}\,|\,[[H_o,\tau_n],\tau_k]\,|\,CC\rangle X_k^C(\omega_2) + \sum_{mk} Y_m^C(\omega_2)\langle\bar{m}\,|\,[[H_o,\tau_n],\tau_k]\,|\,CC\rangle X_k^B(\omega_1)$$

$$+ \sum_{mk}\langle\Lambda\,|\,[[[H_o,\tau_n],\tau_m],\tau_k]\,|\,CC\rangle\times X_m^B(\omega_1)X_k^C(\omega_2) + \sum_m Y_m^B(\omega_1)\langle\bar{m}\,|\,[C,\tau_n]\,|\,CC\rangle + \sum_m Y_m^C(\omega_2)$$

$$\times\langle\bar{m}\,|\,[B,\tau_n]\,|\,CC\rangle\Bigg]. \tag{108}$$

In deriving Eqs. (107) and (108), we have eliminated X^{BC} and Y^{BC}, which depend on two simultaneous perturbations. The evaluation of the quadratic response function is performed in the elementary basis and requires the solution of six first-order response amplitudes: $X_\mu^A(-\omega_1-\omega_2)$, $X_\mu^B(\omega_1)$, $X_\mu^C(\omega_2)$, $Y_\mu^A(-\omega_1-\omega_2)$, $Y_\mu^B(\omega_1)$, and $Y_\mu^C(\omega_2)$.

2. Second-order transition matrix element

In the previous subsection, we showed that the transition matrix element $\Gamma_{o\to k}^A$ differs from $\Gamma_{k\to o}^A$ due to right and left projection used to determine the response parameters. The second-order transition matrix element $\Gamma_{m\to o}^{AB}(\omega_1)$ differs from $\Gamma_{o\to m}^{AB}(\omega_1)$ for the same reason. Equation (12) may be used to determine $\Gamma_{o\to m}^{AB}(\omega_1)$ and Eq. (13) to determine $\Gamma_{m\to o}^{AB}(\omega_1)$. We initially identify $\Gamma_{m\to o}^{AB}(\omega_1)$ from the residue in Eq. (13):

$$\Gamma_{o\to m}^C\Gamma_{m\to o}^{AB}(\omega_1) = -\lim_{\omega_2\to-\omega_m}(\omega_2+\omega_m)\langle\langle A;B;C\rangle\rangle_{\omega_1,\omega_2}$$

$$= \Bigg\{\langle\Lambda\,|\,[C,\tau_m]\,|\,CC\rangle - \sum_k C_k(\omega_m+\omega_k)^{-1}F_{km}\Bigg\}\times\Bigg(\sum_n\Bigg\{\langle\bar{m}\,|\,[A,\tau_k]\,|\,CC\rangle$$

$$+ \sum_k\langle\bar{m}\,|\,[[H_o,\tau_k],\tau_n]\,|\,CC\rangle X_k^A(\omega_m-\omega_1)\Bigg\}X_n^B(\omega_1) + \sum_n\langle\bar{m}\,|\,[B,\tau_n]\,|\,CC\rangle X_n^A(\omega_m-\omega_1)\Bigg). \tag{109}$$

In deriving Eq. (109), we have used the following residue of the first-order response amplitudes:

$$\lim_{\omega_1\to-\omega_k}(\omega_1+\omega_k)Y_n^A(\omega_1) = -\delta_{nk}\Bigg[\langle\Lambda\,|\,[A,\tau_\mu]\,|\,CC\rangle - \sum_m A_m(\omega_k+\omega_m)^{-1}F_{mk}\Bigg]. \tag{110}$$

The second-order transition matrix element $\Gamma_{m\to o}^{AB}(\omega_1)$ is thus seen to be

$$\Gamma_{m\to o}^{AB}(\omega_1) = \sum_n\langle\bar{m}\,|\,[B,\tau_n]\,|\,CC\rangle X_n^A(\omega_m-\omega_1) + \sum_n \Delta_{mn}^A(\omega_m-\omega_1)X_n^B(\omega_1), \tag{111}$$

where we have introduced

$$\Delta_{nm}^A(\omega_1) = \langle\bar{n}\,|\,[A,\tau_m]\,|\,CC\rangle + \sum_k X_k^A(\omega_1)\langle\bar{n}\,|\,[[H_o,\tau_k],\tau_m]\,|\,CC\rangle. \tag{112}$$

The second-order transition matrix element $\Gamma_{o\to m}^{AB}(\omega_1)$ may be determined from Eq. (13):

$$\Gamma_{o \to m}^{AB}(\omega_1) = \sum_n X_n^B(-\omega_1)F_{nm}^A + \sum_n X_n^A(\omega_1 - \omega_m)F_{nm}^B + \sum_n Y_n^B(-\omega_1)\Delta_{nm}^A(\omega_1 - \omega_m) + \sum_n Y_n^B(\omega_1 - \omega_m)$$

$$\times \Delta_{nm}^B(-\omega_1) + \sum_n X_n^A(\omega_1 - \omega_m) \sum_k F_{km}(\omega_m + \omega_k)^{-1}\Delta_{kn}^B(-\omega_1) - \sum_n X_n^B(-\omega_1)\left\{ \sum_k F_{km}(\omega_m \right.$$

$$\left. + \omega_k)^{-1}\langle \overline{k}\,|\,[A,\tau_k]\,|CC\rangle - p\sum_k \langle \Lambda\,|\,[[[H,\tau_k],\tau_n],\tau_m]\,|CC\rangle X_k^A(\omega_1 - \omega_m)\right\}. \tag{113}$$

In deriving Eq. (113), we have used the residue

$$\lim_{\omega_1 \to \omega_k}(\omega_1 - \omega_k)Y_n^A(\omega_1) = -A_n(\omega_n + \omega_k)^{-1}F_{nk}. \tag{114}$$

3. Transition matrix element between excited states

The transition matrix element between excited states may be identified taking the double residue in Eq. (14) of the CCQR:

$$\lim_{\omega_1 \to -\omega_k}(\omega_1 + \omega_k)\left[\lim_{\omega_2 \to \omega_m}(\omega_2 - \omega_m)\langle\langle A;V^{\omega_1};V^{\omega_2}\rangle\rangle_{\omega_1,\omega_2}\right]$$

$$= -\left[\langle \Lambda\,|\,[B,\tau_k]\,|CC\rangle - \sum_n F_{kn}(\omega_k + \omega_n)^{-1}B_n\right]$$

$$\times \left[\langle \overline{k}\,|\,[A,\tau_m]\,|CC\rangle + \sum_n X_n^A(\omega_k - \omega_m)\right.$$

$$\left. \times \langle \overline{k}\,|\,[[H_o,\tau_n],\tau_m]\,|CC\rangle\right] C_m. \tag{115}$$

Comparing with the exact result in Eq. (14) gives the coupled cluster transition matrix element between excited state k and m:

$$\Gamma_{k \to m}^A = \langle \overline{k}\,|\,[A,\tau_m]\,|CC\rangle + \sum_n X_n^A(\omega_k - \omega_m)$$

$$\times \langle \overline{k}\,|\,[[H_o,\tau_n],\tau_m]\,|CC\rangle + \delta_{km}\langle \Lambda\,|A|CC\rangle$$

$$= \Delta_{km}^A(\omega_k - \omega_m) + \delta_{km}\langle \Lambda\,|A|CC\rangle. \tag{116}$$

For $k = m$, Eq. (116) gives the dipole moment for the excited state.

VII. CONCLUSIONS

The linear and quadratic response functions have been determined for a molecular system described by a coupled cluster reference state. From the linear response function, computationally tractable expressions have been derived for excitation energies, transition matrix elements, and second-order frequency-dependent properties. From the quadratic response function, expressions are determined for second-order transition matrix elements, transition matrix elements between excited states, and third-order molecular properties. The derivations are based on a coupled cluster generalization of the Hellmann–Feynman theorem, where the average value is replaced by a transition expectation value with respect to the coupled cluster state and a dual-type state. The first-order response of the coupled

cluster state and of the dual type state appear in the derivation of the linear response function. In the derivation of the quadratic response function, the second-order response appears. Previous derivations of the linear response function required both the first- and second-order responses of the coupled cluster state. The second-order response was eliminated afterwards using difficult algebra.[7] Generalization of the previous derivation to determine the quadratic response function would be rather tedious, as it would require the third-order response of the coupled cluster state to be initially evaluated and eliminated afterwards.

In the limit where no truncation is carried out in the coupled cluster operator, the derivation of this paper describes an alternative derivation of the response functions for the exact case. For truncated manifolds and with time-independent perturbations, the response functions become identical to those which, for example, are obtained using the Lagrangian technique of Ref. 4.

In the subsequent paper, excitation energies have been determined from the linear response eigenvalue equation for a coupled cluster single and double reference state. The results are very encouraging and indicate that it may be very tractable to use response functions to calculate other molecular properties. This is very important, as it would extend significantly the application range of the coupled cluster model.

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