Multiphoton transition moments and absorption cross sections in coupled cluster response theory employing variational transition moment functionals

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(Received 12 November 1997; accepted 19 February 1998)

Based on an analysis of the first residues of coupled cluster response functions we devise variational functionals from which the transition moments for n-photon excitations can be calculated as nth derivatives. Combining these functionals with variational perturbation theory, we obtain a new approach for the derivation of multiphoton transition moments which allows us to utilize the full strengths of variational perturbation theory without the roundabout way via residues of response functions. Coupled cluster multiphoton transition moments derived by this approach are formally equivalent to the one identified from the first residues of the ground state response functions. The introduction of the variational functionals makes the mathematical structure of the transition moments more transparent and provides an interpretation of intermediates in terms of responses of excited state vectors and Lagrangian multipliers. $2n+1$ and $2n+2$ rules are formulated for the transition moments and build the basis for a straightforward derivation of a computational efficient formulation. The strength of the new approach is demonstrated by the derivation of three- and four-photon transition moments. © *1998 American Institute of Physics.* [S0021-9606(98)02520-3]

I. INTRODUCTION

The advances of modern laser technology have in the last decades opened the possibility for exploring various types of multiphoton processes experimentally as high harmonic generation,[1–3] multiphoton excitation (MPE),[4] multiphoton ionization (MPI),[5,6] and above threshold ionization (ATI).[7] Doppler free two-photon absorption (DFTPA)[8] has succesfully been used to study molecular structures and dynamics.[9]

The theoretical description of multiphoton processes is a challenging task because it involves high-order responses of the atoms or molecules to the time-dependent field of the laser light. One of the key properties in the understanding of the various nonlinear optical processes are the multiphoton transition moments and absorption cross sections.[10–12] High-order multiphoton transition moments have been calculated for the hydrogen atom by Karule[13] using a Sturmian expansion method and by Gao and Starace[14] using Slater orbitals. For many-electron systems calculations of high-order multiphoton transition moments have only been carried out at rudimentary levels of theory.[15,16] Formal expressions for two-photon and three-photon transition moments using multiconfigurational self-consistent field (MCSCF) response theory have been derived by Olsen and Jørgensen[17] and an implementation of the two-photon transition moments has been reported by Hettema *et al.*[18] An implementation of MCSCF response theory for the three-photon transition moments has been reported very recently by Jonsson *et al.*[19] The formal expressions for two-photon transition moments for a coupled cluster wave function have been derived by Koch and Jørgensen,[20] but an implementation was not reported.

For exact wave functions multiphoton transition moments can be defined in several equivalent ways: For example, in terms of explicit sum-over-states expressions[10,11] or by projection of the right hand sides of the ground state response equations onto the excited state wave functions.[16] Alternatively they may be identified from the multiphoton absorption cross sections which can be determined as residues of the even order response functions.[17] For approximate wave functions the equivalence between the different definitions may or may not be valid, depending on the introduced approximations. The standard approach for *ab initio* methods has been to identify the multiphoton transition moments from the residues of the response functions.

Recent advances in response theory,[21–26] initiated by the introduction of quasienergy derivatives,[22–28] have now made it possible to derive high-order response functions for non-variational *ab initio* methods in a mathematical simple and transparent way as derivatives of a variational quasienergy Lagrangian. The derivation of computational efficient expressions, that employ the $2n+1$ and $2n+2$ rules of variational perturbation theory,[26,29,30] which some years ago was a difficult task has for that reason become a straightforward exercise. Implementations of coupled cluster response functions formulated as derivatives of a quasienergy Lagrangian have now been presented for the linear, quadratic,[31] cubic,[32] quartic and pentic response functions.[33]

In the present paper we adopt the formulation of coupled cluster response functions as quasienergy derivatives to analyze the general structure of their first residues and to derive expressions for multiphoton transition moments. The identification of the transition moments from the residues of response functions leads in general to computational inefficient expressions which require the solution of unneccessary high-order response equations. The solution of the latter equations

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can be circumvented by *a posteriori* reformulation of the expressions identified from the residues using the so-called interchange technique.[34] However, in higher order this becomes soon a tedious approach. The appearance of the unneccessary high-order response intermediates in the expressions for the transition moments is a consequence of the route taken in the derivation. The $2n+1$ and $2n+2$ rules for the quasienergy Lagrangian provide information about the maximum order of response intermediates needed to calculate the response functions, but this information cannot be straightforwardly transferred to the residues and the transition moments. In Sec. V we show that this shortcoming can be resolved by introducing variational transition moment functionals from which n-photon transition moments can be obtained as nth derivatives. We devise such transition moment functionals for coupled cluster response theory. The transition moments obtained from these functionals are formally equivalent to those identified from the residues of the response functions, but the $2n+1$ and $2n+2$ rules can be applied directly to the expressions for the n-photon transition moments. The efficiency of a variational formulation for the derivation of computational tractable expressions is exemplified by the three- and four-photon transition moments.

II. SUMMARY OF COUPLED CLUSTER GROUND STATE RESPONSE THEORY

We investigate in the following the response of a system described by the Hamiltonian $\hat{H}^{(0)}$ to a time-dependent one-electron perturbation $\hat{V}(t,\boldsymbol{\epsilon})$

$$\hat{H}(t,\boldsymbol{\epsilon})=\hat{H}^{(0)}+\hat{V}(t,\boldsymbol{\epsilon}). \tag{1}$$

It is assumed that the perturbation operator $\hat{V}(t,\boldsymbol{\epsilon})$ can be expanded in a sum over Fourier components as

$$\hat{V}(t,\boldsymbol{\epsilon})=\sum_j \hat{H}^{X_j}\ \epsilon_j(\omega_j)\ e^{-i\omega_j t}, \tag{2}$$

where $\hat{H}^{X_j}$ are Hermitian time-independent one-electron operators and $\epsilon_j(\omega_j)$ the associated field strengths for the frequencies ω_j. We use the letter $\boldsymbol{\epsilon}$ without index as shorthand notation for the set $\{\epsilon_j\}$ of all field strengths. To obtain a Hermitian perturbation operator, we require that the sum in Eq. (2) includes for each term $\hat{H}^{X_j}\epsilon_j(\omega_j)\exp(-i\omega_j t)$ also its complex conjugate $\hat{H}^{X_j}\epsilon_j(-\omega_j)\exp(i\omega_j t)$ with $\epsilon_j(-\omega_j)=\epsilon_j(\omega_j)^*$. For the coupled cluster wave function we use a parametrization, where the oscillating phase factor caused by the so-called level-shift or time-dependent quasienergy $\mathscr{W}(t,\boldsymbol{\epsilon})$ is explicitly isolated:[26,27,35]

$$|\mathrm{CC}(t,\boldsymbol{\epsilon})\rangle=\exp\left(-i\int_{t_0}^{t}\mathscr{W}(t',\boldsymbol{\epsilon})\ dt'\right)\exp(\hat{T}(t,\boldsymbol{\epsilon}))|\mathrm{HF}\rangle, \tag{3}$$

$\hat{T}(t,\boldsymbol{\epsilon})$ is the field- and time-dependent cluster operator $\hat{T}(t,\boldsymbol{\epsilon})=\Sigma_\mu t_\mu(t,\boldsymbol{\epsilon})\hat{\tau}_\mu$. The cluster amplitudes $t_\mu(t,\boldsymbol{\epsilon})$ are expanded in the Fourier components of the applied perturbations and in orders of the perturbation strengths as:

$$\begin{aligned}t_\mu(t,\boldsymbol{\epsilon})=t_\mu^{(0)}&+\sum_j t_\mu^{X_j}(\omega_j)\ \epsilon_j(\omega_j)\ e^{-i\omega_j t}\\&+\frac{1}{2}\sum_j\sum_k t_\mu^{X_jX_k}(\omega_j,\omega_k)\\&\times\epsilon_j(\omega_j)\ \epsilon_k(\omega_k)\ e^{-i(\omega_j+\omega_k)t}+\cdots\\&+\frac{1}{n!}\sum_{j_1}\cdots\sum_{j_n} t_\mu^{X_{j_1}\cdots X_{j_n}}(\omega_{j_1},\cdots,\omega_{j_n})\\&\times\prod_{m=1}^{n}\epsilon_{j_m}(\omega_{j_m})e^{-i\omega_{j_m}t}+\cdots.\end{aligned} \tag{4}$$

Projecting the time-dependent Schrödinger equation

$$\left(\hat{H}(t,\boldsymbol{\epsilon})-i\frac{d}{dt}\right)|\mathrm{CC}(t,\boldsymbol{\epsilon})\rangle=0, \tag{5}$$

onto the Hartree-Fock reference and onto the bra states $\langle\mathrm{HF}|\hat{\tau}_\mu^\dagger\exp(-\hat{T}(t,\boldsymbol{\epsilon}))$ determines the quasienergy

$$\begin{aligned}\mathscr{W}(t,\boldsymbol{\epsilon})&=\left\langle\mathrm{HF}\left|\left(\hat{H}(t,\boldsymbol{\epsilon})-i\frac{d}{dt}\right)\exp(\hat{T}(t,\boldsymbol{\epsilon}))\right|\mathrm{HF}\right\rangle\\&=\langle\mathrm{HF}|\hat{H}(t,\boldsymbol{\epsilon})\exp(\hat{T}(t,\boldsymbol{\epsilon}))|\mathrm{HF}\rangle,\end{aligned} \tag{6}$$

and the time-dependent coupled cluster equations

$$\begin{aligned}&\langle\mathrm{HF}|\hat{\tau}_\mu^\dagger\exp(-\hat{T}(t,\boldsymbol{\epsilon}))\hat{H}(t,\boldsymbol{\epsilon})\exp(\hat{T}(t,\boldsymbol{\epsilon}))|\mathrm{HF}\rangle\\&\quad-i\frac{d}{dt}t_\mu(t,\boldsymbol{\epsilon})=0.\end{aligned} \tag{7}$$

The Hartree-Fock reference of the unperturbed molecule is used throughout. Orbital relaxation is therefore not treated explicitly, but only approximately through the single excitation manifold of the cluster operator. By using nonrelaxed orbitals we circumvent a two step approach which introduces artifacts into the response functions such that, for example, the pole structure is not compatible with the one of the exact response function. Equation (7) may be written in the shorthand form

$$e_\mu(t,\boldsymbol{\epsilon})-i\frac{d}{dt}t_\mu(t,\boldsymbol{\epsilon})=0, \tag{8}$$

where $e_\mu(t,\boldsymbol{\epsilon})$ does not contain derivatives with respect to time. The quasienergy and the time-dependent equations for the coupled cluster methods CCS, CCSD and CCSDT are obtained by truncating the cluster operator after the single, double or triple excitation level, respectively. The CC2 and CC3 methods are defined by further approximations to $e_\mu(t,\boldsymbol{\epsilon})$.[24,25] A variational formulation of coupled cluster response theory is obtained by combining the quasienergy (6) and the time-dependent coupled cluster equations (8) to a quasienergy Lagrangian:

$$L(t,\boldsymbol{\epsilon})=\mathscr{W}(t,\boldsymbol{\epsilon})+\sum_\mu \bar{t}_\mu\left(e_\mu(t,\boldsymbol{\epsilon})-i\frac{d}{dt}t_\mu\right), \tag{9}$$

where $\bar{t}_\mu$ are the Lagrangian multipliers. The time-average of the quasienergy Lagrangian,

$$\{L(t,\epsilon)\}_T = \lim_{t_0\to\infty} \frac{1}{2t_0}\int_{-t_0}^{+t_0} L(t,\epsilon)\, dt, \tag{10}$$

may now be introduced and required to be stationary with respect to variations of the cluster amplitudes and the Lagrangian multipliers.[26,27]

$$\delta\{L(t,\epsilon)\}_T = 0. \tag{11}$$

If the perturbation and Fourier expansion of the cluster amplitudes (4) and an analogous expansion of the Lagrangian multipliers is inserted into Eq. (11), this becomes a variational condition for the individual Fourier components of the amplitudes and the multipliers for each order of $\{L(t,\epsilon)\}_T$ in the perturbation strengths:

$$\frac{d\{L\}_T^{X_1\cdots X_{n+m}}(\omega_1,\cdots,\omega_{n+m})}{d\,\overline{t}_\mu^{X_{n+1}\cdots X_{n+m}}(\omega_{n+1},\cdots,\omega_{n+m})} = 0, \tag{12}$$

$$\frac{d\{L\}_T^{X_1\cdots X_{n+m}}(\omega_1,\cdots,\omega_{n+m})}{dt_\mu^{X_{n+1}\cdots X_{n+m}}(\omega_{n+1},\cdots,\omega_{n+m})} = 0, \tag{13}$$

with

$$\{L\}_T^{X_1\cdots X_{n+m}}(\omega_1,\cdots,\omega_{n+m}) = \left(\frac{d^{n+m}\{L(t,\epsilon)\}_T}{d\epsilon_1(\omega_1)\cdots d\epsilon_{n+m}(\omega_{n+m})}\right)_{\epsilon=0}. \tag{14}$$

In order that $\{L\}_T^{X_1\cdots X_{n+m}}(\omega_1,\cdots,\omega_{n+m})$ is nonvanishing, the Fourier components of the perturbations must compensate each other, i.e., the sum $\omega_1+\cdots+\omega_{n+m}$ must be zero. Equations (12) and (13) determine the cluster amplitudes $t_\mu^{X_1\cdots X_n}(\omega_1,\cdots,\omega_n)$ and the Lagrangian multipliers $\overline{t}_\mu^{X_1\cdots X_n}(\omega_1,\cdots,\omega_n)$. The response equations (12) and (13) may for $n>0$ be written in the form:

$$\frac{d\{L\}_T^{X_1\cdots X_{n+m}}(\omega_1,\cdots,\omega_{n+m})}{d\,\overline{t}^{X_{n+1}\cdots X_{n+m}}(\omega_{n+1},\cdots,\omega_{n+m})} = \xi^{X_1\cdots X_n}(\omega_1,\cdots,\omega_n) + [\boldsymbol{A} - (\omega_1+\cdots+\omega_n)\mathbf{1}] \times t^{X_1\cdots X_n}(\omega_1,\cdots,\omega_n) = 0, \tag{15}$$

and

$$\frac{d\{L\}_T^{X_1\cdots X_{n+m}}(\omega_1,\cdots,\omega_{n+m})}{dt^{X_{n+1}\cdots X_{n+m}}(\omega_{n+1},\cdots,\omega_{n+m})} = \overline{\xi}^{X_1\cdots X_n}(\omega_1,\cdots,\omega_n) + \overline{t}^{X_1\cdots X_n}(\omega_1,\cdots,\omega_n) \times [\boldsymbol{A} + (\omega_1+\cdots+\omega_n)\mathbf{1}] = 0, \tag{16}$$

where $\xi^{X_1\cdots X_n}$ and $\overline{\xi}^{X_1\cdots X_n}$ are the right hand side vectors for, respectively, the amplitude and Lagrangian multiplier response equations of order n. The zeroth-order equations for the cluster amplitudes are the usual coupled cluster equations, $e^{(0)}=0$, and the zeroth-order equations for the Lagrangian multipliers are

$$\eta^{(0)} + \overline{t}^{(0)}\,\boldsymbol{A} = 0. \tag{17}$$

The matrix $\boldsymbol{A}$ is the coupled cluster Jacobian for the unperturbed molecule, defined as

$$\boldsymbol{A}_{\mu\nu} = \left(\frac{\partial^2 L}{\partial\overline{t}_\mu \partial t_\nu}\right)_0 = \left(\frac{\partial e_\mu}{\partial t_\nu}\right)_0, \tag{18}$$

where the index 0 indicates that the derivative is taken for zero perturbation strengths. The vector $\eta^{(0)}$ is defined as derivative of the quasienergy with respect to the cluster amplitudes:

$$\eta_\nu^{(0)} = \left(\frac{\partial \mathscr{W}}{\partial t_\nu}\right)_0. \tag{19}$$

For the first-order response equations the right hand side vectors are given by:

$$\xi^A(\omega_A) = \xi^A, \tag{20}$$

$$\overline{\xi}^A(\omega_A) = \eta^A + \boldsymbol{F}\, t^A(\omega_A), \tag{21}$$

with ξ^A, η^A and $\boldsymbol{F}$ defined as second partial derivatives of the Lagrangian:

$$\xi_\mu^A = \left(\frac{\partial^2 L}{\partial\epsilon_A(\omega_A)\partial\overline{t}_\mu}\right)_0, \tag{22}$$

$$\eta_\mu^A = \left(\frac{\partial^2 L}{\partial\epsilon_A(\omega_A)\partial t_\mu}\right)_0, \tag{23}$$

$$\boldsymbol{F}_{\mu\nu} = \left(\frac{\partial^2 L}{\partial t_\mu \partial t_\nu}\right)_0. \tag{24}$$

Open-ended expressions for the right hand side vectors for higher-order response equations are given in Appendix A. If the response equations have been solved, the response functions are obtained as derivatives of the *real part* of the time-averaged quasienergy:

$$\langle\langle X_1; X_2,\cdots,X_n\rangle\rangle_{\omega_2,\cdots,\omega_n} = \left(\frac{d^n\{(1/2)\,L(t,\epsilon) + (1/2)\,L(t,\epsilon)^*\}_T}{d\epsilon_1(\omega_1)\cdots d\epsilon_n(\omega_n)}\right)_0 = \frac{1}{2}\hat{C}^{\pm\omega}\,\{L\}_T^{X_1,\cdots,X_n}(\omega_1,\cdots,\omega_n), \tag{25}$$

with the frequency $\omega_1 = -\omega_2\cdots-\omega_n$ assigned to X_1. The action of the symmetrizer $\hat{C}^{\pm\omega}$ is defined as:

$$\hat{C}^{\pm\omega}\, f(\omega_1,\cdots,\omega_n) = f(\omega_1,\cdots,\omega_n) + f(-\omega_1,\cdots,-\omega_n)^*. \tag{26}$$

The coupled cluster response functions obtained from Eq. (25) are, as the exact response functions, symmetric with respect to permutation of the operators X_i together with their associated frequencies and with respect to inversion of the signs of all frequencies and simultaneous complex conjugation. Equation (25) differs from the result of the earliest derivations,[36,37,20] as we take the derivative of only the real part of the quasienergy Lagrangian and not of the complete quasienergy. For truncated or approximated coupled cluster models the time-dependent quasienergy and the quasienergy

Lagrangian are in general complex. The imaginary part is an artefact of the projection principle Eq. (6), used to determine the coupled cluster quasienergy and vanishes in the limit of a complete cluster expansion, i.e., in the full CI limit. We note that this problem is not special for time- or frequency-dependent perturbation theory: the standard definition of the coupled cluster energy becomes also complex in the presence of static magnetic fields.

According to the $2n+1$ rule for the amplitudes and the $2n+2$ rule for the Lagrangian multipliers one can calculate from the first-order response amplitudes and multipliers the linear and the quadratic response functions:

$$\langle\langle A;B\rangle\rangle_{\omega_B}=\frac{1}{2}\hat{C}^{\pm\omega}\hat{P}^{AB}\left\{\frac{1}{2}\boldsymbol{F}\ t^A(\omega_A)\ t^B(\omega_B)+\boldsymbol{\eta}^A\ t^B(\omega_B)\right\}, \tag{27}$$

$$\begin{aligned}\langle\langle A;B,C\rangle\rangle_{\omega_B,\omega_C}&=\frac{1}{2}\hat{C}^{\pm\omega}\hat{P}^{ABC}\left\{\frac{1}{6}\boldsymbol{G}t^A(\omega_A)t^B(\omega_B)t^C(\omega_C)\right.\\&+\frac{1}{2}\boldsymbol{F}^A t^B(\omega_B)t^C(\omega_C)+\frac{1}{2}\overline{t^A}(\omega_A)\boldsymbol{B}t^B(\omega_B)t^C(\omega_C)\\&\left.+\overline{t^A}(\omega_A)\boldsymbol{A}^B\ t^C(\omega_C)\right\},\end{aligned} \tag{28}$$

with $\omega_A=-\omega_B$ for the linear and $\omega_A=-(\omega_B+\omega_C)$ for the quadratic response function. The operators $\hat{P}^{AB\cdots}$ symmetrize with respect to the indices A, B, etc. of the perturbation operators and accompanied frequencies. The matrices $\boldsymbol{G}$, $\boldsymbol{B}$, $\boldsymbol{F}^A$ and $\boldsymbol{A}^A$ are defined as partial third derivatives of the Lagrangian:

$$\boldsymbol{G}_{\mu\nu\gamma}=\left(\frac{\partial^3 L}{\partial t_\mu\partial t_\nu\partial t_\gamma}\right)_0, \tag{29}$$

$$\boldsymbol{B}_{\mu\nu\gamma}=\left(\frac{\partial^3 L}{\partial \overline{t}_\mu\partial t_\nu\partial t_\gamma}\right)_0, \tag{30}$$

$$\boldsymbol{F}^A_{\mu\nu}=\left(\frac{\partial^3 L}{\partial \epsilon_A(\omega_A)\partial t_\mu\partial t_\nu}\right)_0, \tag{31}$$

$$\boldsymbol{A}^A_{\mu\nu}=\left(\frac{\partial^3 L}{\partial \epsilon_A(\omega_A)\partial \overline{t}_\mu\partial t_\nu}\right)_0. \tag{32}$$

Open-ended expressions for higher-order response functions are given in Appendix B. If we go beyond quadratic response theory we need in addition to the second partial derivatives of the Lagrangian defined in Eqs. (18) and (22)–(24) and the third partial derivatives defined in Eqs. (29)–(32) the fourth partial derivatives

$$\boldsymbol{H}_{\mu\nu\gamma\delta}=\left(\frac{\partial^4 L}{\partial t_\mu\partial t_\nu\partial t_\gamma\partial t_\delta}\right)_0, \tag{33}$$

$$\boldsymbol{C}_{\mu\nu\gamma\delta}=\left(\frac{\partial^4 L}{\partial \overline{t}_\mu\partial t_\nu\partial t_\gamma\partial t_\delta}\right)_0, \tag{34}$$

$$\boldsymbol{B}^A_{\mu\nu\gamma}=\left(\frac{\partial^4 L}{\partial \epsilon_A(\omega_A)\partial \overline{t}_\mu\partial t_\nu\partial t_\gamma}\right)_0, \tag{35}$$

and the fifth partial derivative

$$\boldsymbol{D}_{\mu\nu\gamma\delta\epsilon}=\left(\frac{\partial^5 L}{\partial \overline{t}_\mu\partial t_\nu\partial t_\gamma\partial t_\delta\partial t_\epsilon}\right)_0. \tag{36}$$

As long as we assume that the perturbation is described by one-electron operators a $\boldsymbol{G}^A$ matrix defined analogously to $\boldsymbol{F}^A$ vanishs as do similarly defined $\boldsymbol{H}^A$, $\boldsymbol{C}^A$ and $\boldsymbol{D}^A$ matrices. A fifth partial derivative of the Lagrangian with respect to the amplitudes t_μ vanishs because the coupled cluster equations are at most quartic in the amplitudes. For the same reason all sixth and higher partial derivatives of the Lagrangian vanish also. In Eqs. (27) and (28) and in the following we use a generalized notation for contractions of these matrices with vectorlike intermediates which implies the summation convention $\overline{t^A}\boldsymbol{A}t^B=\Sigma_{\mu\nu}\overline{t^A_\mu}A_{\mu\nu}t^B_\nu$, $\boldsymbol{F}t^At^B=\Sigma_{\mu\nu}F_{\mu\nu}t^A_\mu t^B_\nu$, $\overline{t^A}\boldsymbol{B}t^Bt^C=\Sigma_{\mu\nu\gamma}\overline{t^A_\mu}B_{\mu\nu\gamma}t^B_\nu t^C_\gamma$, $\boldsymbol{G}t^At^Bt^C=\Sigma_{\mu\nu\gamma}G_{\mu\nu\gamma}t^A_\mu t^B_\nu t^C_\gamma$, etc. We note that the matrices $\boldsymbol{F}$, $\boldsymbol{G}$, and $\boldsymbol{H}$ are symmetric in all their indices, while the matrices $\boldsymbol{B}$, $\boldsymbol{C}$, and $\boldsymbol{D}$ are only symmetric in the second, third, fourth and fifth index. Therefore we indicate a contraction of the first index of $\boldsymbol{A}$, $\boldsymbol{B}$, $\boldsymbol{C}$, or $\boldsymbol{D}$ with a vector by multiplication from the left side, in difference to multiplication from the right side which means a contraction with one of the last indices.

III. MULTIPHOTON TRANSITION MOMENTS FROM THE RESIDUES OF THE GROUND STATE NONLINEAR RESPONSE FUNCTIONS

The response functions for an exact state have poles when either a single frequency or a sum of frequencies equals an excitation energy of the unperturbed molecule. The corresponding first residues of the response functions are equal to products of (multi-) photon transition moments between the ground state and an excited state. Different definitions for n-photon transition moments are in use in the literature,[10–12,16] differing mainly in alternating signs, a complex phase factor or in the incorporation of an amplitude dependent prefactor.[12] We adopt in the following the definition and notation used by Meath and Power,[10] who defined the n-photon transition moment from an initial state i to the final state f as:

$$M^{X_1\cdots X_n}_{f\leftarrow i}(\omega)=\hat{P}^{X_1\cdots X_n}\sum_{l_1}\sum_{l_2}\cdots\sum_{l_{n-1}}\frac{\mu^{X_n}_{fl_{n-1}}\mu^{X_{n-1}}_{l_{n-1}l_{n-2}}\cdots\mu^{X_2}_{l_2l_1}\mu^{X_1}_{l_1i}}{[(n-1)\omega-E_{l_{n-1}i}]\cdots[2\omega-E_{l_{n-2}i}][\omega-E_{l_1i}]}, \tag{37}$$

where $\mu^{X_{l_j}}_{l_jl_k}$ are the transition matrix elements of the operator X_{l_j} between the states l_j and l_k. E_{l_ji} is the excitation energy from

state i to state l_j and ω the photon frequency. $\hat{P}^{X_1\cdots X_n}$ is the symmetrization operator defined in the last section. In Eq. (37) the frequencies were the same for all fields, but the expression for the multiphoton transition moments can straightforwardly be extended to a general polychromatic case:

$$M^{X_1\cdots X_n}_{f\leftarrow i}(\omega_2,\cdots,\omega_n)=\hat{P}^{X_1\cdots X_n}\sum_{l_1}\sum_{l_2}\cdots\sum_{l_{n-1}}\frac{\mu^{X_n}_{fl_{n-1}}\mu^{X_{n-1}}_{l_{n-1}l_{n-2}}\cdots\mu^{X_2}_{l_2l_1}\mu^{X_1}_{l_1i}}{[\omega_1+\cdots+\omega_{n-1}-E_{l_{n-1}i}]\cdots[\omega_1+\omega_2-E_{l_2i}][\omega_1-E_{l_1i}]}. \tag{38}$$

The n photon frequencies that appear in the expression for the n-photon transition moment are not independent: their sum is restricted by a matching condition to $\omega_1+\cdots+\omega_n=E_{fi}$. Equation (38) might be compared with the sum-over-states expression for the (ground state) response function of order n:[38–40]

$$\langle\langle X_1;\cdots X_n\rangle\rangle_{\omega_2,\cdots,\omega_n}=\hat{P}^{X_1\cdots X_n}\sum_{l_1}\sum_{l_2}\cdots\sum_{l_{n-1}}\frac{\mu^{X_n}_{0l_{n-1}}\mu^{X_{n-1}}_{l_{n-1}l_{n-2}}\cdots\mu^{X_2}_{l_2l_1}\mu^{X_1}_{l_10}}{[\omega_1+\cdots+\omega_{n-1}-E_{l_{n-1}0}]\cdots[\omega_1+\omega_2-E_{l_20}][\omega_1-E_{l_10}]}, \tag{39}$$

where now the frequencies are restricted by $\omega_1+\omega_2\cdots+\omega_n=0$. Similar to the response functions, the multiphoton transition moments are symmetric with respect to permutations of the operators X_i together with the accompanied frequencies ω_i. Response functions are also symmetric with respect to the inversion of the signs of the frequency arguments and simultaneous complex conjugation. The corresponding symmetry of the multiphoton transition moments is sligthly more complicated: they are symmetric under sign inversion of the frequency arguments and simultaneous complex conjugation together with an exchange of the state indeces i and f:

$$M^{X_1\cdots X_n}_{f\leftarrow i}(\omega_2,\cdots,\omega_n)^*=\hat{P}^{X_1\cdots X_n}\sum_{l_1\cdots l_{n-1}}\frac{\mu^{X_1}_{il_1}\mu^{X_2}_{l_1l_2}\cdots\mu^{X_{n-1}}_{l_{n-2}l_{n-1}}\mu^{X_n}_{l_{n-1}f}}{[\omega_1-E_{l_1i}][\omega_1+\omega_2-E_{l_2i}]\cdots[\omega_1+\cdots+\omega_{n-1}-E_{l_{n-1}i}]} \tag{40}$$

$$=\hat{P}^{X_1\cdots X_n}\sum_{l_1\cdots l_{n-1}}\frac{\mu^{X_1}_{il_1}\mu^{X_2}_{l_1l_2}\cdots\mu^{X_{n-1}}_{l_{n-2}l_{n-1}}\mu^{X_n}_{l_{n-1}f}}{[-\omega_2\cdots-\omega_n-E_{l_1f}][-\omega_3\cdots-\omega_n-E_{l_2f}]\cdots[-\omega_n-E_{l_{n-1}f}]} \tag{41}$$

$$=\hat{P}^{X_1\cdots X_n}\sum_{l_1\cdots l_{n-1}}\frac{\mu^{X_n}_{il_1}\mu^{X_{n-1}}_{l_1l_2}\cdots\mu^{X_2}_{l_{n-2}l_{n-1}}\mu^{X_1}_{l_{n-1}f}}{[-\omega_{n-1}\cdots-\omega_1-E_{l_1f}][-\omega_{n-2}\cdots-\omega_1-E_{l_2f}]\cdots[-\omega_1-E_{l_{n-1}f}]} \tag{42}$$

$$=M^{X_1\cdots X_n}_{i\leftarrow f}(-\omega_2,\cdots,-\omega_n). \tag{43}$$

In Eq. (41) we used the matching condition to rewrite ω_1 as $E_{fi}-\omega_2\cdots-\omega_n$ and in Eq. (42) we employed the invariance of the expression under permutation of the operators X_i together with their accompanied frequencies ω_i.

For exact states the sum-over-states expression (38) is equivalent to the transition matrix type expressions:[14,16]

$$M^{X_1\cdots X_n}_{f\leftarrow i}(\omega_2,\cdots,\omega_n)=\frac{1}{(n-1)!}\hat{P}^{X_1\cdots X_n}\langle f|H^{X_1}|i^{X_2\cdots X_n}(\omega_2,\cdots,\omega_n)\rangle, \tag{44}$$

$$M^{X_1\cdots X_n}_{i\leftarrow f}(-\omega_2,\cdots,-\omega_n)=\frac{1}{(n-1)!}\hat{P}^{X_1\cdots X_n}\langle i^{X_2\cdots X_n}(\omega_2,\cdots,\omega_n)|H^{X_1}|f\rangle, \tag{45}$$

where $i^{X_2\cdots X_n}(\omega_2,\cdots,\omega_n)$ is the response of order $n-1$ of the wave function for state i to the frequency-dependent fields $X_2,\cdots, X_n$.

The relation between the residues of the response functions and the transition moments for multiphoton excitations can be used to derive expressions for multiphoton transition moments for approximate wave functions.[17,19,20,26] Of particular interest are the first residues of the response functions of order $2n$ which determine the absorption cross sections for n-photon transitions from the ground state 0 to an excited state f:

$$\lim_{\omega_1+\cdots+\omega_n\to\omega_f}(\omega_1+\cdots+\omega_n-\omega_f)\langle\langle X_1;X_2,\cdots,X_{2n}\rangle\rangle_{\omega_2,\cdots,\omega_{2n}}$$

$$=\hat{P}^{X_1\cdots X_n}\sum_{l_1}\sum_{l_2}\cdots\sum_{l_{2n-1}}\lim_{\omega_1+\cdots+\omega_n\to\omega_f}(\omega_1+\cdots+\omega_n-\omega_f)$$

$$\times\frac{\mu^{X_{2n}}_{0l_{2n-1}}\cdots\mu^{X_{n+1}}_{l_{n+1}l_n}\,\mu^{X_n}_{l_nl_{n-1}}\cdots\mu^{X_1}_{l_10}}{[\omega_1+\cdots+\omega_{2n-1}-E_{l_{2n-1}0}]\cdots[\omega_1+\cdots+\omega_n-E_{l_n0}]\cdots[\omega_1-E_{l_10}]} \tag{46}$$

$$=\frac{\mu^{X_{2n}}_{0l_{2n-1}}\cdots\mu^{X_{n+1}}_{l_{n+1}f}}{[\omega_1+\cdots+\omega_{2n-1}-E_{l_{2n-1}0}]\cdots[\omega_1+\cdots+\omega_{n+1}-E_{l_{n+1}0}]}\,\frac{\mu^{X_n}_{fl_{n-1}}\cdots\mu^{X_1}_{l_10}}{[\omega_1+\cdots+\omega_{n-1}-E_{l_{n-1}0}]\cdots[\omega_1-E_{l_10}]} \tag{47}$$

$$=\frac{\mu^{X_{2n}}_{0l_{2n-1}}\cdots\mu^{X_{n+1}}_{l_{n+1}f}}{[\omega_{n+1}\cdots+\omega_{2n-1}-E_{l_{2n-1}f}]\cdots[\omega_{n+1}-E_{l_{n+1}f}]}\,\frac{\mu^{X_n}_{fl_{n-1}}\cdots\mu^{X_1}_{l_10}}{[\omega_1\cdots+\omega_{n-1}-E_{l_{n-1}0}]\cdots[\omega_1-E_{l_10}]} \tag{48}$$

$$=M^{X_{n+1}\cdots X_{2n}}_{0\leftarrow f}(\omega_{n+2},\cdots,\omega_{2n})\;M^{X_1\cdots X_n}_{f\leftarrow 0}(\omega_2,\cdots,\omega_n). \tag{49}$$

Alternatively to Eq. (49) one can use its complex conjugate:

$$\lim_{\omega_{n+1}+\cdots+\omega_{2n}\to-\omega_f}(-\omega_{n+1}\cdots-\omega_{2n}-\omega_f)\langle\langle X_1;X_2,\cdots,X_{2n}\rangle\rangle_{-\omega_2,\cdots,-\omega_{2n}}$$

$$=M^{X_1\cdots X_n}_{0\leftarrow f}(-\omega_2,\cdots,-\omega_n)\;M^{X_{n+1}\cdots X_{2n}}_{f\leftarrow 0}(-\omega_{n+2},\cdots,-\omega_{2n}). \tag{50}$$

In the following we will refer to $M^{X_1\cdots X_n}_{0\leftarrow f}(\omega_2,\cdots,\omega_n)$ as ''left'' and to $M^{X_1\cdots X_n}_{f\leftarrow 0}(\omega_2,\cdots,\omega_n)$ as ''right'' n-photon transition moments from the ground state 0 to the excited state f.

For approximate methods the structure of Eq. (49) is only retained if an orthonormal parametrization for the bra and the ket states is used and if the quasienergy remains real in the presence of a time-dependent perturbation. For methods in which the quasienergy is obtained from a projection type expression, as for the coupled cluster models, the response functions have to be calculated as derivatives of only the real part of the quasienergy, as in Eq. (25). The response functions then consist of two terms which are derivatives of the quasienergy and of its complex conjugate and in general have poles at the same frequencies. Their residues can then only be compared with the symmetrized expression:

$$\lim_{\omega_1+\cdots+\omega_n\to\omega_f}(\omega_1+\cdots+\omega_n-\omega_f)\langle\langle X_1;X_2,\cdots,X_{2n}\rangle\rangle_{\omega_2,\cdots,\omega_{2n}}$$

$$=\frac{1}{2}\{M^{X_{n+1}\cdots X_{2n}}_{0\leftarrow f}(\omega_{n+2},\cdots,\omega_{2n})\;M^{X_1\cdots X_n}_{f\leftarrow 0}(\omega_2,\cdots,\omega_n)$$

$$+(M^{X_1\cdots X_n}_{0\leftarrow f}(-\omega_2,\cdots,-\omega_n))^*$$

$$\times(M^{X_{n+1}\cdots X_{2n}}_{f\leftarrow 0}(-\omega_{n+2},\cdots,-\omega_{2n}))^*\}, \tag{51}$$

and left and right transition moments $M^{X_1\cdots X_n}_{0\leftarrow f}(-\omega_2,\cdots,-\omega_n)$ and $M^{X_1\cdots X_n}_{f\leftarrow 0}(\omega_2,\cdots,\omega_n)$ can no longer be expected to be each others complex conjugate. The structure of the residues in Eq. (51) represents a straightforward generalization for response functions obtained from approximate wave functions with a projection type expression for the quasienergy. A symmetrized biorthogonal structure in principle prohibits the identification of unequivocally defined individual transition moments, but all measurable quantities as optical properties, absorption cross sections, etc., depend only on the product of left and right transition moments which can still unambiguously be identified from residues with this structure. Thus from a practical point of view, we may still identify individual approximate left and right transition moments, but one has to keep in mind that they in general are not each others complex conjugate and that products of left and right transition moments must be substituted by the symmetrized expression

$$\frac{1}{2}\{M^{X_{n+1}\cdots X_{2n}}_{0\leftarrow f}(\omega_{n+2},\cdots,\omega_{2n})\;M^{X_1\cdots X_n}_{f\leftarrow 0}(\omega_2,\cdots,\omega_n)$$

$$+(M^{X_1\cdots X_n}_{0\leftarrow f}(-\omega_2,\cdots,-\omega_n))^*$$

$$\times(M^{X_{n+1}\cdots X_{2n}}_{f\leftarrow 0}(-\omega_{n+2},\cdots,-\omega_{2n}))^*\}. \tag{52}$$

The coupled cluster response functions have poles if a single frequency or a sum of frequencies becomes equal to an eigenvalue of the Jacobian $\boldsymbol{A}$ defined in Eq. (18). Therefore one identifies the eigenvalue ω_f of $\boldsymbol{A}$ as approximation to the excitation energy from the ground state to an excited state f.[20,41] This presupposes that ω_f is real and positive definite. Since the coupled cluster Jacobian $\boldsymbol{A}$ is a nonsymmetric matrix it may in principle have complex eigenvalues. Eigenvalues with a nonzero imaginary part are unphysical and indicate that the ground or the excited state are not well represented by the coupled cluster approximation. However, experience has shown that complex eigenvalues are not a problem in practical calculations and coupled cluster response theory has in numerous applications proven a valuable method for the calculation of excitation energies.[42–45]

The inverse of the Jacobian $\boldsymbol{A}$ plays in coupled cluster response theory the same role as the resolvent in exact state response theory. The nonsymmetric Jacobian may be diagonalized with a biorthonormal set of left and right eigenvectors $\overline{E^f}$ and E^f:

$$\overline{E^f}\boldsymbol{A}\,E^f=\omega_f, \quad \overline{E^i}E^f=\delta_{if}. \tag{53}$$

Expressed in terms of the left and right eigenvectors the coupled cluster resolvent and its residues can be written in a spectral representation as

$$R_{\nu\mu}(\omega)=[-(\boldsymbol{A}-\omega\boldsymbol{1})]^{-1}_{\nu\mu}=\sum_m E^m_\nu \frac{1}{\omega-\omega_m}\overline{E}^m_\mu, \tag{54}$$

and

$$R^f_{\nu\mu}=\lim_{\omega\to\omega_f}(\omega-\omega_f)[-(\boldsymbol{A}-\omega\boldsymbol{1})]^{-1}_{\nu\mu}=E^f_\nu\overline{E}^f_\mu. \tag{55}$$

As in exact state response theory we may identify the residues of the resolvent as projection operators for the excited states f and $\overline{E^f}$ and E^f as representation of the accompanied bra and ket states in the parameter space of the coupled cluster wave function. For the derivation of the transition moments it is convenient to introduce the alternative notation $\overline{E^f}(-\omega_f)$ and $E^f(\omega_f)$ for the excited state vectors, where the left excited state vectors have been associated with minus the excitation energies and the right excited state vectors with plus the excitation energies. The reason for the choice of the signs for ω_f will become apparent in Sec. IV.

The biorthonormality constraints define the eigenvectors of the coupled cluster Jacobian only up to a set of relative scaling factors. One has still the freedom to scale the right eigenvectors by a set of arbitrary nonzero factors, if at the same time the corresponding left eigenvectors are scaled by the inverse factors. Consequently the coupled cluster transition moments are also only defined up to these relative scaling factors. However, this is not a defect of the theory because, as has already been pointed out, it is not the transition moment that is the physical observable but the absorption cross section. The latter property is obtained as product of left and right transition moments and is thus invariant with respect to a relative scaling of the left and right eigenvectors.

In the following sections we show how in coupled cluster response theory the expressions for multiphoton transition moments can be identified from the residues of the response functions of order $2n$ and demonstrate how then the interchange technique can be employed to reformulate the expressions such that they fulfill $2n+1$ and $2n+2$ rules, where n is the photon number of the transition moment. Of course, in high order this approach would become tedious and lengthy. Our goal, however, is to derive the transition moments as derivatives of variational functionals which allow to apply the complete apparatus of variational perturbation theory, including the $2n+1$ and $2n+2$ rules, and make the mathematical structure more apparent. The variational functionals will be derived in Sec. V, after the neccessary prerequisites have been introduced.

A. One-photon transition moments from the linear response function

In Sec. II the linear response function has been obtained as

$$\langle\langle A;B\rangle\rangle_\omega=\frac{1}{2}\hat{C}^{\pm\omega}\hat{P}^{AB}\left\{\left(\eta^A+\frac{1}{2}\boldsymbol{F}t^A(-\omega)\right)t^B(\omega)\right\}. \tag{56}$$

The real eigenvalues of the Jacobian $\boldsymbol{A}$ are usually positive definite and $t^A(\omega)$, $t^B(\omega)$ have only poles for $\omega>0$, while $t^A(-\omega)$ and $t^B(-\omega)$ have poles for $\omega<0$. Therefore one obtains for the residue that determines the one-photon absorption cross section:

$$\begin{aligned}\lim_{\omega\to\omega_f}&(\omega-\omega_f)\langle\langle A;B\rangle\rangle_\omega\\ &=\frac{1}{2}\{(\eta^A+\boldsymbol{F}t^A(-\omega_f))\lim_{\omega\to\omega_f}(\omega-\omega_f)t^B(\omega)\\ &\quad+(\eta^B+\boldsymbol{F}t^B(-\omega_f))^*\lim_{\omega\to\omega_f}(\omega-\omega_f)t^A(\omega)^*\}\end{aligned} \tag{57}$$

$$\begin{aligned}&=\frac{1}{2}\{\overline{\xi^A}(-\omega_f)[-\lim_{\omega\to\omega_f}(\omega-\omega_f)(\boldsymbol{A}-\omega\boldsymbol{1})^{-1}]\xi^B\\ &\quad+\overline{\xi^B}(-\omega_f)^*[-\lim_{\omega\to\omega_f}(\omega-\omega_f)(\boldsymbol{A}-\omega\boldsymbol{1})^{-1}]^*\xi^{A*}\}.\end{aligned} \tag{58}$$

Using the residue of the resolvent $\boldsymbol{R}^f$ we obtain for the residue of the linear response function:

$$\begin{aligned}\lim_{\omega\to\omega_f}&(\omega-\omega_f)\langle\langle A;B\rangle\rangle_\omega\\ &=\frac{1}{2}\{\overline{\xi^A}(-\omega_f)\boldsymbol{R}^f\xi^B+\overline{\xi^B}(-\omega_f)^*\boldsymbol{R}^{f*}\xi^{A*}\}\end{aligned} \tag{59}$$

$$\begin{aligned}&=\frac{1}{2}\{(\overline{\xi^A}(-\omega_f)E^f(\omega_f))(\overline{E^f}(-\omega_f)\xi^B)\\ &\quad+(\overline{\xi^B}(-\omega_f)E^f(\omega_f))^*(\overline{E^f}(-\omega_f)\xi^A)^*\}.\end{aligned} \tag{60}$$

From the last equation one identifies the one-photon transition strengths:

$$S^{0f}_{A,B}=\frac{1}{2}\{M^A_{0\leftarrow f}M^B_{f\leftarrow 0}+(M^B_{0\leftarrow f}M^A_{f\leftarrow 0})^*\}, \tag{61}$$

with the one-photon transition moments:

$$M^A_{0\leftarrow f}=\overline{\xi^A}(-\omega_f)E^f(\omega_f), \tag{62}$$

$$M^A_{f\leftarrow 0}=\overline{E^f}(-\omega_f)\xi^A. \tag{63}$$

The computation of left transition moments $M^A_{0\leftarrow f}$ from the right hand side vectors $\overline{\xi^A}(-\omega_f)$ would require the solution of a set of first-order response equations for $t^A(-\omega_f)$. This can be avoided if one solves instead the additional zeroth-order equation

$$\overline{M^f}(\omega_f)(\boldsymbol{A}+\omega_f\boldsymbol{1})=-\boldsymbol{F}E^f(\omega_f), \tag{64}$$

which can be used to rewrite Eq. (62) as:

$$M^A_{0\leftarrow f}=(\eta^A+Ft^A(-\omega_f))E^f(\omega_f)$$
$$=\eta^A E^f(\omega_f)+\overline{M^f}(\omega_f)\xi^A. \quad (65)$$

Equation (64) is considered to be a zeroth-order response equation since it is independent of perturbation operators. One can interpret the intermediates $\overline{M^f}(\omega_f)$ as a type of Lagrangian multipliers. This will become apparent in the variational formulation derived in Sec. V, which will also allow us to derive general equations for $\overline{M^f}(\omega_f)$ and its responses (see Appendix D).

B. Two-photon transition moments from the cubic response function

The coupled cluster cubic response function was derived in Ref. 32 as

$$\langle\langle A;B,C,D\rangle\rangle_{\omega_B,\omega_C,\omega_D}$$
$$=\frac{1}{2}\hat{C}^{\pm\omega}\hat{P}^{ABCD}\left\{\frac{1}{4}\left(\eta^{CD}+\frac{1}{2}\boldsymbol{F}t^{CD}\right)t^{AB}+\frac{1}{4!}\boldsymbol{H}t^At^Bt^Ct^D\right.$$
$$\left.+\frac{1}{6}\overline{t^A}\boldsymbol{C}t^Bt^Ct^D+\frac{1}{2}\overline{t^A}\boldsymbol{B}^Bt^Ct^D\right\}, \quad (66)$$

where the vector $\eta^{CD}=\overline{\xi^{CD}}-\boldsymbol{F}t^{CD}$ was introduced to separate the contributions of the second-order response amplitudes. For notational convenience the frequency-dependence of the response vectors has been suppressed in Eq. (66) implying that $t^A=t^A(\omega_A)$, $\overline{t^B}=\overline{t^B}(\omega_B)$, etc. The right hand side vectors for the second-order response equations for the cluster amplitudes and Lagrangian multipliers are (cf. Appendix A):

$$\xi^{AB}(\omega_A,\omega_B)=\hat{P}^{AB}\left\{\frac{1}{2}\boldsymbol{B}t^A(\omega_A)t^B(\omega_B)+\boldsymbol{A}^At^B(\omega_B)\right\} \quad (67)$$

$$\overline{\xi}^{AB}(\omega_A,\omega_B)=\boldsymbol{F}t^{AB}(\omega_A,\omega_B)$$
$$+\hat{P}^{AB}\left\{\frac{1}{2}\boldsymbol{G}t^A(\omega_A)t^B(\omega_B)+\boldsymbol{F}^At^B(\omega_B)\right.$$
$$\left.+\overline{t^B}(\omega_B)\boldsymbol{B}t^A(\omega_A)+\overline{t^B}(\omega_B)\boldsymbol{A}^A\right\}. \quad (68)$$

The two-photon absorption cross section is determined by the residue of the cubic response function at $(\omega_A+\omega_B)\rightarrow\omega_f$. Resolvents depending on the frequency $(\omega_A+\omega_B)$ occur only in the second-order response amplitudes $t^{AB}(\omega_A,\omega_B)$ and $t^{CD}(-\omega_C,-\omega_D)$, thus this residue is obtained as

$$\lim_{\omega_A+\omega_B\rightarrow\omega_f}(\omega_A+\omega_B-\omega_f)\langle\langle A;B,C,D\rangle\rangle_{\omega_B,\omega_C,\omega_D}=\lim_{\omega_A+\omega_B\rightarrow\omega_f}(\omega_A+\omega_B-\omega_f)\frac{1}{2}\{(\eta^{CD}(\omega_C,\omega_D)+\boldsymbol{F}t^{CD}(\omega_C,\omega_D))t^{AB}(\omega_A,\omega_B)$$
$$+(\eta^{AB}(-\omega_A,-\omega_B)+\boldsymbol{F}t^{AB}(-\omega_A,-\omega_B))^*t^{CD}(-\omega_C,-\omega_D)^*\} \quad (69)$$

$$=\frac{1}{2}\{(\overline{\xi}^{CD}(-\omega_f-\omega_D,\omega_D)E^f(\omega_f))(\overline{E^f}(-\omega_f)\xi^{AB}(\omega_f-\omega_B,\omega_B))$$
$$+(\overline{\xi}^{AB}(-\omega_f+\omega_B,-\omega_B)E^f(\omega_f))^*(\overline{E^f}(-\omega_f)\xi^{CD}(\omega_f+\omega_D,-\omega_D))^*\}. \quad (70)$$

From the last equation we identify the two-photon transition strength as

$$S^{0f}_{AB,CD}(\omega)=\frac{1}{2}\{M^{AB}_{0\leftarrow f}(-\omega)M^{CD}_{f\leftarrow 0}(\omega)-(M^{CD}_{0\leftarrow f}(-\omega)M^{AB}_{f\leftarrow 0}(\omega))^*\}, \quad (71)$$

with the two-photon transition moments:

$$M^{AB}_{0\leftarrow f}(\omega_B)=\overline{\xi}^{AB}(-\omega_f-\omega_B,\omega_B)E^f(\omega_f), \quad (72)$$

$$M^{AB}_{f\leftarrow 0}(\omega_B)=\overline{E^f}(-\omega_f)\xi^{AB}(\omega_f-\omega_B,\omega_B). \quad (73)$$

Using the interchange technique, the expression for $M^{AB}_{0\leftarrow f}(\omega_B)$ can be rewritten as

$$M^{AB}_{0\leftarrow f}(\omega_B)=\eta^{AB}(-\omega_f-\omega_B,\omega_B)E^f(\omega_f)+\overline{M^f}(\omega_f)\xi^{AB}(-\omega_f-\omega_B,\omega_B). \quad (74)$$

The formulation of Eq. (74) requires a minimal number of response equations to be solved. But in difference to the ground state linear response function the second-order transition properties in the formulation of Eq. (74) require also the first-order ground state Lagrangian multipliers. Using the interchange technique, one can obtain a formulation that is in accord with a $2n+1$ rule for the ground state cluster amplitudes and the excited state vectors and a $2n+2$ rule for the ground state Lagrangian multipliers, where $2n+1/2n+2$ refers to the order of the transition moment rather than to the order of the response function from which is was derived:

$$M^{AB}_{0\leftarrow f}(\omega_B)=[\boldsymbol{G}t^A(-\omega_f-\omega_B)t^B(\omega_B)+\boldsymbol{F}^At^B(\omega_B)+\boldsymbol{F}^Bt^A(-\omega_f-\omega_B)]E^f(\omega_f)+\overline{M}^f(\omega_f)\xi^{AB}(-\omega_f-\omega_B,\omega_B)$$
$$+\overline{t}^A(-\omega_f-\omega_B)[\boldsymbol{B}t^B(\omega_B)+\boldsymbol{A}^B]E^f(\omega_f)+\overline{t}^B(\omega_B)[\boldsymbol{B}t^A(-\omega_f-\omega_B)+\boldsymbol{A}^A]E^f(\omega_f) \quad (75)$$
$$=[\boldsymbol{G}t^A(-\omega_f-\omega_B)t^B(\omega_B)+\boldsymbol{F}^At^B(\omega_B)+\boldsymbol{F}^Bt^A(-\omega_f-\omega_B)]E^f(\omega_f)+\overline{M}^f(\omega_f)\xi^{AB}(-\omega_f-\omega_B,\omega_B)$$
$$+\overline{\xi}^A(-\omega_f-\omega_B)\quad E^{fB}(\omega_f,\omega_B)+\overline{\xi}^B(\omega_B)\quad E^{fA}(\omega_f,-\omega_f-\omega_B). \quad (76)$$

The vectors E^{fA}, E^{fB} are the first-order response of the right eigenvector E^f, obtained in an irregular, i.e., not phase-isolated, response expansion for the excited state vectors (see Sec. IV). They are obtained as solutions of the first-order equations:

$$(\boldsymbol{A}-(\omega_f+\omega)\mathbf{1})\ E^{fA}(\omega_f,\omega)=-(\boldsymbol{B}t^A(\omega)+\boldsymbol{A}^A)E^f(\omega_f). \quad (77)$$

C. Three-photon transition moments from the pentic response function

The three-photon transition moments can be identified from the residue of the pentic response function for $(\omega_A+\omega_B+\omega_C)\rightarrow\omega_f$. The coupled cluster pentic response function is (cf. Appendix B)

$$\langle\langle A;B,C,D,E,F\rangle\rangle_{\omega_B,\omega_C,\omega_D,\omega_E,\omega_F}=\frac{1}{2}\hat{C}^{\pm\omega}\hat{P}^{ABCDEF}\left\{\frac{1}{36}\left(\eta^{ABC}+\frac{1}{2}\boldsymbol{F}t^{ABC}\right)t^{DEF}+\frac{1}{48}\boldsymbol{G}t^{AB}t^{CD}t^{EF}+\frac{1}{16}\overline{t}^{AB}\boldsymbol{B}t^{CD}t^{EF}\right.$$
$$+\frac{1}{16}\boldsymbol{H}t^{AB}t^{CD}t^Et^F+\frac{1}{8}\overline{t}^{AB}\boldsymbol{C}t^{CD}t^Et^F+\frac{1}{8}\overline{t}^A\boldsymbol{C}t^{BC}t^{DE}t^F+\frac{1}{4}\overline{t}^{AB}\boldsymbol{B}^Ct^{DE}t^F$$
$$\left.+\frac{1}{8}\overline{t}^A\boldsymbol{B}^Ct^{BD}t^{EF}+\frac{1}{48}\overline{t}^{AB}\boldsymbol{D}t^Ct^Dt^Et^F+\frac{1}{12}\overline{t}^A\boldsymbol{D}t^{BC}t^Dt^Et^F\right\}, \quad (78)$$

where similar as in second order η^{ABC} is defined as $\overline{\xi}^{ABC}-\boldsymbol{F}t^{ABC}$ and $\overline{\xi}^{ABC}$ is the right hand side vector for the third-order response equation for the Lagrangian multipliers:

$$\overline{\xi}^{ABC}(\omega_A,\omega_B,\omega_C)=\hat{P}^{ABC}\left\{\frac{1}{6}\boldsymbol{H}t^A(\omega_A)t^B(\omega_B)t^C(\omega_C)+\frac{1}{2}\boldsymbol{G}t^{AB}(\omega_A,\omega_B)t^C(\omega_C)+\frac{1}{2}\boldsymbol{F}^At^{BC}(\omega_B,\omega_C)\right.$$
$$+\frac{1}{6}\boldsymbol{F}t^{ABC}(\omega_A,\omega_B,\omega_C)+\frac{1}{2}\overline{t}^{BC}(\omega_B,\omega_C)\boldsymbol{A}^A+\frac{1}{2}\overline{t}^A(\omega_A)\boldsymbol{C}t^B(\omega_B)t^C(\omega_C)+\overline{t}^B(\omega_B)\boldsymbol{B}^Ct^A(\omega_A)$$
$$\left.+\frac{1}{2}\overline{t}^{AB}(\omega_A,\omega_B)\boldsymbol{B}t^C(\omega_C)+\frac{1}{2}\overline{t}^A(\omega_A)\boldsymbol{B}t^{BC}(\omega_B,\omega_C)\right\}. \quad (79)$$

The right hand side vector for the third-order response equation for the coupled cluster amplitudes is

$$\xi^{ABC}(\omega_A,\omega_B,\omega_C)=\hat{P}^{ABC}\left\{\frac{1}{6}\boldsymbol{C}t^A(\omega_A)t^B(\omega_B)t^C(\omega_C)+\frac{1}{2}\boldsymbol{B}^At^B(\omega_B)t^C(\omega_C)\right.$$
$$\left.+\frac{1}{2}\boldsymbol{B}t^{AB}(\omega_A,\omega_B)t^C(\omega_C)+\frac{1}{2}\boldsymbol{A}^At^{BC}(\omega_B,\omega_C)\right\}. \quad (80)$$

Resolvents that depend on the frequency $\omega_A+\omega_B+\omega_C$ occur only in the third-order response vectors $t^{ABC}(\omega_A,\omega_B,\omega_C)$ and $t^{DEF}(-\omega_D,-\omega_E,-\omega_F)$. Consequently we obtain for the three-photon absorption cross section:

$$\lim_{\omega_A+\omega_B+\omega_C\to\omega_f}(\omega_A+\omega_B+\omega_C-\omega_f)\langle\langle A;B,C,D,E,F\rangle\rangle_{\omega_B,\omega_C,\omega_D,\omega_E,\omega_F}$$

$$=\frac{1}{2}\{(\eta^{DEF}(\omega_D,\omega_E,\omega_F)+\boldsymbol{F}t^{DEF}(\omega_D,\omega_E,\omega_F))\boldsymbol{R}^f\xi^{ABC}(\omega_A,\omega_B,\omega_C)+(\eta^{ABC}(-\omega_A,-\omega_B,-\omega_C$$

$$+\boldsymbol{F}t^{ABC}(-\omega_A,-\omega_B,-\omega_C))^*\boldsymbol{R}^{f*}\xi^{DEF}(-\omega_D,-\omega_E,-\omega_f)^*\} \tag{81}$$

$$=\frac{1}{2}\{(\bar{\xi}^{DEF}(\omega_D,\omega_E,\omega_F)E^f(\omega_f))\,(\bar{E}^f(-\omega_f)\xi^{ABC}(\omega_A,\omega_B,\omega_C))+(\bar{\xi}^{ABC}(-\omega_A,-\omega_B,-\omega_C)E^f(\omega_f))^*$$

$$\times(\bar{E}^f(-\omega_f)\xi^{DEF}(-\omega_D,-\omega_E,-\omega_f))^*\}, \tag{82}$$

where in the last two equations $\omega_A=\omega_f-\omega_B-\omega_C$ and $\omega_D=-\omega_f-\omega_E-\omega_F$. From Eq. (82) one identifies the three-photon transition strength as

$$S^{0f}_{ABC,DEF}(\omega_1,\omega_2)=\frac{1}{2}\{M^{ABF}_{0\leftarrow f}(-\omega_1,-\omega_2)M^{DEF}_{f\leftarrow 0}(\omega_1,\omega_2)-(M^{DEF}_{0\leftarrow f}(-\omega_1,-\omega_2)M^{ABD}_{f\leftarrow 0}(\omega_1,\omega_2))^*\}, \tag{83}$$

with the three-photon transition moments:

$$M^{ABC}_{0\leftarrow f}(\omega_B,\omega_C)=\bar{\xi}^{ABC}(-\omega_f-\omega_B-\omega_C,\omega_B,\omega_C)E^f(\omega_f), \tag{84}$$

$$M^{ABC}_{f\leftarrow 0}(\omega_B,\omega_C)=\bar{E}^f(-\omega_f)\xi^{ABC}(\omega_f-\omega_B-\omega_C,\omega_B,\omega_C). \tag{85}$$

If the interchange technique is used to eliminate the third- and second-order response amplitudes and Lagrangian multipliers in the expressions for $M^{ABC}_{0\leftarrow f}(\omega_B,\omega_C)$ one obtains:

$$M^{ABC}_{0\leftarrow f}(\omega_B,\omega_C)=\hat{P}^{ABC}\Bigg\{\left[\frac{1}{6}\boldsymbol{H}t^A(\omega_A)t^B(\omega_B)t^C(\omega_C)+\frac{1}{2}\bar{t}^A(\omega_A)\boldsymbol{C}t^B(\omega_B)t^C(\omega_C)+\bar{t}^B(\omega_B)\boldsymbol{B}^Ct^A(\omega_A)\right]E^f(\omega_f)+\bar{M}^f(\omega_f)$$

$$\times\left[\frac{1}{6}\boldsymbol{C}t^A(\omega_A)t^B(\omega_B)t^C(\omega_C)+\frac{1}{2}\boldsymbol{B}^At^B(\omega_B)t^C(\omega_C)\right]+\left[\frac{1}{2}\boldsymbol{G}t^B(\omega_B)t^C(\omega_C)+\boldsymbol{F}^Bt^C(\omega_C)+\bar{t}^B(\omega_B)\boldsymbol{B}t^C(\omega_C)\right.$$

$$\left.+\bar{t}^C(\omega_C)\boldsymbol{A}^B\right]E^{fA}(\omega_f,\omega_A)+\frac{1}{2}[\boldsymbol{G}t^A(\omega_A)E^f(\omega_f)+\bar{t}^A(\omega_A)\boldsymbol{B}E^f(\omega_f)+\boldsymbol{F}E^{fA}(\omega_f,\omega_A)+\boldsymbol{F}^AE^f(\omega_f)$$

$$+\bar{M}^f(\omega_f)\boldsymbol{B}t^A(\omega_A)+\bar{M}^f(\omega_f)\boldsymbol{A}^A]t^{BC}(\omega_B,\omega_C)\Bigg\} \tag{86}$$

$$=\hat{P}^{ABC}\Bigg\{\frac{1}{6}\boldsymbol{H}t^A(\omega_A)t^B(\omega_B)t^C(\omega_C)E^f(\omega_f)+\bar{t}^A(\omega_A)\left[\frac{1}{2}\boldsymbol{C}t^B(\omega_B)t^C(\omega_C)+\boldsymbol{B}^Ct^B(\omega_B)\right]E^f(\omega_f)+\bar{M}^f(\omega_f)$$

$$\times\left[\frac{1}{6}\boldsymbol{C}t^B(\omega_B)t^C(\omega_C)+\frac{1}{2}\boldsymbol{B}^Ct^B(\omega_B)\right]t^A(\omega_A)+\frac{1}{2}\eta^{BC}(\omega_B,\omega_C)E^{fA}(\omega_f,\omega_A)$$

$$+\frac{1}{2}\bar{M}^{fA}(\omega_f,\omega_A)\xi^{BC}(\omega_B,\omega_C)\Bigg\}. \tag{87}$$

The first-order Lagrangian multipliers $\bar{M}^{fA}$ are obtained from the response equation (see Sec. V A):

$$\bar{M}^{fA}(\omega_f,\omega)(\boldsymbol{A}+(\omega_f+\omega)\boldsymbol{1})=-(\boldsymbol{G}\;t^A(\omega)\;E^f(\omega_f)+\bar{t}^A(\omega)\;\boldsymbol{B}\;E^f(\omega_f)+\boldsymbol{F}^A\;E^f(\omega_f)+\boldsymbol{F}\;E^{fA}(\omega_f,\omega)+\bar{M}^f(\omega_f)\;\boldsymbol{B}\;t^A(\omega_A)$$

$$+\bar{M}^f(\omega_f)\;\boldsymbol{A}^A). \tag{88}$$

In a similar way the second-order amplitudes can be eliminated from the expression for the right form of the three-photon transition matrix element $M^{ABC}_{f\leftarrow 0}(\omega_B,\omega_C)$:

$$M^{ABC}_{f\leftarrow 0}(\omega_B,\omega_C)=\hat{P}^{ABC}\Big\{\overline{E^f}(-\omega_f)\Big(\frac{1}{6}\boldsymbol{C}t^A(\omega_A)t^B(\omega_B)t^C(\omega_C)+\frac{1}{2}\boldsymbol{B}^A t^B(\omega_B)t^C(\omega_C)\Big)$$
$$+\frac{1}{2}(\overline{E^f}(-\omega_f)\boldsymbol{B}t^A(\omega_A)+\overline{E^f}(-\omega_f)\boldsymbol{A}^A)t^{BC}(\omega_B,\omega_C)\Big\} \quad (89)$$

$$=\hat{P}^{ABC}\Big\{\overline{E^f}(-\omega_f)\Big(\frac{1}{6}\boldsymbol{C}t^A(\omega_A)t^B(\omega_B)t^C(\omega_C)+\frac{1}{2}\boldsymbol{B}^A t^B(\omega_B)t^C(\omega_C)\Big)$$
$$+\overline{E^{fA}}(-\omega_f,\omega_A)\Big(\frac{1}{2}\boldsymbol{B}t^B(\omega_B)t^C(\omega_C)+\boldsymbol{A}^B t^C(\omega_C)\Big)\Big\}. \quad (90)$$

The vectors $\overline{E^{fA}}$ represent the first-order response of the left excited state eigenvectors in an irregular, non-phase-isolated response expansion (cf. Sec. IV). They are obtained from the first-order response equations:

$$\overline{E^{fA}}(-\omega_f,\omega)(\boldsymbol{A}+(\omega-\omega_f)\mathbf{1})$$
$$=-(\overline{E^f}(-\omega_f)\boldsymbol{B}t^A(\omega)+\overline{E^f}(-\omega_f)\boldsymbol{A}^A). \quad (91)$$

D. The general case: n-photon transition moments from the response function of order 2n

To derive an open-ended formula for the coupled cluster n-photon transition moments, we consider the response functions of order $2n$ and their functional dependence on the response of the amplitudes and Lagrangian multipliers of order n. First we note that one of the many equivalent variational conditions for the determination of the multipliers of order n is given by (cf. Eq. 16, see also Appendix A):

$$\frac{d\{L\}_T^{X_1\cdots X_{2n}}}{dt^{X_{n+1}\cdots X_{2n}}(\omega_{n+1},\cdots,\omega_{2n})}$$
$$=\frac{d}{dt^{X_{n+1}\cdots X_{2n}}(\omega_{n+1},\cdots,\omega_{2n})}\times\Big\{\frac{\partial^{2n}L}{d\epsilon_{X_1}(\omega_1)\cdots d\epsilon_{X_{2n}}(\omega_{2n})}\Big\}_T \quad (92)$$
$$=\overline{\xi}^{X_1\cdots X_n}(\omega_1,\cdots,\omega_n)+\overline{t}^{X_1\cdots X_n}(\omega_1,\cdots,\omega_n)\times(\boldsymbol{A}+(\omega_1+\cdots+\omega_n)\mathbf{1})$$
$$=0. \quad (93)$$

Similarly, one of the many equivalent variational conditions for the response of the amplitudes of order n is obtained from

$$\frac{d\{L\}_T^{X_1\cdots X_{2n}}}{d\overline{t}^{X_1\cdots X_n}(\omega_1,\cdots,\omega_n)}=\frac{\partial}{d\overline{t}^{X_1\cdots X_n}(\omega_1,\cdots,\omega_n)}\Big\{\frac{\partial^{2n}L}{d\epsilon_{X_1}(\omega_1)\cdots d\epsilon_{X_{2n}}(\omega_{2n})}\Big\}_T \quad (94)$$

$$=(\boldsymbol{A}-(\omega_{n+1}\cdots+\omega_{2n})\mathbf{1})t^{X_{n+1}\cdots X_{2n}}(\omega_{n+1},\cdots,\omega_{2n})+\xi^{X_{n+1}\cdots X_{2n}}(\omega_{n+1},\cdots,\omega_{2n})=0. \quad (95)$$

Analogous equations hold for all permutations of the operators $X_1,\cdots,X_{2n}$ together with their associated frequencies $\omega_1,\cdots,\omega_{2n}$. The right hand side vectors for the cluster amplitude response equations $\xi^{X_1\cdots X_n}$ are independent of response vectors of order n, and the right hand side vectors $\overline{\xi}^{X_1\cdots X_n}$ can be written as $\eta^{X_1\cdots X_n}+\boldsymbol{F}t^{X_1\cdots X_n}$ (see Appendix A), where $\eta^{X_1\cdots X_n}$ is also independent of response vectors of order n. Thus the time-averaged Lagrangian of order $2n$ can, before the $2n+1$ and $2n+2$ rules have been applied, be written in the form

$$\{L\}_T^{X_1\cdots X_{2n}}=L_<^{X_1\cdots X_{2n}}+L_>^{X_1\cdots X_{2n}}+\frac{1}{n!n!}\hat{P}^{X_1\cdots X_{2n}}\times\Big\{\Big(\eta^{X_1\cdots X_n}(\omega_1,\cdots,\omega_n)+\frac{1}{2}\boldsymbol{F}t^{X_1\cdots X_n}(\omega_1,\cdots,\omega_n)\Big)$$
$$\times t^{X_{n+1}\cdots X_{2n}}(\omega_{n+1},\cdots,\omega_{2n})+\overline{t}^{X_1\cdots X_n}(\omega_1,\cdots,\omega_n)(\boldsymbol{A}+(\omega_1+\cdots+\omega_n)\mathbf{1})$$
$$\times t^{X_{n+1}\cdots X_{2n}}(\omega_{n+1},\cdots,\omega_{2n})+\overline{t}^{X_1\cdots X_n}(\omega_1,\cdots,\omega_n)\xi^{X_{n+1}\cdots X_{2n}}(\omega_{n+1},\cdots,\omega_{2n})\Big\}, \quad (96)$$

where we collected in $L_<^{X_1\cdots X_{2n}}$ all terms that depend only on response amplitudes and multipliers up to order $n-1$ and

$L_{>}^{X_1\cdots X_{2n}}$ is the sum of all terms that depend on response amplitudes and multipliers of orders $m>n$. Both, $L_{<}^{X_1\cdots X_{2n}}$ and $L_{>}^{X_1\cdots X_{2n}}$ are independent of the amplitudes and multipliers of order n. The terms collected in $L_{>}^{X_1\cdots X_{2n}}$ vanish due to the $2n+1$ rule for the amplitudes and the multipliers and the varitional condition (94) can be used to eliminate the terms proportional to the response multipliers of order n. One obtains for the response function of order $2n$ then the expression:

$$\langle\langle X_1;X_2,\cdots,X_{2n}\rangle\rangle_{\omega_2,\cdots,\omega_{2n}}=\frac{1}{2}\hat{C}^{\pm\omega}\Bigg\{L_{<}^{X_1\cdots X_{2n}}+\frac{1}{n!n!}\hat{P}^{X_1\cdots X_{2n}}\Bigg(\eta^{X_1\cdots X_n}(\omega_1,\cdots,\omega_n)+\frac{1}{2}\boldsymbol{F}t^{X_1\cdots X_n}(\omega_1,\cdots,\omega_n)\Bigg)$$
$$\times t^{X_{n+1}\cdots X_{2n}}(\omega_{n+1},\cdots,\omega_{2n})\Bigg\}. \tag{97}$$

If one now takes the residue for $\omega_1+\cdots+\omega_n\rightarrow\omega_f$, only the second term can contribute since all the terms collected in $L_{<}^{X_1\cdots X_{2n}}$ do not contain a resolvent that depends on the frequency sum $\omega_1+\cdots+\omega_n$. From the second term we obtain:

$$\lim_{\omega_1+\cdots+\omega_n\rightarrow\omega_f}(\omega_1+\cdots+\omega_n-\omega_f)\langle\langle X_1;X_2,\cdots,X_{2n}\rangle\rangle_{\omega_2,\cdots,\omega_{2n}}$$
$$=\frac{1}{2}\overline{\xi}^{X_{n+1}\cdots X_{2n}}(\omega_{n+1},\omega_{n+2},\cdots,\omega_{2n})\ \boldsymbol{R}^f\ \xi^{X_1\cdots X_n}(\omega_1,\omega_2,\cdots,\omega_n)$$
$$+\frac{1}{2}(\overline{\xi}^{X_1\cdots X_n}(-\omega_1,-\omega_2,\cdots,-\omega_n)\ \boldsymbol{R}^f\ \xi^{X_{n+1}\cdots X_{2n}}(-\omega_{n+1},-\omega_{n+2}\cdots,-\omega_n))^* \tag{98}$$
$$=\frac{1}{2}(\overline{\xi}^{X_{n+1}\cdots X_{2n}}(\omega_{n+1},\omega_{n+2},\cdots,\omega_{2n})E^f(\omega_f))\ (\overline{E^f}(-\omega_f)\xi^{X_1\cdots X_n}(\omega_1,\omega_2,\cdots,\omega_n))$$
$$+\frac{1}{2}(\overline{\xi}^{X_1\cdots X_n}(-\omega_1,-\omega_2,\cdots,-\omega_n)E^f(\omega_f))^*\ (\overline{E^f(-\omega_f)}\xi^{X_{n+1}\cdots X_{2n}}(-\omega_{n+1},-\omega_{n+2},\cdots,-\omega_n))^*, \tag{99}$$

where in the last two equations $\omega_1=\omega_f-\omega_2\cdots-\omega_n$ and $\omega_{n+1}=-\omega_f-\omega_{n+2}\cdots-\omega_{2n}$. Thus we get for the ''left'' and ''right'' n-photon transition moments with $n>0$ the general expressions:

$$M_{0\leftarrow f}^{(n)}(\omega_2,\cdots,\omega_n)=\overline{\xi^{(n)}}(\omega_1,\omega_2,\cdots,\omega_n)E^f(\omega_f),$$
$$\omega_1=-\omega_f-\omega_2\cdots-\omega_n, \tag{100}$$
$$M_{f\leftarrow 0}^{(n)}(\omega_2,\cdots,\omega_n)=\overline{E^f}(-\omega_f)\xi^{(n)}(\omega_1,\omega_2,\cdots,\omega_n),$$
$$\omega_1=\omega_f-\omega_2\cdots-\omega_n. \tag{101}$$

If we include the excitation frequency ω_f, we get, as for response functions, the rule that the frequencies in the expressions for the transition moments add up to zero. From Eqs. (100) and (101) it follows that the right and left approximations to the multiphoton transition moments are related in a simple way to the residues of the response amplitudes and the Lagrangian multipliers:

$$\lim_{\omega_1+\cdots+\omega_n\rightarrow\omega_f}(\omega_1+\cdots+\omega_n-\omega_f)t^{(n)}(+\omega_1,\cdots,+\omega_n)$$
$$=E^f(\omega_f)M_{f\leftarrow 0}^{(n)}(\omega_2,\cdots,\omega_n), \tag{102}$$
$$\lim_{\omega_1+\cdots+\omega_n\rightarrow\omega_f}(\omega_1+\cdots+\omega_n-\omega_f)\overline{t^{(n)}}(-\omega_1,\cdots,-\omega_n)$$
$$=M_{0\leftarrow f}^{(n)}(-\omega_2,\cdots,-\omega_n)\overline{E^f}(-\omega_f). \tag{103}$$

The Eqs. (100) and (101) can also be compared with the expressions of the n-photon transition moments for exact states, (44) and (45): $(1/(n-1)!)P^{X_1\cdots X_n}H^{X_1}|i^{X_2\cdots X_n}(\omega_2,\cdots,\omega_n)\rangle$ is identical to the right hand side vector for the nth-order response equation for the exact state wave function.[14,16,27]

According to Eqs. (100) and (101), the n-photon transition moments could be calculated as simple scalar products once the eigenvectors and the right hand side vectors for the response equations of order n are available. But from a computational point of view this would lead to an inefficient implementation, as the calculation of the right hand side vectors of order n requires the solution of the response equations for $t^{(n-1)}$, $\overline{t}^{(n-1)}$ and $t^{(n)}$. The most convenient way to obtain computational efficient expressions which require only the solution of a minimal set of response equations is to derive multiphoton transition moments as derivatives of variational functionals.

IV. THE RESPONSE OF THE EXCITED STATE VECTORS TO TIME-DEPENDENT PERTURBATIONS

Before we are going to derive in Sec. V such variational functionals for the multiphoton transition moments between the ground state and an excited state, we will take a closer look on the response of the left and right excited state vectors to a time-dependent perturbation. In Sec. III the excited state vectors have been defined for the unperturbed system as the left and right eigenvectors of the Jacobian $\boldsymbol{A}$, normalized such that they form a biorthonormal basis $\overline{E^i}E^f=\delta_{if}$. For a time-dependent ansatz the eigenvalue equations must be generalized to time-dependent differential equations or to a

time-dependent variation principle and a time-dependent parametrization must be chosen for the excited state vectors, such that for the unperturbed system the time-dependent left and right excited state vectors become equal to $\overline{E^f}(-\omega_f)\exp(+i\omega_f t)$ and $E^f(\omega_f)\exp(-i\omega_f t)$, respectively. Several perturbation expansions of the excited states would be conceivable, differing mainly in the normalization and in the incorporation of a quasienergy-dependent phase factor. In the following we will study an expansion that is only phase-isolated with respect to the ground state quasienergy, but not with respect to the quasienergy difference between the ground state and the excited state. We choose this expansion because it is most closely related to the expressions identified from the residues and leads immediately to the Eqs. (77) and (91).

A parametrization of the excited state vectors that is not phase-isolated with respect to the quasienergy difference between the ground and excited state is obtained by the ansatz:

$$E^f(t,\boldsymbol{\epsilon}) = E^f(\omega_f)e^{-i\omega_f t} + \sum_j \boldsymbol{\epsilon}_j(\omega_j)\; E^{fX_j}(\omega_f,\omega_j)\; e^{-i(\omega_j+\omega_f)t} + \cdots, \tag{104}$$

$$\overline{E^f}(t,\boldsymbol{\epsilon}) = \overline{E^f}(-\omega_f)e^{+i\omega_f t} + \sum_j \boldsymbol{\epsilon}_j(\omega_j)\; \overline{E^{fX_j}}(-\omega_f,\omega_j)\; e^{-i(\omega_j-\omega_f)t} + \cdots. \tag{105}$$

The time-dependent excited state vectors are determined from a time-dependent variation principle analogous to the symmetrized Frenkel variation principle in the form of Langhoff, Epstein and Karplus:[27]

$$\delta^E\left(\overline{E^f}(t,\boldsymbol{\epsilon})\left[\boldsymbol{A}(t,\boldsymbol{\epsilon}) - i\frac{d}{dt}\right]E^f(t,\boldsymbol{\epsilon})\right) + i\frac{d}{dt}\left(\overline{E^f}(t,\boldsymbol{\epsilon})\,\delta^E E^f(t,\boldsymbol{\epsilon})\right) = 0, \tag{106}$$

where δ^E denotes variations with respect to the variables of the excited vectors, i.e., the coefficients of the Fourier components of the left and right excited state vectors. If we take the time-average of Eq. (106), the second term vanishes, because we assumed that $\overline{E^f}(t,\boldsymbol{\epsilon})$ and $E^f(t,\boldsymbol{\epsilon})$ are (quasi-) periodic functions of the time:

$$\delta^E\left\{\overline{E^f}(t,\boldsymbol{\epsilon})\left[\boldsymbol{A}(t,\boldsymbol{\epsilon}) - i\frac{d}{dt}\right]E^f(t,\boldsymbol{\epsilon})\right\}_T = 0. \tag{107}$$

Alternatively, Eq. (106) can be rewritten as

$$\left(\delta\overline{E^f}(t,\boldsymbol{\epsilon})\right)\left[\boldsymbol{A}(t,\boldsymbol{\epsilon}) - i\frac{d}{dt}\right]E^f(t,\boldsymbol{\epsilon}) + \left(\overline{E^f}(t,\boldsymbol{\epsilon})\boldsymbol{A}(t,\boldsymbol{\epsilon}) + i\frac{d\overline{E^f}(t,\boldsymbol{\epsilon})}{dt}\right)\delta E^f(t,\boldsymbol{\epsilon}) = 0. \tag{108}$$

Because the variations of the left and the right excited state vectors, $\delta\overline{E^f}(t,\boldsymbol{\epsilon})$ and $\delta E^f(t,\boldsymbol{\epsilon})$, are independent, Eq. (108) gives two independent time-dependent differential equations:

$$\left[\boldsymbol{A}(t,\boldsymbol{\epsilon}) - i\frac{d}{dt}\right]E^f(t,\boldsymbol{\epsilon}) = 0, \tag{109}$$

$$\overline{E^f}(t,\boldsymbol{\epsilon})\boldsymbol{A}(t,\boldsymbol{\epsilon}) + i\frac{d\overline{E^f}(t,\boldsymbol{\epsilon})}{dt} = 0. \tag{110}$$

Thus in a time-dependent approach the static eigenvalue equations become effective time-dependent Schrödinger equations for the excited state vectors. The time- and field-dependent Jacobian is defined as the derivative

$$\boldsymbol{A}(t,\boldsymbol{\epsilon})_{\mu\nu} = \frac{d\; e_\mu(t,\boldsymbol{\epsilon})}{dt_\nu}. \tag{111}$$

Its expansion in Fourier components and the strengths of the external fields is up to second order given by:

$$\begin{aligned}\boldsymbol{A}(t,\boldsymbol{\epsilon}) = \boldsymbol{A} &+ \sum_j \boldsymbol{\epsilon}_j(\omega_j)\; e^{-i(\omega_j)t}[\boldsymbol{B}t^{X_j}(\omega_j) + A^{X_j}] \\ &+ \frac{1}{2}\sum_{jk} \boldsymbol{\epsilon}_j(\omega_j)\; \boldsymbol{\epsilon}_k(\omega_k)\; e^{-i(\omega_j+\omega_k)t} \\ &\times[\boldsymbol{C}t^{X_j}(\omega_j)t^{X_k}(\omega_k) + \boldsymbol{B}t^{X_jX_k}(\omega_j,\omega_k) \\ &+ \boldsymbol{B}^{X_j}t^{X_k}(\omega_k) + \boldsymbol{B}^{X_k}t^{X_j}(\omega_j)] + \cdots.\end{aligned} \tag{112}$$

Introducing the expansion (112) and the ansatz for the right excited state vectors (104) into Eq. (109) one obtains the usual right eigenvector equations

$$(\boldsymbol{A} - \omega_f\mathbf{1})\; E^f(\omega_f) = 0, \tag{113}$$

and the first- and second-order response equations:

$$\begin{aligned}&(\boldsymbol{A} - (\omega_f+\omega_A)\mathbf{1})\; E^{fA}(\omega_f,\omega_A) \\ &\quad = -[\boldsymbol{B}t^A(\omega_A) + \boldsymbol{A}^A]\; E^f(\omega_f),\end{aligned} \tag{114}$$

$$\begin{aligned}&(\boldsymbol{A} - (\omega_f+\omega_A+\omega_B)\mathbf{1})\; E^{fAB}(\omega_f,\omega_A,\omega_B) \\ &\quad = -\hat{P}^{AB}\left\{\left[\frac{1}{2}\boldsymbol{C}t^A(\omega_A)t^B(\omega_B) + \frac{1}{2}\boldsymbol{B}t^{AB}(\omega_A,\omega_B) + \boldsymbol{B}^A t^B(\omega_B)\right]E^f(\omega_f) + [\boldsymbol{B}t^A(\omega_A) + \boldsymbol{A}^A] \times E^{fB}(\omega_f,\omega_B)\right\}.\end{aligned} \tag{115}$$

For the left excited state vectors one obtains in the same way the left eigenvector equations

$$\overline{E^f}(-\omega_f)\; (\boldsymbol{A} - \omega_f\mathbf{1}) = 0, \tag{116}$$

and the first- and second-order response equations:

$$\begin{aligned}&\overline{E^{fA}}(-\omega_f,\omega_A)\; (\boldsymbol{A} + (\omega_A-\omega_f)\mathbf{1}) \\ &\quad = -\overline{E^f}(-\omega_f)\; [\boldsymbol{B}t^A(\omega_A) + \boldsymbol{A}^A],\end{aligned} \tag{117}$$

$$\overline{E}^{fAB}(-\omega_f,\omega_A,\omega_B)\ (\boldsymbol{A}+(\omega_A+\omega_B-\omega_f)\mathbf{1})$$
$$=-\hat{P}^{AB}\Bigg\{\overline{E}^{f}(-\omega_f)\Bigg[\frac{1}{2}\boldsymbol{C}t^A(\omega_A)t^B(\omega_B)+\frac{1}{2}\boldsymbol{B}t^{AB}(\omega_A,\omega_B)$$
$$+\boldsymbol{B}^A t^B(\omega_B)\Bigg]+\overline{E}^{fB}(-\omega_f,\omega_B)[\boldsymbol{B}t^A(\omega_A)+\boldsymbol{A}^A]\Bigg\}. \quad (118)$$

The excited states response equations have in general the form:

$$(\boldsymbol{A}-(\omega_f+\omega_1+\cdots)\mathbf{1})E^{fX_1\cdots}(\omega_f,\omega_1,\cdots)$$
$$=-\xi^{fX_1\cdots}(\omega_f,\omega_1,\cdots), \quad (119)$$

$$\overline{E}^{fX_1\cdots}(-\omega_f,\omega_1,\cdots)(\boldsymbol{A}+(-\omega_f+\omega_1+\cdots)\mathbf{1})$$
$$=-\overline{\xi}^{fX_1\cdots}(-\omega_f,\omega_1,\cdots). \quad (120)$$

Expressions for the right hand side vectors $\xi^{fX_1\cdots X_n}$ and $\overline{\xi}^{fX_1\cdots X_n}$ are given in Appendix C.

The derivation of the foregoing response expansion followed closely what for exact states is known as the Dirac variation-of-constant method,[27,46–48] adopted for the special case of periodic perturbations and a biorthonormal parametrization. Thereby, the responses of the excited state vectors satisfy for order $n>0$ the normalization conditions

$$\hat{P}^{X_1\cdots X_n}\sum_{k=0}^{n}\frac{1}{k!(n-k)!}\overline{E}^{fX_1\cdots X_k}(-\omega_f,\omega_1,\cdots,\omega_k)$$
$$\times E^{fX_{k+1}\cdots X_n}(\omega_f,\omega_{k+1},\cdots,\omega_n)=0. \quad (121)$$

Thus if the unperturbed eigenvectors are normalized to $\overline{E}^{f}(-\omega_f)E^f(\omega_f)=1$, this normalization is retained by the time-dependent vectors $\overline{E}^{f}(t,\epsilon)$, $E^f(t,\epsilon)$ in the presence of an oscillating perturbation order by order.

The coefficient matrices $(\boldsymbol{A}-(\omega_f\pm\omega_1\pm\cdots\pm\omega_n)\mathbf{1})$ contain the eigenvalue ω_f of $\boldsymbol{A}$ in the constant added to the diagonal while the right hand side vectors are in general not orthogonal to the unperturbed state f. Thus the coefficient matrices become irregular in the limit of $\omega_1+\cdots+\omega_n\rightarrow 0$ and the response equations (119) and (120) have then no solution. In practice this means that the response vectors will diverge if a single frequency or a sum of frequencies becomes zero. These divergencies are a consequence of the so-called secular terms that appear in the perturbation expansion of the non-phase-isolated excited state vectors similar to the secular terms encountered in a perturbation expansion of the non-phase-isolated exact state wave function.[27] The parametrization (104) and (105) is phase-isolated only with respect to the ground state quasienergy via the phase-isolated parametrization for the ground state wave function. The secular terms describe an overall time-dependent phase-factor which arises from a shift in the difference between the ground-state and the excited state quasienergies. One can avoid these singlularities by a completely phase-isolated perturbation expansion for the excited state vectors. However, since the expressions for the transition moments are most closely related to a non-phase-isolated expansion, we will in the following only consider the foregoing expansion. A completely phase-isolated expansion for the excited state vectors will be discussed in a forthcoming publication on excited state nonlinear optical properties.[49]

V. VARIATIONAL FORMULATION

The derivation of multiphoton transition moments from the residues of the ground state response functions, as described in Sec. III, is in principle straightforward, but has the disadvantage that computationally efficient expressions are only obtained after rather ''hand-made'' algebraic reformulations using the interchange rule. Such an approach is difficult to generalize and becomes in higher order very tedious and error prone. Thus it would certainly be advantageous if one could instead derive these expressions as derivatives of a variational functional.

A. The Lagrangian for the left transition moments

To find such a variational functional for the left transition moments between the ground state and an excited state we use a two step approach: First we show that the left n-photon transition moments are the nth derivatives of a function. Then we complement this function to a variational Lagrangian. We start from the expression for the left transition moments derived in Sec. III:

$$M^{X_1\cdots X_n}_{0\leftarrow f}(\omega_2,\cdots,\omega_n)=\overline{\xi}^{X_1\cdots X_n}(\omega_1,\omega_2,\cdots,\omega_n)\ E^f(\omega_f),$$
$$\omega_1=-\omega_f-\omega_2\cdots-\omega_n. \quad (122)$$

The vectors $\overline{\xi}^{X_1\cdots X_m}(\omega_1,\omega_2,\cdots,\omega_m)$ are the right hand side vectors for the response equations of the ground state Lagrangian multipliers $\overline{t}^{X_1\cdots X_m}(\omega_1,\omega_2,\cdots,\omega_m)$. Thus we can arbitrarly add to $M^{X_1\cdots X_n}_{0\leftarrow f}$ terms of the form

$$\{\overline{\xi}^{X_1\cdots X_m}(\omega_1,\omega_2,\cdots,\omega_m)$$
$$+\overline{t}^{X_1\cdots X_m}(\omega_1,\omega_2,\cdots,\omega_m)(\boldsymbol{A}+(\omega_1\cdots+\omega_m)\mathbf{1})\}$$
$$\times E^{fX_{m+1}\cdots X_n}(\omega_f,\omega_{m+1},\cdots,\omega_n)=0, \quad (123)$$

without changing the value of the transition moment. The vector E^f is an eigenvector of the Jacobian $\boldsymbol{A}$ with the eigenvalue ω_f. This allows us to add to $M^{X_1\cdots X_n}_{0\leftarrow f}$ also the term

$$\lim_{\omega_1+\cdots+\omega_n\rightarrow-\omega_f}\overline{t}^{X_1\cdots X_n}(\omega_1,\omega_2,\cdots,\omega_n)(\boldsymbol{A}-\omega_f\mathbf{1})E^f(\omega_f)=0, \quad (124)$$

where we impose the limes in order to guarantee that the equality still holds, when the sum of the frequencies approaches minus the excitation energy. Thus, we can rewrite $M^{X_1\cdots X_n}_{0\leftarrow f}$ as

$$M_{0\leftarrow f}^{X_1\cdots X_n}(\omega_2,\cdots,\omega_n)=\overline{\xi}^{X_1\cdots X_n}(\omega_1,\omega_2,\cdots,\omega_n)\ E^f(\omega_f)+\lim_{\omega_1+\cdots+\omega_n\rightarrow-\omega_f}\overline{t}^{X_1\cdots X_n}(\omega_1,\omega_2,\cdots,\omega_n)(\boldsymbol{A}-\omega_f\mathbf{1})E^f(\omega_f)$$

$$+\hat{P}^{X_1\cdots X_n}\sum_{m=0}^{n-1}\frac{1}{m!(n-m)!}[\overline{\xi}^{X_1\cdots X_m}(\omega_1,\omega_2,\cdots,\omega_m)+\overline{t}^{X_1\cdots X_m}(\omega_1,\omega_2,\cdots,\omega_m)$$

$$\times(\boldsymbol{A}+(\omega_1\cdots+\omega_m)\mathbf{1})]\times E^{fX_{m+1}\cdots X_n}(\omega_f,\omega_{m+1},\cdots,\omega_n) \tag{125}$$

$$=\lim_{\omega_1+\cdots+\omega_n\rightarrow-\omega_f}\hat{P}^{X_1\cdots X_n}\sum_{m=0}^{n}\frac{1}{m!(n-m)!}\frac{d\{L\}_T^{X_1\cdots X_n}(\omega_1,\cdots,\omega_n)}{dt^{X_{m+1}\cdots X_n}(\omega_{m+1},\cdots,\omega_n)}E^{fX_{m+1}\cdots X_n}(\omega_f,\omega_{m+1},\cdots,\omega_n) \tag{126}$$

$$=\lim_{\omega_1+\cdots+\omega_n\rightarrow-\omega_f}\hat{P}^{X_1\cdots X_n}\sum_{m=0}^{n}\frac{1}{m!(n-m)!}\left(\frac{d^m\{\eta(t,\epsilon)+\overline{t}(t,\epsilon)(\boldsymbol{A}(t,\epsilon)+(\omega_1\cdots+\omega_n))\}}{d\epsilon_1(\omega_1)\cdots d\epsilon_m(\omega_m)}\right)_0$$

$$\times\left(\frac{d^{n-m}E^f(t,\epsilon)}{d\epsilon_{m+1}(\omega_{m+1})\cdots d\epsilon_n(\omega_n)}\right)_0 \tag{127}$$

$$=\left(\frac{d^n}{d\epsilon_1(\omega_1)\cdots d\epsilon_n(\omega_n)}\left\{\lim_{\rho\rightarrow0}e^{\rho t}\left[\eta(t,\epsilon)+\overline{t}(t,\epsilon)\left(\boldsymbol{A}(t,\epsilon)-i\frac{d}{dt}\right)\right]E^f(t,\epsilon)\right\}_T\right)_0. \tag{128}$$

The time- and field-dependent vector $\eta(t,\epsilon)$ is defined as

$$\eta_\mu(t,\epsilon)=\frac{d}{dt_\mu}\mathscr{W}(t,\epsilon). \tag{129}$$

The time- and field-dependent Jacobian $\boldsymbol{A}(t,\epsilon)$ was defined in Sec. IV. Thus the left multiphoton transition moments are the derivatives of the time-average of the ''left transition moment function'':

$$\mathscr{T}(t,\epsilon)=\lim_{\rho\rightarrow0}e^{\rho t}\left[\eta(t,\epsilon)+\overline{t}(t,\epsilon)\left(\boldsymbol{A}(t,\epsilon)-i\frac{d}{dt}\right)\right]E^f(t,\epsilon). \tag{130}$$

The time-average of this function is found to be variational in the Fourier components of $\overline{t}(t,\epsilon)$ and $E^f(t,\epsilon)$. To obtain a Lagrangian functional that is *stationary in all* its parameters, we complement $\mathscr{T}(t,\epsilon)$ with the constraints for the coupled cluster amplitudes $t(t,\epsilon)$ multiplied by ''transition moment'' Lagrangian multipliers:

$$L^{0f}(t,\epsilon)=\lim_{\rho\rightarrow0}\left\{e^{\rho t}\left[\eta(t,\epsilon)+\overline{t}(t,\epsilon)\left(\boldsymbol{A}(t,\epsilon)-i\frac{d}{dt}\right)\right]\right.$$

$$\times E^f(t,\epsilon)+e^{\rho t}\overline{M}^f(t,\epsilon)$$

$$\left.\times\left(e(t,\epsilon)-i\frac{d}{dt}t(t,\epsilon)\right)\right\}. \tag{131}$$

Per construction the same response equations for the ground state amplitudes t and Lagrangian multipliers $\overline{t}$ are obtained from the stationarity conditions for the time-average of the left transition moment Lagrangian $\{L^{0f}\}_T$ as were obtained from the time-average of the ground state quasienergy Lagrangian. From the stationarity of $\{L^{0f}\}_T$ in the Fourier components of $\overline{t}$ one gets the response equations for the right excited state vector $E^f(t,\epsilon)$ in the irregular perturbation expansion, derived in Sec. IV and from the stationarity of $\{L^{0f}\}_T$ in the coupled cluster amplitudes one obtains the response equations for the transition Lagrangian multipliers $\overline{M}^f$. The variational transition moment Lagrangian thus provides the means for a straightforward derivation and a clear mathematical interpretation of the intermediates $E^{fX_1\cdots X_n}$ and $\overline{M}^{fX_1\cdots X_n}$ as response of the right excited state vectors and transition Lagrangian multipliers, respectively.

Up to now we have ignored that in Eq. (125) a term was added to the transition moment $M_{0\leftarrow f}^{X_1\cdots X_n}$ which contained the singular response multipliers $\overline{t}^{X_1\cdots X_n}(\omega_1,\cdots,\omega_n)$ with $\omega_1=-\omega_f-\omega_2\cdots-\omega_n$. Due to the dependence of the transition moment Lagrangian multipliers $\overline{M}^f$ on the ground state quasienergy Lagrangian multipliers $\overline{t}$ the functional $\{L^{0f}\}_T^{(n)}$ contains a second singular term: $\overline{M}^{fX_1\cdots X_n}(\omega_1,\cdots,\omega_n)\ e^{(0)}$. In order to obtain well defined results we had to take the limes in Eqs. (124)–(131). For the derivatives of the time-average of $L^{0f}(t,\epsilon)$ the limes for $\rho\rightarrow0$ becomes limes for $\omega_1\rightarrow-\omega_f-\omega_2\cdots-\omega_n$. These singularities are a consequence of the fact that one calculates a response for a combination of frequencies that equals an excitation energy. We note that they do not pose a practical problem, because the singular terms are eliminated from the expressions for the transition moments when the $2n+1$ and $2n+2$ rules are applied.

There are two other aspects in which the transition moment Lagrangian differs from a quasienergy Lagrangian: The zeroth-order term of the transition moment Lagrangian van-

ishes. There exists no physical transition property that corresponds to the unperturbed energy in ground state response calculations. In difference to the quasienergy Lagrangian where time-averaging leads to the condition that the sum of the frequencies associated with the external fields is zero, time-averaging of the transition moment Lagrangian leads to the condition that the sum of the external field frequencies is equal to minus the excitation energy ω_f.

In the following paragraphs it will be shown that from the derivatives of the time-averaged left transition moment Lagrangian,

$$M^{X_1\cdots X_n}_{0\leftarrow f}(\omega_2,\cdots,\omega_n)=\left(\frac{d^n\{L^{0f}\}_T}{d\epsilon_1(\omega_1)\cdots d\epsilon_n(\omega_n)}\right)_0, \qquad (132)$$

the same expressions for the left form of the transition moments are obtained, as were found from the first residues of the ground state response functions, and how the variational formulation can be employed for a compact derivation of computational efficient expressions which are in accord with the $2n+1$ and $2n+2$ rules for the parameters and for the multipliers, respectively.

1. The first derivative of the time-averaged left transition moment Lagrangian

The first derivative of the time-averaged transition moment Lagrangian is found as

$$\left(\frac{d\{L^{0f}\}_T}{d\epsilon_A(-\omega_f)}\right)_0 = \lim_{\omega_A\rightarrow-\omega_f}\{[\eta^A+\overline{t^A}(\omega_A)(\boldsymbol{A}-\omega_f) + \boldsymbol{F}t^A(\omega_A)]E^f(\omega_f)+[\eta^{(0)}+\overline{t^{(0)}}\boldsymbol{A}] \times E^{fA}(\omega_f,\omega_A)+\overline{M}^{fA}(\omega_f,\omega_A)e^{(0)} + \overline{M}^f(\omega_f)[\xi^A+(\boldsymbol{A}+\omega_f)t^A(\omega_A)]. \qquad (133)$$

The stationarity conditions for the first derivatives of $\{L^{0f}\}_T$ with respect to its zeroth- and first-order variables gives the zeroth- and first-order response equations for t, $\overline{t}$, E^f, and $\overline{M}^f$. For the ground state amplitudes and Lagrangian multipliers, t and $\overline{t}$, one obtains the same equations as have been obtained from the ground state quasienergy Lagrangian, and the zeroth-order equation found for E^f is the usual excited state eigenvector equation. For the transition moment Lagrangian multipliers one finds the zeroth-order response Eq. (64).

According to the $2n+1$ and $2n+2$ rules, the zeroth-order response equations can now be employed to eliminate from Eq. (133) all terms containing first-order parameters or multipliers. The remaining terms are

$$M^A_{0\leftarrow f}=\left(\frac{d\{L^{0f}\}_T}{d\epsilon_A(-\omega_f)}\right)_0=\eta^A E^f(\omega_f)+\overline{M}^f(\omega_f)\xi^A. \qquad (134)$$

2. The second derivative of the time-averaged left transition moment Lagrangian

Before the $2n+1$ and $2n+2$ rules have been employed, the second derivative of the time-averaged left transition moment Lagrangian has the lenghty form:

$$\left(\frac{d^2\{L^{0f}\}^{AB}_T}{d\epsilon_A(-\omega_f-\omega_B)\ d\epsilon_B(\omega_B)}\right)_0$$

$$= \lim_{\omega_A\rightarrow-\omega_f-\omega_B}\hat{P}^{AB}\left\{\left[\frac{1}{2}\boldsymbol{G}t^A(\omega_A)t^B(\omega_B)+\frac{1}{2}\boldsymbol{F}t^{AB}(\omega_A,\omega_B)+\boldsymbol{F}^At^B(\omega_B)+\overline{t^A}(\omega_A)\boldsymbol{A}^B+\overline{t^A}(\omega_A)\boldsymbol{B}t^B(\omega_B)+\overline{t^{AB}}(\boldsymbol{A}-\omega_f\boldsymbol{1})\right]\right.$$
$$\times E^f(\omega_f)+[\eta^A+\boldsymbol{F}t^A(\omega_A)+\overline{t^A}(\omega_A)(\boldsymbol{A}-(\omega_f-\omega_B)\boldsymbol{1})]E^{fB}(\omega_f,\omega_B)$$
$$+\frac{1}{2}[\eta^{(0)}+\overline{t^{(0)}}\boldsymbol{A}]E^{fAB}(\omega_f,\omega_A,\omega_B)+\frac{1}{2}\overline{M}^{fAB}(\omega_f,\omega_A,\omega_B)e^{(0)}+\overline{M}^{fA}(\omega_f,\omega_A)[\xi^B+(\boldsymbol{A}-\omega_B)t^B(\omega_B)]+\overline{M}^f(\omega_f)$$
$$\left.\times\left[(\boldsymbol{A}-\omega_A-\omega_B)t^{AB}(\omega_A,\omega_B)+\frac{1}{2}\boldsymbol{B}t^B(\omega_B)t^A(\omega_A)+\boldsymbol{A}^Bt^A(\omega_A)\right]\right\}. \qquad (135)$$

From the stationarity conditions for the second derivatives of $\{L^{0f}\}_T$ one obtains the usual first-order equations for the ground state amplitudes and Lagrangian multipliers. For the right excited state vector and the transition moment Lagrangian multipliers one obtains the first-order response equations for E^{fA} and $\overline{M}^{fA}$, Eqs. (77) and (88), which in Sec. III could only be identified after repetitive application of the interchange technique. Employing the $2n+1$ and $2n+2$ rules one obtains the two-photon transition matrix element in the form of Eq. (76):

$$M^{AB}_{0\leftarrow f}(\omega_B)=\hat{P}^{AB}\left\{\left[\frac{1}{2}\boldsymbol{G}t^A(\omega_A)t^B(\omega_B)+\boldsymbol{F}^At^B(\omega_B)\right]E^f(\omega_f)+\overline{\xi^A}(\omega_A)E^{fB}(\omega_f,\omega_B)+\overline{M}^f(\omega_f)\left[\frac{1}{2}\boldsymbol{B}t^B(\omega_B)t^A(\omega_A)+\boldsymbol{A}^Bt^A(\omega_A)\right]\right\}, \qquad (136)$$

with $\omega_A=-\omega_f-\omega_B$.

3. The third and fourth derivative of the time-averaged left transition moment Lagrangian

Employing the $2n+1$ and $2n+2$ rules one obtains from the left transition moment Lagrangian immediately a computationaly efficient expression for the left form of the three-photon transition matrix element:

$$\begin{aligned}M^{ABC}_{0\leftarrow f}(\omega_B,\omega_C) = \hat{P}^{ABC}\Big\{&\frac{1}{6}\boldsymbol{H}E^f(\omega_f)t^A(\omega_A)t^B(\omega_B)t^C(\omega_C)+\frac{1}{6}\overline{M}^f(\omega_f)\boldsymbol{C}t^A(\omega_A)t^B(\omega_B)t^C(\omega_C)\\
&+\frac{1}{2}\overline{t}^A(\omega_A)\boldsymbol{C}E^f(\omega_f)t^B(\omega_B)t^C(\omega_C)+\frac{1}{2}\boldsymbol{G}E^{fA}(\omega_f,\omega_A)t^B(\omega_B)t^C(\omega_C)+\frac{1}{2}\overline{M}^{fA}(\omega_f,\omega_A)\boldsymbol{B}t^B(\omega_B)t^C(\omega_C)\\
&+\overline{t}^A(\omega_A)\boldsymbol{B}E^{fB}(\omega_f,\omega_B)t^C(\omega_C)+\boldsymbol{F}^AE^{fB}(\omega_f,\omega_B)t^C(\omega_C)+\overline{t}^A(\omega_A)\boldsymbol{B}^BE^f(\omega_f)t^C(\omega_C)\\
&+\frac{1}{2}\overline{M}^f(\omega_f)\boldsymbol{B}^At^B(\omega_B)t^C(\omega_C)+\overline{t}^A(\omega_A)\boldsymbol{A}^BE^{fC}(\omega_f,\omega_C)+\overline{M}^{fA}(\omega_f,\omega_A)\boldsymbol{A}^Bt^C(\omega_C)\Big\} \qquad (137)\\
=\hat{P}^{ABC}\Big\{&\frac{1}{2}\eta^{AB}(\omega_A,\omega_B)E^{fC}(\omega_f,\omega_C)+\frac{1}{2}\overline{M}^{fC}(\omega_f,\omega_C)\xi^{AB}(\omega_A,\omega_B)+\Big[\frac{1}{6}\boldsymbol{H}t^A(\omega_A)t^B(\omega_B)t^C(\omega_C)\\
&+\frac{1}{2}\overline{t}^A(\omega_A)\boldsymbol{C}t^B(\omega_B)t^C(\omega_C)+\overline{t}^A(\omega_A)\boldsymbol{B}^Bt^C(\omega_C)\Big]E^f(\omega_f)+\frac{1}{2}\overline{M}^f(\omega_f)\Big[\frac{1}{6}\boldsymbol{C}t^A(\omega_A)t^B(\omega_B)t^C(\omega_C)\\
&+\boldsymbol{B}^At^B(\omega_B)t^C(\omega_C)\Big]\Big\}, \qquad (138)\end{aligned}$$

where $\omega_A=-\omega_f-\omega_B-\omega_C$. If the eigenvector E^f and the eigenvalue ω_f are known, we can thus calculate the three-photon transition matrix element for a given pair of frequencies ω_B, ω_C by solving the two zeroth-order equations for $\overline{t}^{(0)}$ and $\overline{M}^f$ and the first-order equations for t^X, $\overline{t}^X$, E^{fX} and $\overline{M}^{fX}$. No second-order equations have to be solved.

The four-photon transition moments are obtained as

$$\begin{aligned}M^{ABCD}_{0\leftarrow f}(\omega_B,\omega_C,\omega_D) = \hat{P}^{ABCD}\Big\{&\frac{1}{4}\overline{\xi}^{AB}(\omega_A,\omega_B)E^{fCD}(\omega_f,\omega_C,\omega_D)+\frac{1}{6}\overline{M}^{fA}\xi^{BCD}(\omega_B,\omega_C,\omega_D)+\Big[\frac{1}{6}\boldsymbol{H}t^B(\omega_B)t^C(\omega_C)t^D(\omega_D)\\
&+\frac{1}{2}\boldsymbol{G}t^{BC}(\omega_B,\omega_C)t^D(\omega_D)+\frac{1}{2}\boldsymbol{F}^Bt^{CD}(\omega_C,\omega_D)+\frac{1}{2}\overline{t}^B(\omega_B)\boldsymbol{C}t^C(\omega_C)t^D(\omega_D)\\
&+\frac{1}{2}\overline{t}^B(\omega_B)\boldsymbol{B}t^{CD}(\omega_C,\omega_D)+\overline{t}^B(\omega_B)\boldsymbol{B}^Ct^D(\omega_D)\Big]E^{fA}(\omega_f,\omega_A)+\Big[\frac{1}{4}\boldsymbol{H}t^{AB}(\omega_A,\omega_B)t^C(\omega_C)t^D(\omega_D)\\
&+\frac{1}{8}\boldsymbol{G}t^{AB}(\omega_A,\omega_B)t^{CD}(\omega_C,\omega_D)+\frac{1}{6}\overline{t}^A(\omega_A)\boldsymbol{D}t^B(\omega_B)t^C(\omega_C)t^D(\omega_D)\\
&+\frac{1}{2}\overline{t}^A(\omega_A)\boldsymbol{C}t^{BC}(\omega_B,\omega_C)t^D(\omega_D)+\frac{1}{2}\overline{t}^A(\omega_A)\boldsymbol{B}^Bt^{CD}(\omega_C,\omega_D)\Big]E^f(\omega_f)\\
&+\overline{M}^f\Big[\frac{1}{24}\boldsymbol{D}t^A(\omega_A)t^B(\omega_B)t^C(\omega_C)t^D(\omega_D)+\frac{1}{4}\boldsymbol{C}t^{AB}(\omega_A,\omega_B)t^C(\omega_C)t^D(\omega_D)\\
&+\frac{1}{8}\boldsymbol{B}t^{AB}(\omega_A,\omega_B)t^{CD}(\omega_C,\omega_D)+\frac{1}{2}\boldsymbol{B}^At^{BC}(\omega_B,\omega_C)t^D(\omega_D)\Big]\Big\}, \qquad (139)\end{aligned}$$

with $\omega_A=-\omega_f-\omega_B-\omega_C-\omega_D$. Using the interchange technique, one can write the first term $\frac{1}{4}\overline{\xi}^{AB}(\omega_A,\omega_B)E^{fCD}(\omega_f,\omega_C,\omega_D)$ alternatively as $\frac{1}{4}\overline{t}^{AB}(\omega_A,\omega_B)\xi^{fCD}(\omega_f,\omega_C,\omega_D)$. This means that one has the choice to solve either the second-order equations for the ground-state Lagrangian multipliers or the second-order equations for the excited state vectors. In addition one has to solve the second-order equations for the ground state cluster amplitudes.

B. The Lagrangian for the right transition moments

To derive a Lagrangian for the right transition moments we can proceed along the same lines as for left transition moments: We start from the expression derived in Sec. III:

$$M^{X_1\cdots X_n}_{f\leftarrow 0}(\omega_2,\cdots,\omega_n)=\overline{E^f}(-\omega_f)\;\xi^{X_1\cdots X_n}(\omega_1,\omega_2,\cdots,\omega_n),$$
$$\omega_1=\omega_f-\omega_2\cdots-\omega_n. \qquad (140)$$

To find the function of which $M^{X_1\cdots X_n}_{f\leftarrow 0}$ is the nth derivative we add response equations for lower-order amplitudes multiplied by left excited state response vectors:

$$E^{fX_{m+1}\cdots X_n}(-\omega_f,\omega_{m+1},\cdots,\omega_n)\{\xi^{X_1\cdots X_m}(\omega_1,\omega_2,\cdots,\omega_m)+(\boldsymbol{A}-(\omega_1\cdots-\omega_m)\boldsymbol{1})t^{X_1\cdots X_m}(\omega_1,\omega_2,\cdots,\omega_m)\}=0, \qquad (141)$$

and the eigenvector equation for $\overline{E^f}$ multiplied by $t^{X_1\cdots X_n}$:

$$\lim_{\omega_1+\cdots+\omega_n\to\omega_f} \overline{E^f}(-\omega_f)(\boldsymbol{A}-\omega_f\mathbf{1})\; t^{X_1\cdots X_n}(\omega_1,\omega_2,\cdots,\omega_n)=0. \tag{142}$$

This allows us to rewrite $M^{X_1\cdots X_n}_{f\leftarrow 0}$ as

$$\begin{aligned} M^{X_1\cdots X_n}_{f\leftarrow 0}(\omega_2,\cdots,\omega_n) &= \overline{E^f}(-\omega_f)\,\xi^{X_1\cdots X_n}(\omega_1,\cdots,\omega_n)+\lim_{\omega_1+\cdots+\omega_n\to\omega_f}\overline{E^f}(-\omega_f)(\boldsymbol{A}-\omega_f\mathbf{1})t^{X_1\cdots X_n}(\omega_1,\cdots,\omega_n)\\ &\quad+\hat{P}^{X_1\cdots X_n}\sum_{m=0}^{n-1}\frac{1}{m!(n-m)!}\overline{E^f}^{X_{m+1}\cdots X_n}(-\omega_f,\omega_{m+1},\cdots,\omega_n)[\,\xi^{X_1\cdots X_m}(\omega_1,\omega_2,\cdots,\omega_m)\\ &\quad\times(\boldsymbol{A}-(\omega_1\cdots-\omega_m)\mathbf{1})+t^{X_1\cdots X_m}(\omega_1,\omega_2,\cdots,\omega_m)] \end{aligned} \tag{143}$$

$$=\lim_{\omega_1+\cdots+\omega_n\to\omega_f}\hat{P}^{X_1\cdots X_n}\sum_{m=0}^{n}\frac{1}{m!(n-m)!}\overline{E^f}^{X_{m+1}\cdots X_n}(-\omega_f,\omega_{m+1},\cdots,\omega_n)\frac{d\{L\}_T(\omega_1,\cdots,\omega_n)}{d\overline{t^X}_{m+1}\cdots X_n(\omega_{m+1},\cdots,\omega_n)} \tag{144}$$

$$=\lim_{\omega_1+\cdots+\omega_n\to\omega_f}\hat{P}^{X_1\cdots X_n}\sum_{m=0}^{n}\frac{1}{m!(n-m)!}\left(\frac{d^{n-m}\overline{E^f}(t,\epsilon)}{d\epsilon_{m+1}(\omega_{m+1})\cdots d\epsilon_n(\omega_n)}\right)_0\left(\frac{d(e(t,\epsilon)-i\,(d/dt)\,t(t,\epsilon))}{d\epsilon_1(\omega_1)\cdots d\epsilon_m(\omega_m)}\right)_0 \tag{145}$$

$$=\left(\frac{d}{d\epsilon_1(\omega_1)\cdots d\epsilon_n(\omega_n)}\left\{\lim_{\rho\to 0}e^{\rho t}\overline{E^f}(t,\epsilon)\left(e(t,\epsilon)-i\frac{d}{dt}t(t,\epsilon)\right)\right\}_T\right)_0. \tag{146}$$

From Eq. (146) we identify as the ''right transition moment'' the time-dependent coupled cluster equations multiplied by the left excited state vectors:

$$\mathscr{T}^{f0}(t,\epsilon)=\lim_{\rho\to 0}e^{\rho t}\overline{E^f}(t,\epsilon)\left(e(t,\epsilon)-i\frac{d}{dt}t(t,\epsilon)\right). \tag{147}$$

The time-average of $\mathscr{T}^{f0}$ is found to be variational in the Fourier components of $\overline{E^f}(t,\epsilon)$ and $t(t,\epsilon)$ and thus $\mathscr{T}^{f0}(t,\epsilon)$ is already the searched for variational functional:

$$L^{f0}(t,\epsilon)=\mathscr{T}^{f0}(t,\epsilon). \tag{148}$$

The right transition moment functional has a distinctly simpler structure as the left transition moment Lagrangian: Only two types of response equations have to be solved to calculate the right transition moments: the ground state cluster amplitude and the left excited state response equations. Similar as for the left transition moment function, we added in the derivation of $\mathscr{T}^{f0}(t,\epsilon)$ a term to the transition moments which is proportional to the amplitude responses $t^{X_1\cdots X_n}(\omega_1,\cdots,\omega_n)$ with $\omega_1=\omega_f-\omega_2\cdots-\omega_n$. Again, these singularities will not hinder the applicability of the right transition moment functional, because these terms are eliminated from the expressions for the transition moments, if the $2n+1$ and $2n+2$ rules are applied.

As for the left transition moments, the right transition moment Lagrangian differs from a quasienergy Lagrangian in that there exists no zeroth-order term. For the right transition moment Lagrangian time-averaging leads to the constraint that the sum of the frequencies of the external perturbations must be equal to the excitation energy of the considered state, in contrast to the minus sign found for the left transition moment Lagrangian.

1. The first derivative of the time-averaged right transition moment Lagrangian

The first derivative of the right transition moment Lagrangian is found as

$$\begin{aligned}\left(\frac{d\{L^{f0}\}_T}{d\epsilon_A(\omega_f)}\right)_0 &= \lim_{\omega_A\to\omega_f}\overline{E^f}(-\omega_f)[\,\xi^A+(\boldsymbol{A}-\omega_f)t^A(\omega_A)]\\ &\quad+\overline{E^f}^A(-\omega_f,\omega_A)e^{(0)}.\end{aligned} \tag{149}$$

From the stationarity conditions for the first derivatives of $\{L^{f0}\}_T$ one identifies the usual zeroth-order equations for the coupled cluster amplitudes and the eigenvector equations for the left excited state. Employing the $2n+1$ rule Eq. (149) reduces to

$$M^A_{f\leftarrow 0}=\left(\frac{d\{L^{f0}\}_T}{d\epsilon_A(\omega_f)}\right)_0=\overline{E^f}(-\omega_f)\,\xi^A. \tag{150}$$

2. The second derivative of the time-averaged right transition moment Lagrangian

The second derivative of the time-averaged right transition moment Lagrangian is found as

$$\left\langle \frac{d^2\{L^{f0}\}_T}{d\epsilon_A(\omega_f-\omega_B)\, d\epsilon_B(\omega_B)} \right\rangle_0 = \lim_{\omega_A\to\omega_f-\omega_B} \hat{P}^{AB}\Big\{ \overline{E^f}(-\omega_f)\Big[\frac{1}{2}(\boldsymbol{A}-\omega_f\mathbf{1})t^{AB}(\omega_A,\omega_B)+\frac{1}{2}\boldsymbol{B}t^A(\omega_A)t^B(\omega_B)+\boldsymbol{A}^A t^B(\omega_B)\Big] + \overline{E^{fA}}(-\omega_f,\omega_A)[\xi^B+(\boldsymbol{A}-\omega_B\mathbf{1})t^B(\omega_B)]+\frac{1}{2}\overline{E^{fAB}}(-\omega_f,\omega_A,\omega_B)e^{(0)}\Big\}. \tag{151}$$

From the variational condition for the second derivatives of $\{L^{f0}\}_T$ one obtains the usual first-order response equations for the ground state amplitudes and the first-order response equations for the left excited state vectors, Eq. (117), in the irregular response expansion as derived in Sec. IV. Employing the $2n+1$ and $2n+2$ rules one obtains for the right two-photon transition moments immediately the expression:

$$M^{AB}_{f\leftarrow 0}(\omega_B)=\hat{P}^{AB}\Big\{\overline{E^f}(-\omega_f)\Big[\frac{1}{2}\boldsymbol{B}t^A(\omega_A)t^B(\omega_B)+\boldsymbol{A}^B t^A(\omega_A)\Big]\Big\} \tag{152}$$

with $\omega_A=\omega_f-\omega_B$.

3. The third and fourth derivatives of the time-averaged right transition moment Lagrangian

Similarly one finds for the right three-photon transition moment the expression:

$$M^{ABC}_{f\leftarrow 0}(\omega_B,\omega_C)=\hat{P}^{ABC}\Big\{\frac{1}{6}\overline{E^f}(-\omega_f)\boldsymbol{C}t^A(\omega_A)t^B(\omega_B)t^C(\omega_C)+\frac{1}{2}\overline{E^f}(-\omega_f)\boldsymbol{B}^A t^B(\omega_B)t^C(\omega_C) + \frac{1}{2}\overline{E^{fA}}(-\omega_f,\omega_A)\boldsymbol{B}t^B(\omega_B)t^C(\omega_C)+\overline{E^{fA}}(-\omega_f,\omega_A)\boldsymbol{A}^B t^C(\omega_C)\Big\}, \tag{153}$$

with $\omega_A+\omega_B+\omega_C=\omega_f$ and for the four-photon transition moments:

$$M^{ABCD}_{f\leftarrow 0}(\omega_B,\omega_C,\omega_D)=\hat{P}^{ABCD}\Big\{\frac{1}{6}\overline{E^{fA}}(-\omega_f,\omega_A)\xi^{BCD}(\omega_B,\omega_C,\omega_D)+\overline{E^f}(-\omega_f)\Big[\frac{1}{4}\boldsymbol{C}t^{AB}(\omega_A,\omega_B)t^C(\omega_C)t^D(\omega_D) + \frac{1}{2}\boldsymbol{B}^A t^{BC}(\omega_B,\omega_C)t^D(\omega_D)+\frac{1}{4}\boldsymbol{B}t^{AB}(\omega_A,\omega_B)t^{CD}(\omega_C,\omega_D)+\frac{1}{24}\boldsymbol{D}t^A(\omega_A)t^B(\omega_B)t^C(\omega_C)t^D(\omega_D)\Big]\Big\}, \tag{154}$$

with $\omega_A+\omega_B+\omega_C+\omega_D=\omega_f$. As for the left transition moments, one has for the right three-photon transition moments only to solve first-order equations. First for the four-photon transition moments also the second-order response equations for the ground state cluster amplitudes have to be solved.

VI. DISCUSSION

Recent developments in coupled cluster response theory have made coupled cluster response functions available through high order.[26,31–33] Essential for this development has been the introduction of variational quasienergy Lagrangians[21–26] which made the mathematical structure more transparent and made it feasible to derive in a compact way computational tractable expressions for high-order coupled cluster response functions. In Appendixes A and B we give open-ended formulas for the coupled cluster response equations and for the response functions, in accord with the $2n+1$ and $2n+2$ rules.

In the present paper we used the mathematical framework of the coupled cluster quasienergy Lagrangian to analyze the general structure of the first residues of the ground state response functions. These residues are related to multiphoton transition moments and to absorption cross sections between the ground state and excited states. We showed that the first residues of the coupled cluster response functions have a similar structure as the residues of the exact response functions. They differ, however, in an explicit symmetrization as a consequence of the projection that is used in the definition of the coupled cluster energy and which leads to a biorthonormal representation for bra and ket states. Left and right transition moments obtained within the biorthonormal representation are different and physical observables f.x. as the absorption cross section are related to symmetrized products of left and right transition moments.

For exact states, left and right transition moments are related in a simple way to the projection of the right hand sides for the nth order response equations onto the excited state wave functions. We showed that similar equations hold in coupled cluster response theory: The ground to excited state n-photon transition moments are equal to the projections onto the excited state vectors of the right hand side vectors for the nth order response equations for the ground state cluster amplitudes and Lagrangian multipliers. These relations and the excited state response equations obtained in Sec. IV were used to derive left and right transition moment Lagrangians, from which the coupled cluster response expressions for multiphoton transition moments can be obtained as derivatives. The introduction of variational Lagrangians makes the mathematical structure of the coupled

cluster multiphoton transition moments more transparent and provides an interpretation of the intermediates as responses of the excited state vectors and transition moment Lagrangian multipliers. The variational formulation allows us to apply $2n+1$ and $2n+2$ rules directly without the roundabout way via the residues of the ground state response functions and facilitates a straightforward derivation of computational efficient expressions for high-order multiphoton transition moments.

A clear understanding of the mathematical structure of the multiphoton transition moments builds the basis for the derivation of efficient formulations of multiphoton transition moments between excited states and of excited states response functions. Both properties can be derived from the second residues of the ground state response functions or, alternatively, from the first residues of the multiphoton transition moments. An extension of the present approach in this direction will be subject to a forthcoming publication. The derivations given in the present paper were specialized to coupled cluster theory, but the approach developed here can likely serve as a model to obtain an efficient formulation for multiphoton transition moments for other *ab initio* methods. The first implementation and calculations of coupled cluster two-photon transition moments, based on the equations derived in Sec. V, are reported in the following article.[50]

ACKNOWLEDGMENTS

One of the authors (C.H.) thanks the Deutsche Forschungsgemeinschaft for financial support through a research fellowship (HA 2588/1-1). This work has been supported by the Danish Natural Science Research Council (Grant No. 9600856).

APPENDIX A: CLOSED EXPRESSIONS FOR THE RIGHT HAND SIDE VECTORS FOR THE *n*TH-ORDER RESPONSE EQUATIONS

The equations for the response of the amplitudes in order n are obtained from the requirement that the time-averaged Lagrangian of order $n+m$ is stationary with respect to variations in the Lagrangian multipliers of order m:

$$\frac{d\{L\}_T^{(n+m)}}{d\bar{t}^{(m)}(\omega_{n+1},\cdots,\omega_{n+m})} = \frac{d}{d\bar{t}^{(m)}(\omega_{n+1},\cdots,\omega_{n+m})} \times\left\{\frac{d^{n+m}L(,\epsilon)}{d\epsilon_1(\omega_1)\cdots d\epsilon_{n+m}(\omega_{n+m})}\right\} = 0. \tag{A1}$$

To this derivative of the Lagrangian contribute terms of the form $\boldsymbol{A}t^{(p)}$, $\boldsymbol{B}t^{(p)}t^{(q)}$, $\boldsymbol{C}t^{(p)}t^{(q)}t^{(r)}$, $\boldsymbol{D}t^{(p)}t^{(q)}t^{(r)}t^{(s)}$, ξ^X, $\boldsymbol{A}^X t^{(p)}$, or $\boldsymbol{B}^X t^{(p)}t^{(q)}$ where the sum of the orders of the response amplitudes is n for the first four types of terms and $n-1$ for the last two types of terms. The vector ξ^X contributes only in first-order. For $n>1$ one obtains for the derivative of Eq. (A1):

$$(\boldsymbol{A}-(\omega_1+\cdots+\omega_n)\mathbf{1})t^{X_1\cdots X_n}+\xi^{X_1\cdots X_n}=0, \tag{A2}$$

with the right hand side vectors:

$$\begin{aligned}\xi^{X_1\cdots X_n} = \hat{P}^{X_1\cdots X_n}\Bigg\{ &\frac{1}{(n-1)!}\boldsymbol{A}^{X_1}t^{X_2\cdots X_n} + \frac{1}{2}\sum_{i=1}^{n-1}\frac{1}{i!(n-i)!}\boldsymbol{B}t^{X_1\cdots X_i}t^{X_{i+1}\cdots X_n} + \frac{1}{2}\sum_{i=1}^{n-2}\frac{1}{i!(n-i-1)!}\boldsymbol{B}^{X_1}t^{X_2\cdots X_{i+1}}t^{X_{i+2}\cdots X_n} \\ &+\frac{1}{6}\sum_{i=2}^{n-1}\sum_{j=1}^{i-1}\frac{1}{j!(i-j)!(n-i)!}\boldsymbol{C}t^{X_1\cdots X_j}t^{X_{j+1}\cdots X_i}t^{X_{i+1}\cdots X_n} \\ &+\frac{1}{24}\sum_{i=3}^{n-1}\sum_{j=2}^{i-1}\sum_{k=1}^{j-1}\frac{1}{k!(j-k)!(i-j)!(n-i)!}\boldsymbol{D}t^{X_1\cdots X_k}t^{X_{k+1}\cdots X_j}t^{X_{j+1}\cdots X_i}t^{X_{i+1}\cdots X_n}\Bigg\}.\end{aligned} \tag{A3}$$

The response equations for the Lagrange multipliers of order n are obtained from the variational condition for the cluster amplitudes

$$\frac{d\{L\}_T^{(n+m)}}{dt^{(m)}(\omega_{n+1},\cdots,\omega_{n+m})} = \frac{d}{dt^{(m)}(\omega_{n+1},\cdots,\omega_{n+m})} \times\left\{\frac{d^{n+m}L(t,\epsilon)}{d\epsilon_1(\omega_1)\cdots d\epsilon_{n+m}(\omega_{n+m})}\right\} = 0. \tag{A4}$$

The expressions for these derivatives have a similar form as the respective derivatives with respect to the multiplers, but are more lengthy as now more types contribute: $\bar{t}^{(p)}\boldsymbol{A}$, $\boldsymbol{F}t^{(p)}$, $\bar{t}^{(p)}\boldsymbol{B}t^{(q)}$, $\boldsymbol{G}\bar{t}^{(p)}t^{(q)}$, $\bar{t}^{(p)}\boldsymbol{C}t^{(q)}t^{(r)}$, $\boldsymbol{H}t^{(p)}t^{(q)}t^{(r)}$, $\bar{t}^{(p)}\boldsymbol{D}t^{(q)}t^{(r)}t^{(s)}$, η^X, $\bar{t}^{(p)}\boldsymbol{A}^X$, $\boldsymbol{F}^X t^{(p)}$, $\bar{t}^{(p)}\boldsymbol{B}^X t^{(q)}$. The vector η^X contributes only in first-order. For $n>1$ the response equations for the Lagrangian multipliers become:

$$\bar{t}^{X_1\cdots X_n}(\boldsymbol{A}+(\omega_1+\cdots+\omega_n)\mathbf{1})+\bar{\xi}^{X_1\cdots X_n}=0, \tag{A5}$$

with the right hand side vectors:

$$\overline{\xi}^{X_1\cdots X_n}=\hat{P}^{X_1\cdots X_n}\Bigg\{\frac{1}{n!}\boldsymbol{F}t^{X_1\cdots X_n}+\frac{1}{(n-1)!}(\overline{t}^{X_2\cdots X_n}\boldsymbol{A}^{X_1}+\boldsymbol{F}^{X_1}t^{X_2\cdots X_n})+\sum_{i=1}^{n-1}\frac{1}{i!(n-i)!}\left(\overline{t}^{X_1\cdots X_i}\boldsymbol{B}+\frac{1}{2}\boldsymbol{G}t^{X_1\cdots X_i}\right)t^{X_{i+1}\cdots X_n}$$

$$+\frac{1}{2}\sum_{i=1}^{n-2}\frac{1}{i!(n-i-1)!}\overline{t}^{X_2\cdots X_{i+1}}\boldsymbol{B}^{X_1}t^{X_{i+2}\cdots X_n}+\sum_{i=2}^{n-1}\sum_{j=1}^{i-1}\frac{1}{j!(i-j)!(n-i)!}\left(\frac{1}{2}\overline{t}^{X_1\cdots X_j}\boldsymbol{C}+\frac{1}{6}\boldsymbol{H}t^{X_1\cdots X_j}\right)t^{X_{j+1}\cdots X_i}t^{X_{i+1}\cdots X_n}$$

$$+\frac{1}{6}\sum_{i=3}^{n-1}\sum_{j=2}^{i-1}\sum_{k=1}^{j-1}\frac{1}{k!(j-k)!(i-j)!(n-i)!}\overline{t}^{X_1\cdots X_k}\boldsymbol{D}t^{X_{k+1}\cdots X_j}t^{X_{j+1}\cdots X_i}t^{X_{i+1}\cdots X_n}\Bigg\}. \tag{A6}$$

APPENDIX B: CLOSED EXPRESSIONS FOR *n*TH-ORDER RESPONSE FUNCTION EMPLOYING THE $2n+1$ AND $2n+2$ RULES

1. Response functions of order $2n+1$

According to the $2n+1$ and $2n+2$ rules contribute to response function of order $2n+1$ only terms that contain the responses of the amplitudes and of the multipliers up to order n. The response functions of order $2n+1$ with $n>1$ are thus found as

$$\langle\langle X_1;X_2\cdots X_{2n+1}\rangle\rangle_{\omega_2\cdots\omega_{2n+1}}=\frac{1}{2}\,\hat{C}^{\pm\omega}\hat{P}^{X_1\cdots X_{2n+1}}\Bigg\{\frac{1}{n!n!}\left(\overline{t}^{X_1\cdots X_n}\,\boldsymbol{A}^{X_{2n+1}}+\frac{1}{2}\boldsymbol{F}^{X_{2n+1}}\,t^{X_1\cdots X_n}\right)t^{X_{n+1}\cdots X_{2n}}$$

$$+\sum_{j=\max(n+1,2)}^{2n}\sum_{i=\max(j-n,1)}^{\min(j-1,n)}\frac{1}{i!(j-i)!(2n+1-j)!}\left(\frac{1}{2}\overline{t}^{X_1\cdots X_i}\,\boldsymbol{B}+\frac{1}{6}\boldsymbol{G}\,t^{X_1\cdots X_i}\right)$$

$$\times t^{X_{i+1}\cdots X_j}t^{X_{j+1}\cdots X_{2n+1}}$$

$$+\sum_{j=\max(n,2)}^{2n-1}\sum_{i=\max(j-n,1)}^{\min(j-1,n)}\frac{1}{i!(j-i)!(2n-j)!2}\overline{t}^{X_1\cdots X_i}\,\boldsymbol{B}^{X_{2n+1}}\,t^{X_{i+1}\cdots X_j}t^{X_{j+1}\cdots X_{2n}}$$

$$+\sum_{k=\max(n+1,3)}^{2n}\sum_{j=\max(k-n,2)}^{k-1}\sum_{i=\max(j-n,1)}^{\min(j-1,n)}\frac{1}{i!(j-i)!(k-j)!(2n+1-k)!}$$

$$\times\left(\frac{1}{6}\overline{t}^{X_1\cdots X_i}\,\boldsymbol{C}+\frac{1}{24}\boldsymbol{H}\,t^{X_1\cdots X_i}\right)t^{X_{i+1}\cdots X_j}t^{X_{j+1}\cdots X_k}t^{X_{k+1}\cdots X_{2n+1}}$$

$$+\sum_{l=\max(n+1,4)}^{2n}\sum_{k=\max(l-n,3)}^{l-1}\sum_{j=\max(k-n,2)}^{k-1}\sum_{i=\max(j-n,1)}^{\min(j-1,n)}\frac{1}{i!(j-i)!(k-j)!(l-k)!(2n+1-l)!}$$

$$\times\frac{1}{24}\overline{t}^{X_1\cdots X_i}\,\boldsymbol{D}\,t^{X_{i+1}\cdots X_j}\,t^{X_{j+1}\cdots X_k}\,t^{X_{k+1}\cdots X_l}\,t^{X_{l+1}\cdots X_{2n+1}}\Bigg\}. \tag{B1}$$

2. Response functions of order $2n+2$:

To the response function of order $2n+2$ contribute terms with responses of amplitudes up to order $n+1$ and responses of the multipliers up to order n. For $n>1$ these response functions have the structure:

$$\langle\langle X_1;X_2\cdots X_{2n+2}\rangle\rangle_{\omega_2\cdots\omega_{2n+2}}=\frac{1}{2}\hat{C}^{\pm\omega}\hat{P}^{X_1\cdots X_{2n+2}}\Bigg\{\frac{1}{(n+1)!(n+1)!2}\boldsymbol{F}\ t^{X_1\cdots X_{n+1}}\ t^{X_{n+2}\cdots X_{2n+2}}$$

$$+\frac{1}{n!(n+1)!}(\overline{t}^{X_1\cdots X_n}\boldsymbol{A}^{X_{2n+2}}+\boldsymbol{F}^{X_{2n+2}}\ t^{X_1\cdots X_n})\ t^{X_{n+1}\cdots X_{2n+1}}$$

$$+\sum_{j=\max(n+1,2)}^{2n+1}\sum_{i=\max(j-n-1,1)}^{\min(j-1,n)}\frac{1}{i!(j-i)!(2n+2-j)!2}\overline{t}^{X_1\cdots X_i}\boldsymbol{B}\ t^{X_{i+1}\cdots X_j}t^{X_{j+1}\cdots X_{2n+2}}$$

$$+\sum_{j=\max(n+1,2)}^{2n+1}\sum_{i=\max(j-n-1,1)}^{\min(j-1,n+1)}\frac{1}{i!(j-i)!(2n+2-j)!6}\boldsymbol{G}\ t^{X_1\cdots X_i}\ t^{X_{i+1}\cdots X_j}t^{X_{j+1}\cdots X_{2n+2}}$$

$$+\sum_{j=\max(n,2)}^{2n}\sum_{i=\max(j-n-1,1)}^{\min(j-1,n)}\frac{1}{i!(j-i)!(2n+1-j)!2}\overline{t}^{X_1\cdots X_i}\boldsymbol{B}^{X_{2n+2}}\ t^{X_{i+1}\cdots X_j}t^{X_{j+1}\cdots X_{2n+1}}$$

$$+\sum_{k=\max(n+1,3)}^{2n+1}\sum_{j=\max(k-n-1,2)}^{k-1}\sum_{i=\max(j-n-1,1)}^{\min(j-1,n)}\frac{1}{i!(j-i)!(k-j)!(2n+2-k)!}$$

$$\times\frac{1}{6}\overline{t}^{X_1\cdots X_i}\boldsymbol{C}\ t^{X_{i+1}\cdots X_j}t^{X_{j+1}\cdots X_k}t^{X_{k+1}\cdots X_{2n+2}}+\sum_{k=\max(n+1,3)}^{2n+1}\sum_{j=\max(k-n-1,2)}^{k-1}\sum_{i=\max(j-n-1,1)}^{\min(j-1,n+1)}$$

$$\times\frac{1}{i!(j-i)!(k-j)!(2n+2-k)!}\frac{1}{24}\boldsymbol{H}\ t^{X_1\cdots X_i}\ t^{X_{i+1}\cdots X_j}t^{X_{j+1}\cdots X_k}t^{X_{k+1}\cdots X_{2n+2}}$$

$$+\sum_{l=\max(n+1,4)}^{2n+1}\sum_{k=\max(l-n-1,3)}^{l-1}\sum_{j=\max(k-n-1,2)}^{k-1}\sum_{i=\max(j-n-1,1)}^{\min(j-1,n)}$$

$$\times\frac{1}{i!(j-i)!(k-j)!(l-k)!(2n+2-l)!24}$$

$$\times\overline{t}^{X_1\cdots X_i}\boldsymbol{D}\ t^{X_{i+1}\cdots X_j}\ t^{X_{j+1}\cdots X_k}\ t^{X_{k+1}\cdots X_l}\ t^{X_{l+1}\cdots X_{2n+2}}\Bigg\}. \tag{B2}$$

APPENDIX C: CLOSED EXPRESSIONS FOR THE RIGHT HAND SIDE VECTORS FOR THE *n*TH-ORDER EXCITED STATE RESPONSE EQUATIONS

The response equations for the excited state amplitudes are obtained by expansion of Eqs. (109) and (110) in orders of the perturbation strengths. Choosing $\omega_\sigma=\omega_1+\cdots+\omega_n$ we get for the left and right excited state response vectors of order n the equations:

$$\sum_{m=0}^{n}\frac{1}{m!(n-m)!}\hat{P}^{X_1\cdots X_n}\left(\frac{d^m(\boldsymbol{A}(t,\epsilon)-(\omega_\sigma+\omega_f)\boldsymbol{1})}{d\epsilon_1(\omega_1)\cdots d\epsilon_m(\omega_m)}\right)_0\left(\frac{d^{n-m}E^f(t,\epsilon)}{d\epsilon_{m+1}(\omega_{m+1})\cdots d\epsilon_n(\omega_n)}\right)_0=0, \tag{C1}$$

$$\sum_{m=0}^{n}\frac{1}{m!(n-m)!}\hat{P}^{X_1\cdots X_n}\left(\frac{d^{n-m}\overline{E^f}(t,\epsilon)}{d\epsilon_{m+1}(\omega_{m+1})\cdots d\epsilon_n(\omega_n)}\right)_0\left(\frac{d^m(\boldsymbol{A}(t,\epsilon)+(\omega_\sigma-\omega_f)\boldsymbol{1})}{d\epsilon_1(\omega_1)\cdots d\epsilon_m(\omega_m)}\right)_0=0. \tag{C2}$$

The first derivative of the Jacobian $\boldsymbol{A}(t,\epsilon)$ with respect to the field strengths is

$$\left(\frac{d\boldsymbol{A}(t,\epsilon)}{d\epsilon_1(\omega_1)}\right)_0=\boldsymbol{B}t^{X_1}+\boldsymbol{A}^{X_1}, \tag{C3}$$

and the higher derivatives are obtained as

$$\left(\frac{d^n\boldsymbol{A}(t,\epsilon)}{d\epsilon_1(\omega_1)\cdots d\epsilon_n(\omega_n)}\right)_0=\hat{P}^{X_1\cdots X_n}\Bigg\{\frac{1}{n!}\boldsymbol{B}t^{X_1\cdots X_n}+\frac{1}{(n-1)!}\boldsymbol{B}^{X_1}t^{X_2\cdots X_n}+\frac{1}{2}\sum_{k=1}^{n-1}\frac{1}{k!(n-k)!}\boldsymbol{C}t^{X_1\cdots X_k}t^{X_{k+1}\cdots X_n}$$

$$+\frac{1}{6}\sum_{l=2}^{n-1}\sum_{k=1}^{k-1}\frac{1}{k!(l-k)!(n-l)!}\boldsymbol{D}t^{X_1\cdots X_k}t^{X_{k+1}\cdots X_l}t^{X_{l+1}\cdots X_n}\Bigg\}. \tag{C4}$$

If we insert this expansion into Eqs. (C1) and (C2) we get for the right excited state vectors the response equations:

$$(\boldsymbol{A}-(\omega_f+\omega_1+\cdots+\omega_n)\boldsymbol{1})E^{fX_1\cdots X_n}(\omega_f,\omega_1,\cdots,X_n)=-\xi^{fX_1\cdots X_n}(\omega_f,\omega_1,\cdots,X_n), \tag{C5}$$

with the right hand side vectors:

$$\xi^{fX_1\cdots X_n}=\hat{P}^{X_1\cdots X_n}\Bigg\{\frac{1}{(n-1)!}\boldsymbol{A}^{X_1}E^{fX_2\cdots X_n}+\sum_{i=1}^{n-1}\frac{1}{i!(n-i)!}\boldsymbol{B}E^{fX_1\cdots X_i}t^{X_{i+1}\cdots X_n}+\sum_{i=1}^{n-2}\frac{1}{i!(n-i-1)!}\boldsymbol{B}^{X_1}E^{fX_2\cdots X_{i+1}}t^{X_{i+2}\cdots X_n}$$
$$+\frac{1}{2}\sum_{i=2}^{n-1}\sum_{j=1}^{i-1}\frac{1}{j!(i-j)!(n-i)!}\boldsymbol{C}E^{fX_1\cdots X_j}t^{X_{j+1}\cdots X_i}t^{X_{i+1}\cdots X_n}$$
$$+\frac{1}{6}\sum_{i=3}^{n-1}\sum_{j=2}^{i-1}\sum_{k=1}^{j-1}\frac{1}{k!(j-k)!(i-j)!(n-i)!}\boldsymbol{D}E^{fX_1\cdots X_k}t^{X_{k+1}\cdots X_j}t^{X_{j+1}\cdots X_i}t^{X_{i+1}\cdots X_n}\Bigg\}. \tag{C6}$$

Similarly, we get for the left excited state response vectors the equations:

$$(\boldsymbol{A}+(\omega_1+\cdots+\omega_n-\omega_f)\boldsymbol{1})\bar{E}^{fX_1\cdots X_n}(\omega_f,\omega_1,\cdots,X_n)=-\xi^{fX_1\cdots X_n}(\omega_f,\omega_1,\cdots,X_n), \tag{C7}$$

$$\xi^{fX_1\cdots X_n}=\hat{P}^{X_1\cdots X_n}\Bigg\{\frac{1}{(n-1)!}\bar{E}^{fX_2\cdots X_n}\boldsymbol{A}^{X_1}+\sum_{i=1}^{n-1}\frac{1}{i!(n-i)!}\bar{E}^{fX_1\cdots X_i}\boldsymbol{B}t^{X_{i+1}\cdots X_n}+\sum_{i=1}^{n-2}\frac{1}{i!(n-i-1)!}\bar{E}^{fX_2\cdots X_{i+1}}\boldsymbol{B}^{X_1}t^{X_{i+2}\cdots X_n}$$
$$+\frac{1}{2}\sum_{i=2}^{n-1}\sum_{j=1}^{i-1}\frac{1}{j!(i-j)!(n-i)!}\bar{E}^{fX_1\cdots X_j}\boldsymbol{C}t^{X_{j+1}\cdots X_i}t^{X_{i+1}\cdots X_n}$$
$$+\frac{1}{6}\sum_{i=3}^{n-1}\sum_{j=2}^{i-1}\sum_{k=1}^{j-1}\frac{1}{k!(j-k)!(i-j)!(n-i)!}\bar{E}^{fX_1\cdots X_k}\boldsymbol{D}t^{X_{k+1}\cdots X_j}t^{X_{j+1}\cdots X_i}t^{X_{i+1}\cdots X_n}\Bigg\}. \tag{C8}$$

APPENDIX D: THE *n*TH-ORDER RESPONSE EQUATIONS FOR THE TRANSITION MOMENT LAGRANGIAN MULTIPLIERS

The response equations for the Lagrangian multipliers $\bar{M}^f$ are obtained by requiring that the derivatives of the time-averaged left transition moment Lagrangian are stationary in the ground-state cluster amplitudes:

$$\frac{d}{dt^{(m)}_{-\omega_\sigma}}\left\{\frac{d^{n+m}L^{0f}}{d\epsilon_1(\omega_1)\cdots d\epsilon_{n+m}(\omega_{n+m})}\right\}_T=0. \tag{D1}$$

One obtains for the response equations:

$$\bar{M}^{fX_1\cdots X_n}(\boldsymbol{A}+(\omega_f+\omega_1+\cdots+\omega_f)\boldsymbol{1})=-\hat{P}^{X_1\cdots X_n}\Bigg\{\frac{1}{n!}\boldsymbol{F}E^{fX_1\cdots X_n}+\frac{1}{(n-1)!}\bar{M}^{fX_2\cdots X_n}\boldsymbol{A}^{X_1}+\frac{1}{(n-1)!}\boldsymbol{F}^{X_1}E^{fX_2\cdots X_n}$$
$$+\sum_{i=0}^{n-1}\frac{1}{i!(n-i)!}(\bar{M}^{fX_1\cdots X_i}\boldsymbol{B}+\boldsymbol{G}E^{fX_1\cdots X_i})t^{X_{i+1}\cdots X_n}$$
$$+\sum_{i=1}^{n}\frac{1}{i!(n-i)!}\bar{t}^{X_1\cdots X_i}\boldsymbol{B}E^{fX_{i+1}\cdots X_n}+\sum_{i=1}^{n-2}\frac{1}{i!(n-i-1)!}(\bar{M}^{fX_2\cdots X_{i+1}}\boldsymbol{B}^{X_1}t^{X_{i+2}\cdots X_n}$$
$$+\bar{t}^{X_2\cdots X_{i+1}}\boldsymbol{B}^{X_1}E^{fX_{i+2}\cdots X_n})+\frac{1}{2}\sum_{i=1}^{n-1}\sum_{j=0}^{i-1}\frac{1}{j!(i-j)!(n-i)!}(\bar{M}^{fX_1\cdots X_j}\boldsymbol{C}$$
$$+\boldsymbol{H}E^{fX_1\cdots X_j})t^{X_{j+1}\cdots X_i}t^{X_{i+1}\cdots X_n}$$
$$+\sum_{i=1}^{n-1}\sum_{j=1}^{i}\frac{1}{j!(i-j)!(n-i)!}\bar{t}^{X_1\cdots X_j}\boldsymbol{C}E^{fX_{j+1}\cdots X_i}t^{X_{i+1}\cdots X_n}$$
$$+\frac{1}{6}\sum_{i=2}^{n-1}\sum_{j=1}^{i-1}\sum_{k=0}^{j-1}\frac{1}{k!(j-k)!(i-j)!(n-i)!}\bar{M}^{fX_1\cdots X_k}\boldsymbol{D}t^{X_{k+1}\cdots X_j}t^{X_{j+1}\cdots X_i}t^{X_{i+1}\cdots X_n}$$
$$+\frac{1}{2}\sum_{i=2}^{n-1}\sum_{j=1}^{i-1}\sum_{k=1}^{j}\frac{1}{k!(j-k)!(i-j)!(n-i)!}\bar{t}^{X_1\cdots X_k}\boldsymbol{D}E^{fX_{k+1}\cdots X_j}t^{X_{j+1}\cdots X_i}t^{X_{i+1}\cdots X_n}\Bigg\}. \tag{D2}$$

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