Derivation of coupled cluster excited states response functions and multiphoton transition moments between two excited states as derivatives of variational functionals

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Based on an analysis of the second residues of the coupled cluster ground state response functions, general expressions are derived for multiphoton transition moments between two excited states and for excited states response functions. The second residues are rewritten as derivatives of variational functionals and computational efficient expressions are obtained in accordance with the $2n+1$ and $2n+2$ rules. For the excited state response functions secular divergent terms are removed by reformulating the expressions that are identified from the second residues of the ground state response functions as derivatives of an excited state quasienergy Lagrangian. Explicit expressions are given for coupled cluster one-, two- and three-photon transition moments between two excited states and for excited states first-order properties and linear and quadratic response functions.
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I. INTRODUCTION

Quantum-mechanical calculations of transition moments and excited state properties have in the past mainly been performed by carrying out an explicit optimization of the excited state wave functions. This requires often a multiconfigurational wave function ansatz and, if dynamical electron correlation effects need to be considered, demanding multireference correlation methods must be used. Olsen and Jørgensen demonstrated in their derivation of response theory for exact and MCSCF wave functions[1,2] how poles and residues of ground state response functions can be utilized to obtain an alternative approach for excited state calculations. Excitation energies were obtained from the poles of the response functions and from the first residues of the linear, quadratic and cubic response functions they identified formulas for one-, two- and three-photon transition moments. From the second residues of the quadratic and cubic response functions expressions were derived for excited states first- and second-order properties.[1] Implementations of this approach for SCF and MCSCF wave functions were reported in Refs. 3–6.

In coupled cluster theory, the determination of excitation energies as poles of the ground state response functions has been used successfully[7–10] and accurate excitation energies have been obtained employing hierarchies of coupled cluster models.[11–15] Analytic excited state first-order properties and energy gradients based on the response approach to excitation energies have been implemented f.x. for the coupled cluster singles and doubles (CCSD) method in the context of the equation-of-motion coupled cluster approach[16,17] and the theory of second derivatives of excited states with respect to general frequency-independent perturbations was derived by Stanton and Gauss in Ref. 18. Recently an AO integral-direct implementation has been reported for one- and two-photon transition moments and for excited states first-order properties in the framework of coupled cluster response theory for the coupled cluster models CCS, CC2 and CCSD.[19,20]

In Ref. 21 we analyzed the structure of the first residues of coupled cluster response functions and derived the expressions for multiphoton transition moments between the ground state and an excited state. We formulated the multiphoton transition moments as derivatives of variational transition moment functionals and used variational perturbation theory to obtain expressions in accord with $2n+1$ and $2n+2$ rules.[22–24]

In the present paper we extend the derivation of Ref. 21 to transition moments between two excited states and to frequency-dependent excited state properties. These quantities can be obtained from the second residues of ground state response functions or equivalently from the first residues of ground to excited state multiphoton transition moments. We analyze the structure of these residues and derive expressions for multiphoton transition moments between two excited states and for excited state response functions.

The expressions identified from the residues have two disadvantages: They involve unnecessary high-order response intermediates and for excited state properties they contain so-called secular divergencies, terms which become singular in the static limit but cancel each other mutually. The unnecessary high-order response intermediates can be removed if the multiphoton transition moments are rewritten as derivatives of a variational functional. This allows us to apply variational perturbation theory to derive expressions which obey the $2n+1$ and $2n+2$ rules. We derive such a variational functional in Sec. IV and exemplify its use in Sec. V by the derivation of expressions for the one- through three-photon transition moments. In Sec. VI we discuss a phase-isolated perturbation expansion for the excited state wave functions in coupled cluster response theory. This alternative parametrization of the excited states is used to remove the secular divergent terms in the excited state response functions. We devise in Sec. VII an excited state

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quasienergy Lagrangian which leads to excited state response functions and response equations which are free of secular divergent terms and therefore are numerical stable in the static limit. Explicit expressions are derived for coupled cluster excited states linear and quadratic response functions.

II. MULTIPHOTON TRANSITION MOMENTS IN COUPLED CLUSTER RESPONSE THEORY

To introduce the notation and the basic concepts of coupled cluster response theory a brief review of the derivation of coupled cluster response functions and multiphoton transition moments between an excited state and the ground state will be in place. For details of the derivations we refer to Refs. 21, 25 and references cited therein. Coupled cluster response functions are most conveniently derived using the quasienergy Lagrangian:[13,21,25–27]

$$L(t,\boldsymbol{\epsilon})=\mathscr{W}(t,\boldsymbol{\epsilon})+\sum_{\mu}\overline{t}_{\mu}(t,\boldsymbol{\epsilon})\left(e_{\mu}(t,\boldsymbol{\epsilon})-i\frac{d}{dt}t_{\mu}(t,\boldsymbol{\epsilon})\right), \tag{1}$$

with the quasienergy defined as

$$\mathscr{W}(t,\boldsymbol{\epsilon})=\langle \mathrm{HF}|\hat{H}(t,\boldsymbol{\epsilon})\exp(\hat{T}(t,\boldsymbol{\epsilon}))|\mathrm{HF}\rangle, \tag{2}$$

and

$$e_{\mu}(t,\boldsymbol{\epsilon})=\langle\overline{\mu}|\exp(-\hat{T}(t,\boldsymbol{\epsilon}))\hat{H}(t,\boldsymbol{\epsilon})\exp(\hat{T}(t,\boldsymbol{\epsilon}))|\mathrm{HF}\rangle. \tag{3}$$

The cluster operator is defined as $\hat{T}(t,\boldsymbol{\epsilon})=\Sigma_{\mu}t_{\mu}(t,\boldsymbol{\epsilon})\hat{\tau}_{\mu}$ and $\overline{t}_{\mu}(t,\boldsymbol{\epsilon})$ are Lagrangian multipliers. We consider a (quasi-)periodic time-dependent perturbation, which can be decomposed into a sum over Fourier components as:

$$\hat{H}(t,\boldsymbol{\epsilon})=\hat{H}^{(0)}+\hat{V}(t,\boldsymbol{\epsilon}), \tag{4}$$

$$\hat{V}(t,\boldsymbol{\epsilon})=\sum_{j}\hat{H}^{X_j}\boldsymbol{\epsilon}_j(\omega_j)e^{-i\omega_j t}, \tag{5}$$

where $\hat{H}^{X_j}$ are time-independent hermitian one-electron operators. $\hat{V}(t,\boldsymbol{\epsilon})$ is assumed to be Hermitian. Therefore the field strengths are required to fulfill $\boldsymbol{\epsilon}_j(-\omega_j)=\boldsymbol{\epsilon}_j(\omega_j)^*$. The time-evolution is determined by the condition that the time-average of the quasienergy Lagrangian is stationary with respect to variations of the cluster amplitudes and the Lagrangian multipliers:[25,28]

$$\delta\{L(t,\boldsymbol{\epsilon})\}_T=\delta\left\{\lim_{t_0\to\infty}\frac{1}{2t_0}\int_{-t_0}^{+t_0}L(t,\boldsymbol{\epsilon})dt\right\}=0. \tag{6}$$

If one expands the cluster amplitudes and the Lagrangian multipliers in orders of the field strengths

$$t_{\mu}(t,\boldsymbol{\epsilon})=\sum_{n=0}^{\infty}\frac{1}{n!}\sum_{j_1}\cdots\sum_{j_n}t_{\mu}^{X_{j_1}\cdots X_{j_n}}(\omega_{j_1},\ldots,\omega_{j_n})\times\prod_{m=1}^{n}\boldsymbol{\epsilon}_{j_m}(\omega_{j_m})e^{-i\omega_{j_m}t}, \tag{7}$$

$$\overline{t}_{\mu}(t,\boldsymbol{\epsilon})=\sum_{n=0}^{\infty}\frac{1}{n!}\sum_{j_1}\cdots\sum_{j_n}\overline{t}_{\mu}^{X_{j_1}\cdots X_{j_n}}(\omega_{j_1},\ldots,\omega_{j_n})\times\prod_{m=1}^{n}\boldsymbol{\epsilon}_{j_m}(\omega_{j_m})e^{-i\omega_{j_m}t}. \tag{8}$$

Equation (6) becomes a set of response equations for the Fourier components of $t_{\mu}(t,\boldsymbol{\epsilon})$ and $\overline{t}_{\mu}(t,\boldsymbol{\epsilon})$. For order $n>0$ these equations can be written in the form

$$(\mathbf{A}-(\omega_1+\ldots+\omega_n)\mathbf{1})t^{X_1\cdots X_n}(\omega_1,\ldots,\omega_n)=-\xi^{X_1\cdots X_n}(\omega_1,\ldots,\omega_n), \tag{9}$$

$$\overline{t}^{X_1\cdots X_n}(\omega_1,\ldots,\omega_n)(\mathbf{A}+(\omega_1+\ldots+\omega_n)\mathbf{1})=-\overline{\xi}^{X_1\cdots X_n}(\omega_1,\ldots,\omega_n), \tag{10}$$

where the matrix $\mathbf{A}$ is the coupled cluster Jacobian:

$$A_{\mu\nu}=\left(\frac{\partial^2 L}{\partial\overline{t}_{\mu}\partial t_{\nu}}\right)_{\epsilon_j(\omega_j)=0}. \tag{11}$$

Explicit expressions for the right hand side vectors $\xi^{X_1\cdots X_n}$ and $\overline{\xi}^{X_1\cdots X_n}$ have been derived in Appendix A of Ref. 21. The response functions are obtained as derivatives of the real part of the time-averaged quasienergy Lagrangian with respect to the field strengths:[25,26,29,30]

$$\langle\langle X_1;X_2,\ldots,X_n\rangle\rangle_{\omega_1,\ldots,\omega_n}=\left(\frac{d^n\{\frac{1}{2}L(t,\boldsymbol{\epsilon})+\frac{1}{2}L(t,\boldsymbol{\epsilon})^*\}_T}{d\boldsymbol{\epsilon}_1(\omega_1)\ldots d\boldsymbol{\epsilon}_n(\omega_n)}\right)_{\epsilon_i(\omega_i)=0}. \tag{12}$$

The right hand side of Eq. (12) is explicitly symmetrized with respect to complex conjugation of $L(t,\boldsymbol{\epsilon})$. This is necessary because the coupled cluster (quasi-)energy is defined by the projection type expression $\langle\mathrm{HF}|\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle$ which without such a symmetrization would give an artificial imaginary contribution if complex Hermitian operators, as for example the time-dependent perturbation $\hat{V}(t,\boldsymbol{\epsilon})$, are included in the Hamiltonian. In the limit of a complete cluster expansion this symmetrization becomes, as in exact state response theory, redundant.

The coupled cluster approximation for ground–excited state multiphoton transition moments can be identified from the first residues of the response functions. Of particular interest are the first residues of the even order response functions which determine the absorption cross sections for multiphoton transitions. For exact states these residues take the form:

$$\lim_{\omega_1+\ldots+\omega_n\to\omega_f}(\omega_1+\ldots+\omega_n-\omega_f)\langle\langle X_1;X_2,\ldots,X_{2n}\rangle\rangle_{\omega_2,\ldots,\omega_{2n}}=M_{0\leftarrow f}^{X_{n+1}\cdots X_{2n}}(\omega_{n+2},\ldots,\omega_{2n})M_{f\leftarrow 0}^{X_1\cdots X_n}(\omega_2,\ldots,\omega_n), \tag{13}$$

where $M_{0\leftarrow f}^{X_1\cdots X_n}(\omega_2,\ldots,\omega_n)$ and $M_{f\leftarrow 0}^{X_1\cdots X_n}(\omega_2,\ldots,\omega_n)$ are left and right n-photon transition moments between the ground state and the excited state f. With ω_f we denote the excitation energy from the ground state to state f.

For exact states, left and right transition moments for the same operators and for frequencies of the same absolute values but of opposite signs are related by complex conjugation:[21] $M^{X_1\ldots X_n}_{f\leftarrow i}(\omega_2,\ldots,\omega_n)^* = M^{X_1\ldots X_n}_{i\leftarrow f}(-\omega_2,\ldots,-\omega_n)$. This symmetry is not retained in coupled cluster response theory. As a consequence of the symmetrization with respect to complex conjugation in Eq. (12) the first residues of the coupled cluster response functions have to be compared with the explicitly symmetrized expression:

$$\lim_{\omega_1+\ldots+\omega_n\rightarrow\omega_f}(\omega_1+\ldots+\omega_n-\omega_f)\langle\langle X_1;\ X_2,\ldots,X_{2n}\rangle\rangle_{\omega_2,\ldots,\omega_{2n}}$$
$$=\tfrac{1}{2}\{M^{X_{n+1}\ldots X_{2n}}_{0\leftarrow f}(\omega_{n+2},\ldots,\omega_{2n})M^{X_1\ldots X_n}_{f\leftarrow 0}(\omega_2,\ldots,\omega_n)$$
$$+M^{X_1\ldots X_n}_{0\leftarrow f}(-\omega_2,\ldots,-\omega_n)^*$$
$$\times M^{X_{n+1}\ldots X_{2n}}_{f\leftarrow 0}(-\omega_{n+2},\ldots,-\omega_{2n})^*\}. \tag{14}$$

In Ref. 21 we showed that the first residues of the coupled cluster response functions have the structure

$$\lim_{\omega_1,\ldots,\omega_n\rightarrow\omega_f}(\omega_1+\ldots\omega_n-\omega_f)\langle\langle X_1;\ X_2,\ldots,X_{2n}\rangle\rangle_{\omega_2,\ldots,\omega_{2n}}$$
$$=\tfrac{1}{2}([\overline{\xi}^{X_{n+1}\ldots X_{2n}}(\omega_{n+1},\omega_{n+2},\ldots,\omega_{2n})E^f(\omega_f)]$$
$$\times[\overline{E}^f(-\omega_f)\xi^{X_1\ldots X_n}(\omega_1,\omega_2,\ldots,\omega_n)]$$
$$+[\overline{\xi}^{X_1\ldots X_n}(-\omega_1,-\omega_2,\ldots,-\omega_n)E^f(\omega_f)]^*$$
$$\times[\overline{E}^f(-\omega_f)\xi^{X_{n+1}\ldots X_{2n}}(-\omega_{n+1},-\omega_{n+2},\ldots,-\omega_{2n})]^*), \tag{15}$$

where on the right hand side $\omega_1=\omega_f-\omega_2\ldots-\omega_n$ and $\omega_{n+1}=-\omega_f-\omega_{n+2}\ldots-\omega_{2n}$. The intermediates $\overline{E}^f(-\omega_f)$ and $E^f(\omega_f)$ are the left and right eigenvectors of the coupled cluster Jacobian $\mathbf{A}$ for the eigenvalue ω_f. From the last equation we identified for the left and right coupled cluster n-photon transition moments between the ground state and an excited state f the expressions:[21]

$$M^{X_1\ldots X_n}_{0\leftarrow f}(\omega_2,\ldots,\omega_n)=\overline{\xi}^{X_1\ldots X_n}(\omega_1,\ldots,\omega_n)E^f(\omega_f),$$
$$\omega_1=-\omega_f-\omega_2\ldots-\omega_n, \tag{16}$$
$$M^{X_1\ldots X_n}_{f\leftarrow 0}(\omega_2,\ldots,\omega_n)=\overline{E}^f(-\omega_f)\xi^{X_1\ldots X_n}(\omega_1,\ldots,\omega_n),$$
$$\omega_1=\omega_f-\omega_2\ldots-\omega_n. \tag{17}$$

Equations (16) and (17) provide a simple basis for the derivation of closed expressions for the coupled cluster ground–excited state transition moments, but are not efficient from a computational point of view, because the right hand side vectors $\xi^{X_1\ldots X_n}$ and $\overline{\xi}^{X_1\ldots X_n}$ require the solution of response equations up to order $(n-1)$ for the Lagrange multipliers $\overline{t}$ and up to order n for the cluster amplitudes t. These high-order response vectors can be eliminated if one solves instead for some additional low-order intermediates. In Ref. 21 we showed that Eqs. (16) and (17) can be formulated as nth derivatives of two time-averaged functionals which, augmented with the constraints for the wave function variables, could be used as variational ''transition moment Lagrangians,'' from which expressions for multiphoton transition moments are obtained as derivatives:

$$\{L^{0f}\}_T=\lim_{\rho\rightarrow 0}\left\{e^{\rho t}\left[\eta(t,\epsilon)+\overline{t}(t,\epsilon)\left(\mathbf{A}(t,\epsilon)-i\frac{d}{dt}\right)\right]E^f(t,\epsilon)\right.$$
$$\left.+e^{\rho t}\overline{M}^f(t,\epsilon)\left(e(t,\epsilon)-i\frac{d}{dt}t(t,\epsilon)\right)\right\}_T, \tag{18}$$

$$\{L^{f0}\}_T=\lim_{\rho\rightarrow 0}\left\{e^{\rho t}\overline{E}^f(t,\epsilon)\left(e(t,\epsilon)-i\frac{d}{dt}t(t,\epsilon)\right)\right\}_T. \tag{19}$$

The field- and time-dependent vector $\eta(t,\epsilon)$ and the Jacobian $\mathbf{A}(t,\epsilon)$ are defined as derivatives of the ground state quasienergy and the coupled cluster equations:

$$\eta_\mu(t,\epsilon)=\frac{d}{dt_\mu}\mathscr{W}(t,\epsilon), \tag{20}$$

$$\mathbf{A}(t,\epsilon)_{\mu\nu}=\frac{d}{dt_\nu}e_\mu(t,\epsilon). \tag{21}$$

The damping factor $e^{\rho t}$ was introduced to ensure the proper convergence of the transition moment functionals when the sum of the external field frequencies approaches the excitation energy ω_f. $\overline{E}^f(t,\epsilon)$ and $E^f(t,\epsilon)$ are field- and time-dependent left and right excited state vectors:

$$\overline{E}^f(t,\epsilon)=\sum_{n=0}^{\infty}\frac{1}{n!}\sum_{j_1}\ldots\sum_{j_n}\overline{E}^{fX_{j_1}\ldots X_{j_n}}(-\omega_f,\omega_{j_1},\ldots,\omega_{j_n})$$
$$\times e^{i\omega_f t}\prod_{m=1}^{n}\epsilon_{j_m}(\omega_{j_m})e^{-i\omega_{j_m}t}, \tag{22}$$

$$E^f(t,\epsilon)=\sum_{n=0}^{\infty}\frac{1}{n!}\sum_{j_1}\ldots\sum_{j_n}E^{fX_{j_1}\ldots X_{j_n}}(\omega_f,\omega_{j_1},\ldots,\omega_{j_n})$$
$$\times e^{-i\omega_f t}\prod_{m=1}^{n}\epsilon_{j_m}(\omega_{j_m})e^{-i\omega_{j_m}t}. \tag{23}$$

$\overline{M}^f(t,\epsilon)$ are Lagrangian multipliers that impose the coupled cluster equations as constraints for the cluster amplitudes $t(t,\epsilon)$. From the Lagrangian $\{L^{0f}\}_T$, the left ground state–excited state multiphoton transition moments are obtained as:

$$M^{X_1\ldots X_n}_{0\leftarrow f}(\omega_2,\ldots,\omega_n)=\left(\frac{d^n\{L^{0f}\}_T}{d\epsilon_1(\omega_1)\ldots d\epsilon_n(\omega_n)}\right)_0. \tag{24}$$

Similarly, the right ground state–excited state transition moments are obtained as:

$$M^{X_1\ldots X_n}_{f\leftarrow 0}(\omega_2,\ldots,\omega_n)=\left(\frac{d^n\{L^{f0}\}_T}{d\epsilon_1(\omega_1)\ldots d\epsilon_n(\omega_n)}\right)_0. \tag{25}$$

The variational conditions for the time-averaged Lagrangians $\{L^{0f}\}_T$ and $\{L^{f0}\}_T$ determine the time-evolution of the variables $t(t,\epsilon)$, $\overline{t}(t,\epsilon)$, $E^f(t,\epsilon)$, $\overline{E}^f(t,\epsilon)$, and $\overline{M}^f(t,\epsilon)$. By construction, the transition moment functionals give for the cluster amplitudes and the ground state Lagrang-

ian multipliers the same response equations as obtained from the ground state quasienergy Lagrangian $\{L\}_T$. For the left and right excited state vectors one obtains in zeroth-order the eigenvalue equations for the unperturbed left and right excited state vectors,

$$\overline{E}^f(-\omega_f)(\mathbf{A}-\omega_f\mathbf{1})=0, \tag{26}$$

$$(\mathbf{A}-\omega_f\mathbf{1})E^f(\omega_f)=0, \tag{27}$$

and the higher-order response equations can be cast into the form

$$\overline{E}^{fX_1\ldots X_n}(-\omega_f,\omega_1,\ldots,\omega_n)(\mathbf{A}+(\omega_1+\ldots+\omega_n-\omega_f)\mathbf{1}) = -\overline{\xi}^{fX_1\ldots X_n}(-\omega_f,\omega_1,\ldots,\omega_n), \tag{28}$$

$$(\mathbf{A}-(\omega_1+\ldots+\omega_n+\omega_f)\mathbf{1})E^{fX_1\ldots X_n}(\omega_f,\omega_1,\ldots,\omega_n) = -\xi^{fX_1\ldots X_n}(\omega_f,\omega_1,\ldots,\omega_n). \tag{29}$$

The equations for the excited state vectors obtained from the transition moment Lagrangians $\{L^{f0}\}_T$ and $\{L^{0f}\}_T$ are equivalent to the equations obtained by expansion of the effective Schrödinger equations:

$$\mathbf{A}(t,\boldsymbol{\epsilon})E^f(t,\boldsymbol{\epsilon})=i\frac{d}{dt}E^f(t,\boldsymbol{\epsilon}), \tag{30}$$

$$\overline{E}^f(t,\boldsymbol{\epsilon})\mathbf{A}(t,\boldsymbol{\epsilon})=-i\frac{d}{dt}\overline{E}^f(t,\boldsymbol{\epsilon}), \tag{31}$$

which can be derived from a generalized Frenkel variation principle.[21] The response equations for the transition moment Lagrangian $\overline{M}^{fX_1\ldots X_n}$ multipliers are of the form

$$\overline{M}^{fX_1\ldots X_n}(\omega_f,\omega_1,\ldots,\omega_n)(\mathbf{A}+(\omega_1+\ldots+\omega_n+\omega_f)\mathbf{1}) = -\overline{m}^{fX_1\ldots X_n}(\omega_f,\omega_1,\ldots,\omega_n). \tag{32}$$

Explicit expressions for the right hand side vectors $\overline{\xi}^{fX_1\ldots X_n}$, $\xi^{fX_1\ldots X_n}$ and $\overline{m}^{fX_1\ldots X_n}$ can be found in Appendices C and D of Ref. 21.

From the variational formulation of the transition moments it follows immediately that one can formulate $2n+1$ and $2n+2$ rules for the response intermediates: The responses of the cluster amplitudes and the right eigenvectors up to order n are sufficient to calculate transition moments up to photon number $2n+1$, and from the responses of the Lagrangian multipliers $\overline{t}$ and $\overline{M}^f$ and the left eigenvectors up to order n one can calculate transition moments up to photon number $2n+2$.

III. ANALYSIS OF THE SECOND RESIDUES OF COUPLED CLUSTER RESPONSE FUNCTIONS

The expressions for multiphoton transition moments in Eqs. (16) and (17) were obtained from an analysis of the first residues of the coupled cluster ground state response functions. From the second residues of the ground state response functions or equivalently from the first residues of the ground–excited state transition moments one can derive expressions for transition moments between two excited states and for excited state response functions.[1] This may be verified for exact wave functions starting from the sum-over-states expression for multiphoton transition moments:[21,31]

$$M_{0\leftarrow f}^{X_1\ldots X_{n+1}}(\omega_2,\ldots,\omega_{n+1})=\hat{P}^{X_1\ldots X_{n+1}}\sum_{l_1}\ldots\sum_{l_n}\frac{\mu_{0l_n}^{X_{n+1}}\mu_{l_nl_{n-1}}^{X_n}\ldots\mu_{l_2l_1}^{X_2}\mu_{l_1f}^{X_1}}{[\omega_1+\ldots+\omega_n-E_{l_nf}]\ldots[\omega_1+\omega_2-E_{l_2f}][\omega_1-E_{l_1f}]}, \tag{33}$$

where $\omega_1=-(\omega_2+\ldots+\omega_{n+1}+\omega_f)$ and $\mu_{jk}^{X_i}=\langle j|X_i|k\rangle$ and $E_{ij}=E_j-E_i$. Taking into account the sum over all permutations of operator/frequency pairs and the summations over all states (which include the excited states as well as the ground state), we obtain two contributions to the residue at $\omega_{n+1}\rightarrow-\omega_i$:

$$\lim_{\omega_{n+1}\rightarrow-\omega_i}(-\omega_{n+1}-\omega_i)M_{0\leftarrow f}^{X_1\ldots X_{n+1}}(\omega_2,\ldots,\omega_{n+1})=\mu_{0i}^{X_{n+1}}\hat{P}^{X_1\ldots X_n}\sum_{l_1}\ldots\sum_{l_{n-1}}\frac{\mu_{il_{n-1}}^{X_n}\ldots\mu_{l_2l_1}^{X_2}\mu_{l_1f}^{X_1}}{[\omega_1+\ldots+\omega_{n-1}-E_{l_{n-1}f}]\ldots[\omega_1-E_{l_1f}]} - \delta_{if}\mu_{0f}^{X_{n+1}}\hat{P}^{X_1\ldots X_n}\sum_{l_1}\ldots\sum_{l_{n-1}}\frac{\mu_{0l_{n-1}}^{X_n}\ldots\mu_{l_2l_1}^{X_2}\mu_{l_10}^{X_1}}{[\omega_1+\ldots+\omega_{n-1}-E_{l_{n-1}0}]\ldots[\omega_1-E_{l_10}]}. \tag{34}$$

If i and f are two different states one thus obtains:

$$\lim_{\omega_{n+1}\rightarrow-\omega_i}(-\omega_{n+1}-\omega_i)M_{0\leftarrow f}^{X_1\ldots X_{n+1}}(\omega_2,\ldots,\omega_{n+1})=M_{0\leftarrow i}^{X_{n+1}}M_{i\leftarrow f}^{X_1\ldots X_n}(\omega_2,\ldots,\omega_n). \tag{35}$$

When the two excited states i and f are identical, this residue becomes equal to the difference between the excited state and the ground state response functions:

$$\lim_{\omega_{n+1}\rightarrow-\omega_f}(-\omega_{n+1}-\omega_f)M_{0\leftarrow f}^{X_1\ldots X_{n+1}}(\omega_2,\ldots,\omega_{n+1})=M_{0\leftarrow f}^{X_{n+1}}(\langle\langle X_1;\ X_2\ldots X_n\rangle\rangle_{\omega_2,\ldots,\omega_n}^{(f)}-\langle\langle X_1;\ X_2\ldots X_n\rangle\rangle_{\omega_2,\ldots,\omega_n}^{(0)}), \tag{36}$$

where we used that the response functions for exact states can be written in a sum-over-states form as:

$$\langle\langle X_1;\ X_2 \ldots X_n\rangle\rangle^{(i)}_{\omega_2,\ldots,\omega_n} = \hat{P}^{X_1\ldots X_n} \sum_{l_1} \ldots \sum_{l_n} \frac{\mu^{X_n}_{l_i l_{n-1}} \ldots \mu^{X_2}_{l_2 l_1} \mu^{X_1}_{l_1 i}}{[\omega_1 + \ldots + \omega_{n-1} - E_{l_{n-1} i}] \ldots [\omega_1 + \omega_2 - E_{l_2 i}][\omega_1 - E_{l_1 i}]}. \tag{37}$$

The analogous residues of the right transition moments $M^{X_1\ldots X_{n+1}}_{f\leftarrow 0}$ follow from the symmetry of the transition moments and the response functions with respect to complex conjugation and inversion of the signs of the frequency arguments:

$$\lim_{\omega_{n+1}\rightarrow +\omega_i} (+\omega_{n+1} - \omega_i) M^{X_1\ldots X_{n+1}}_{f\leftarrow 0}(\omega_2,\ldots,\omega_{n+1}) = M^{X_1\ldots X_n}_{f\leftarrow i}(\omega_2,\ldots,\omega_n) M^{X_{n+1}}_{i\leftarrow 0}, \tag{38}$$

for $i \neq f$ and for the diagonal case $i = f$:

$$\lim_{\omega_{n+1}\rightarrow +\omega_f} (+\omega_{n+1} - \omega_f) M^{X_1\ldots X_{n+1}}_{f\leftarrow 0}(\omega_2,\ldots,\omega_{n+1}) = (\langle\langle X_1;\ X_2 \ldots X_n\rangle\rangle^{(f)}_{\omega_2,\ldots,\omega_n} - \langle\langle X_1;\ X_2 \ldots X_n\rangle\rangle^{(0)}_{\omega_2,\ldots,\omega_n}) M^{X_{n+1}}_{f\leftarrow 0}. \tag{39}$$

As an example of the use of the above equations, we apply them in the following paragraphs to coupled cluster wave functions, where we determine the one- and two-photon transition moments between two excited states and the first- and second-order properties for excited states. Before doing so, we recall that in coupled cluster theory the quasienergy is calculated by projection $\langle \mathrm{HF}|\hat{H}\ \exp(\hat{T})|\mathrm{HF}\rangle$ and is in general a complex quantity. The response functions are therefore obtained as derivatives of only the real part of the quasienergy which imposes an explicit symmetrization with respect to complex conjugation and inversion of the signs of the frequencies. The equivalent symmetrization for the residues [cp. Eq. (14)] becomes:

$$\begin{aligned} &\lim_{\omega_{n+1}\rightarrow -\omega_i} (-\omega_{n+1} - \omega_i)[\lim_{\omega_{n+2}\rightarrow \omega_f} (\omega_{n+2} - \omega_f)\langle\langle X_1;\ X_2 \ldots X_{n+2}\rangle\rangle_{\omega_2,\ldots,\omega_{n+2}}] \\ &= \lim_{\omega_{n+1}\rightarrow -\omega_i} (-\omega_{n+1} - \omega_i) \tfrac{1}{2}\{M^{X_1\ldots X_{n+1}}_{0\leftarrow f}(\omega_2,\ldots,\omega_{n+1}) M^{X_{n+2}}_{f\leftarrow 0} + (M^{X_{n+2}}_{0\leftarrow f})^*(M^{X_1\ldots X_{n+1}}_{f\leftarrow 0}(-\omega_2,\ldots,-\omega_{n+1}))^*\}. \end{aligned} \tag{40}$$

The left and right transition moments for excitations from the ground state to an excited state f are thus not related by complex conjugation and inversion of the frequency signs and it is thus a nontrivial question, if the residues from Eqs. (35) and (38) will lead to equivalent expressions for the transition moments between two excited states and if Eqs. (36) and (39) will lead to the same expressions for excited state response functions. We will in the following paragraphs show that this is indeed the case and that the second residue in Eq. (40) therefore can be rewritten as:

$$\begin{aligned} &\lim_{\omega_{n+1}\rightarrow -\omega_i} (-\omega_{n+1} - \omega_i)[\lim_{\omega_{n+2}\rightarrow \omega_f} (\omega_{n+2} - \omega_f)\langle\langle X_1;\ X_2 \ldots X_{n+2}\rangle\rangle_{\omega_2,\ldots,\omega_{n-2}}] \\ &\times \begin{cases} = \tfrac{1}{2}\{M^{X_{n+1}}_{0\leftarrow i} M^{X_1\ldots X_n}_{i\leftarrow f}(\omega_2,\ldots,\omega_n) M^{X_{n+2}}_{f\leftarrow 0} + (M^{X_{n+2}}_{0\leftarrow f})^*(M^{X_1\ldots X_n}_{f\leftarrow i}(-\omega_2,\ldots,-\omega_n))^*(M^{X_{n+1}}_{i\leftarrow 0})^*\}, & \text{for } i \neq f \\ = \tfrac{1}{2}\{M^{X_{n+1}}_{0\leftarrow i} \Delta\mathscr{W}^{X_1\ldots X_n}_{0f}(\omega_1,\omega_2,\ldots,\omega_n) M^{X_{n+2}}_{f\leftarrow 0} + (M^{X_{n+2}}_{0\leftarrow f})^*(\Delta\mathscr{W}^{X_1\ldots X_n}_{0f}(-\omega_1,-\omega_2,\ldots,-\omega_n))^*(M^{X_{n+1}}_{i\leftarrow 0})^*\}, & \text{for } i = f \end{cases} \end{aligned} \tag{41}$$

where we define $\Delta\mathscr{W}^{X_1\ldots X_n}_{0f}(-\omega_1,\ldots,-\omega_n)$ implicitly through the last equation with $\omega_1 = -\omega_2 - \ldots - \omega_n$. The asymmetry of the Jacobian, Eq. (11), and the biorthogonality of the left and right eigenvectors introduce an asymmetry between the left and right transition moments between two excited states, $M^{X_1\ldots X_n}_{i\leftarrow f}(\omega_2,\ldots,\omega_n)$ and $M^{X_1\ldots X_n}_{f\leftarrow i}(-\omega_2,\ldots,-\omega_n)$, and between $\Delta\mathscr{W}^{X_1\ldots X_n}_{0f}(\omega_1,\omega_2,\ldots,\omega_n)$ and $\Delta\mathscr{W}^{X_1\ldots X_n}_{0f}(-\omega_1,-\omega_2,\ldots,-\omega_n)$. The transition strengths between two excited states must therefore, as the strengths for the ground–excited state transitions, be calculated from the symmetrized expressions:[19,21]

$$\begin{aligned} &S^{if}_{X_1\ldots X_n, X_{n+1}\ldots X_{2n}}(\omega_2,\ldots,\omega_n) \\ &= \tfrac{1}{2}\{M^{X_1\ldots X_n}_{i\leftarrow f}(\omega_2,\ldots,\omega_n)\ M^{X_{n+1}\ldots X_{2n}}_{f\leftarrow i}(-\omega_2,\ldots,-\omega_n) \\ &\quad + (M^{X_{n+1}\ldots X_{2n}}_{i\leftarrow f}(\omega_2,\ldots,\omega_n))^* \\ &\quad \times (M^{X_1\ldots X_n}_{f\leftarrow i}(-\omega_2,\ldots,-\omega_n))^*\}. \end{aligned} \tag{42}$$

The coupled cluster excited state response functions are identified with the expressions:

$$\begin{aligned} &\langle\langle X_1;\ X_2,\ldots,X_n\rangle\rangle^{(f)}_{\omega_2,\ldots,\omega_n} \\ &= \langle\langle X_1;\ X_2,\ldots,X_n\rangle\rangle^{(0)}_{\omega_2,\ldots,\omega_n} \\ &\quad + \tfrac{1}{2}\Delta\mathscr{W}^{X_1\ldots X_n}_{0f}(\omega_1,\omega_2,\ldots,\omega_n) \\ &\quad + \tfrac{1}{2}(\Delta\mathscr{W}^{X_1\ldots X_n}_{0f}(-\omega_1,-\omega_2,\ldots,-\omega_n))^*. \end{aligned} \tag{43}$$

The quantities $\Delta\mathscr{W}^{X_1\ldots X_n}_{0f}$ are identified with derivatives of the quasienergy difference between the state f and the ground state with respect to the strengths of the external perturbations.

A. One-photon transition moments between two excited states from the residues of the two-photon transition moments

The left form of the two-photon transition moment for a ground state to excited state transition was derived in Ref. 21 as:

$$M^{AB}_{0\leftarrow f}(\omega_B)=\hat{P}^{AB}[\tfrac{1}{2}\mathbf{G}t^A(\omega_A)t^B(\omega_B)+\mathbf{F}^A t^B(\omega_B)+\tfrac{1}{2}\mathbf{F}t^{AB}(\omega_A,\omega_B)+\overline{t}^B(\omega_B)\mathbf{B}t^A(\omega_A)+\overline{t}^B(\omega_B)\mathbf{A}^A]E^f(\omega_f), \quad (44)$$

with $\omega_A=-\omega_f-\omega_B$. The only terms which do not vanish if we take the residue $\lim_{\omega_B\rightarrow-\omega_i}(-\omega_B-\omega_i)$ are those proportional to the first-order Lagrangian multipliers $\overline{t}^B(\omega_B)$. If we introduce the coupled cluster reduced resolvent $\mathbf{R}(\omega)$:[21]

$$R_{\mu\nu}(\omega)=[-(\mathbf{A}-\omega\mathbf{1})^{-1}]_{\mu\nu}=\sum_m E^m_\mu\frac{1}{\omega-\omega_m}\overline{E}^m_\nu, \quad (45)$$

the first-order Lagrangian multipliers can be written as $\overline{t}^B(\omega_B)=\overline{\xi}^B\mathbf{R}(-\omega_B)$, and the residues of $\overline{t}^B(\omega_B)$ in the limit $\omega_B\rightarrow-\omega_i$ are found as:

$$\lim_{\omega_B\rightarrow-\omega_i}(-\omega_B-\omega_i)\overline{t}^B(\omega_B)=[\overline{\xi}^B E^i(\omega_i)]\overline{E}^i(-\omega_i)=M^B_{0\leftarrow i}\overline{E}^i(-\omega_i). \quad (46)$$

The residue of the two-photon transition moment thus becomes

$$\lim_{\omega_B\rightarrow-\omega_i}(-\omega_B-\omega_i)M^{AB}_{0\leftarrow f}(\omega_B)=M^B_{0\leftarrow i}\overline{E}^i(-\omega_i)(\mathbf{B}t^A(\omega_i-\omega_f)+\mathbf{A}^A)E^f(\omega_f), \quad (47)$$

and one identifies the one-photon transition moment between two excited states as:

$$M^A_{i\leftarrow f}=\overline{E}^i(-\omega_i)(\mathbf{B}t^A(\omega_i-\omega_f)+\mathbf{A}^A)E^f(\omega_f). \quad (48)$$

The right ground to excited state two-photon transition moment was derived in Ref. 21 as:

$$M^{AB}_{f\leftarrow 0}(\omega_B)=\overline{E}^f(-\omega_f)(\mathbf{B}t^A(\omega_f-\omega_B)t^B(\omega_B)+\mathbf{A}^A t^B(\omega_B)+\mathbf{A}^B t^A(\omega_f-\omega_B)). \quad (49)$$

Its residue is determined in a similar manner as:

$$\lim_{\omega_B\rightarrow\omega_i}(\omega_B-\omega_i)M^{AB}_{f\leftarrow 0}(\omega_B)=\overline{E}^f(-\omega_f)(\mathbf{B}t^A(\omega_f-\omega_i)+\mathbf{A}^A)E^i(\omega_i)M^B_{i\leftarrow 0}, \quad (50)$$

where we used that the residues of the first-order cluster amplitude responses are:

$$\lim_{\omega_B\rightarrow\omega_i}(\omega_B-\omega_i)t^B(\omega_B)=\lim_{\omega_B\rightarrow\omega_i}(\omega_B-\omega_i)\mathbf{R}(\omega_B)\xi^B(\omega_B)=E^i(-\omega_i)M^B_{i\leftarrow 0}. \quad (51)$$

From Eq. (50) one identifies:

$$M^A_{f\leftarrow i}=\overline{E}^f(-\omega_f)(\mathbf{B}t^A(\omega_f-\omega_i)+\mathbf{A}^A)E^i(\omega_i). \quad (52)$$

The two expressions, Eqs. (48) and (52), for the transition moment between two excited states obtained from the residues of the left and right two-photon transition moments differ only in the dummy indices for the excited state and are thus obviously equivalent. The one-photon transition strength between two excited states is thus obtained as:

$$S^{if}_{X_1,X_2}=\tfrac{1}{2}\{M^{X_1}_{i\leftarrow f}M^{X_2}_{f\leftarrow i}+(M^{X_2}_{i\leftarrow f})^*(M^{X_1}_{f\leftarrow i})^*\}. \quad (53)$$

The calculation of the transition moments according to the expression obtained from the residues of the ground–excited state two-photon transition moments would require the solution of first-order response equations for the coupled cluster amplitudes. This can be avoided if one solves instead the zeroth-order equations:

$$(\mathbf{A}+\omega_i-\omega_f)\overline{N}^{fi}(-\omega_i,\omega_f)=-\overline{E}^f(-\omega_f)\mathbf{B}E^i(\omega_i). \quad (54)$$

With the intermediates $\overline{N}^{fi}$ the transition moments between two excited states can be rewritten as:[25]

$$M^A_{f\leftarrow i}=\overline{N}^{fi}(-\omega_f,\omega_i)\xi^A+\overline{E}^f(-\omega_f)\mathbf{A}^A E^i(\omega_i). \quad (55)$$

For $i=f$ one obtains the expression for the difference between the excited state and the ground state first-order properties:

$$\langle A\rangle^{(f)}-\langle A\rangle^{(0)}=\tfrac{1}{2}\{\overline{N}^{ff}(-\omega_f,\omega_f)\xi^A+\overline{E}^f(-\omega_f)\mathbf{A}^A E^f(\omega_f)+(\overline{N}^{ff}(-\omega_f,\omega_f)\xi^A)^*+(\overline{E}^f(-\omega_f)\mathbf{A}^A E^f(\omega_f))^*\}. \quad (56)$$

In accord with the $2n+1$ and $2n+2$ rules, the calculation of one-photon transition moments between two excited states and of excited states first-order properties requires in the formulation Eqs. (55)–(56) only solution of zeroth-order equations. Using the right hand side vectors for the response equations for the left and right excited state vectors $\overline{\xi}^{fA}$ and ξ^{iA} (see Appendix A of Ref. 21), Eq. (52) may be expressed in a form similar to expressions (16) and (17) for the ground–excited state transition moments:

$$M^A_{f\leftarrow i}=\overline{\xi}^{fA}(-\omega_f,\omega_f-\omega_i)E^f(\omega_f)=\overline{E}^f(-\omega_f)\xi^{iA}(\omega_i,\omega_f-\omega_i). \quad (57)$$

B. Two-photon transition moments between two excited states from the residues of the three-photon transition moments

To find the residues of the coupled cluster left three-photon transition moments we start from the expression:[21]

$$M^{ABC}_{0\leftarrow f}(\omega_B,\omega_C)=\hat{P}^{ABC}\{\tfrac{1}{3!}\mathbf{H}t^A(\omega_A)t^B(\omega_B)t^C(\omega_C)+\tfrac{1}{2}\mathbf{G}t^{AB}(\omega_A,\omega_B)t^C(\omega_C)+\tfrac{1}{2}\mathbf{F}^A t^{BC}(\omega_B,\omega_C)+\tfrac{1}{3!}\mathbf{F}t^{ABC}(\omega_A,\omega_B,\omega_C)+\overline{t}^C(\omega_C)[\tfrac{1}{2}\mathbf{C}t^A(\omega_A)t^B(\omega_B)+\tfrac{1}{2}\mathbf{B}t^{AB}(\omega_A,\omega_B)+\mathbf{B}^A t^B(\omega_B)]+\tfrac{1}{2}\overline{t}^{BC}(\omega_B,\omega_C)[\mathbf{A}^A+\mathbf{B}t^A(\omega_A)]\}E^f(\omega_f), \quad (58)$$

and take the residue for $\omega_C \rightarrow -\omega_i$. The Resolvent $\mathbf{R}(-\omega_C)$ occurs in the first-order multipliers $\overline{t}(\omega_C)$ and in the second-order multipliers $\overline{t}^{AC}(\omega_A,\omega_C)$ and $\overline{t}^{BC}(\omega_B,\omega_C)$. For the latter one the residue for $\omega_C \rightarrow -\omega_i$ becomes:

$$\begin{aligned}
&\lim_{\omega_C \rightarrow -\omega_i} (-\omega_C-\omega_i)\overline{t}^{BC}(\omega_B,\omega_C) \\
&\quad = M^C_{0\leftarrow i}\overline{E}^i(-\omega_i)(\mathbf{B}t^B(\omega_B)+\mathbf{A}^B)\mathbf{R}(\omega_i-\omega_B) \\
&\quad = M^C_{0\leftarrow i}\overline{E}^{iB}(-\omega_i,\omega_B). \qquad (59)
\end{aligned}$$

Using Eqs. (46) and (59) the residue of the left three-photon transition moment is obtained as:

$$\begin{aligned}
&\lim_{\omega_C \rightarrow -\omega_i} (-\omega_C-\omega_i)M^{ABC}_{0\leftarrow f}(\omega_B,\omega_C) \\
&\quad = M^C_{0\leftarrow i}(\hat{P}^{AB}\overline{E}^i(-\omega_i)[\tfrac{1}{2}\mathbf{C}t^A(\omega_A)t^B(\omega_B) \\
&\qquad + \tfrac{1}{2}\mathbf{B}t^{AB}(\omega_A,\omega_B)+\mathbf{B}^A t^B(\omega_B)] \\
&\qquad + \hat{P}^{AB}\overline{E}^{iB}(-\omega_i,\omega_B)[\mathbf{B}t^A(\omega_A)+\mathbf{A}^A])E^f(\omega_f). \qquad (60)
\end{aligned}$$

The term in parentheses is the right hand side vector $\overline{\xi}^{iAB}(-\omega_i,\omega_A,\omega_B)$ for the second-order response equations for the left excited state vectors.[21] Thus we obtain for the two-photon transition moment between two excited states an expression which has the same structure as Eqs. (57) and (16):

$$M^{AB}_{i\leftarrow f}(\omega_B)=\overline{\xi}^{iAB}(-\omega_i,\omega_A,\omega_B)E^f(\omega_f). \qquad (61)$$

Using the interchange technique Eq. (61) can be rewritten in a form which is analogous to Eq. (17):

$$M^{AB}_{i\leftarrow f}(\omega_B)=\overline{E}^i(-\omega_i)\xi^{fAB}(\omega_f,\omega_A,\omega_B). \qquad (62)$$

Alternatively, one can reformulate $M^{AB}_{i\leftarrow f}(\omega_B)$ in a computational more efficient form as

$$\begin{aligned}
M^{AB}_{i\leftarrow f}(\omega_B) &= \hat{P}^{AB}(\overline{E}^i(-\omega_i)[\tfrac{1}{2}\mathbf{C}t^A(\omega_A)t^B(\omega_B)+\mathbf{B}^A t^B(\omega_B)] \\
&\quad \times E^f(\omega_f)+\overline{\xi}^{iB}(-\omega_i,\omega_B)E^{fA}(\omega_f,\omega_A) \\
&\quad + \tfrac{1}{2}\overline{N}^{if}(-\omega_i,\omega_f)\xi^{AB}(\omega_A,\omega_B)). \qquad (63)
\end{aligned}$$

In the last expression we have eliminated the second-order response of the ground state cluster amplitudes, to obtain an expression which is in accordance with a $2n+1$ rule for the coupled cluster amplitudes and the right excited state vectors and a $2n+2$ rule for the Lagrangian multipliers and the left excited state vectors.

The coupled cluster right three-photon transition moment in Ref. 21 was derived as:

$$\begin{aligned}
M^{ABC}_{f\leftarrow 0}(\omega_B,\omega_C) &= \overline{E}^f(-\omega_f)(\hat{P}^{ABC}\{[\tfrac{1}{6}\mathbf{C}t^A(\omega_A)+\tfrac{1}{2}\mathbf{B}^A] \\
&\quad \times t^B(\omega_B)t^C(\omega_C)+\tfrac{1}{2}[\mathbf{B}t^A(\omega_A)+\mathbf{A}^A] \\
&\quad \times t^{BC}(\omega_B,\omega_C)\}). \qquad (64)
\end{aligned}$$

To determine the residue of the expression in Eq. (64) we need the residue of the second-order response of the coupled cluster amplitudes:

$$\lim_{\omega_C \rightarrow \omega_i} (\omega_C-\omega_i)t^{BC}(\omega_B,\omega_C)=E^{iB}(\omega_i,\omega_B)M^C_{i\leftarrow 0}. \qquad (65)$$

Using Eqs. (51) and (65), the residue of the right three-photon transition matrix element is found as:

$$\begin{aligned}
&\lim_{\omega_C \rightarrow \omega_i} (\omega_C-\omega_i)M^{ABC}_{f\leftarrow 0}(\omega_B,\omega_C) \\
&\quad = \overline{E}^f(-\omega_f)(\hat{P}^{AB}[\tfrac{1}{2}\mathbf{C}t^A(\omega_A)t^B(\omega_B)+\tfrac{1}{2}\mathbf{B}^A t^B(\omega_B) \\
&\qquad + \tfrac{1}{2}\mathbf{B}t^{AB}(\omega_A,\omega_B)]E^i(\omega_i)+\hat{P}^{AB}[\mathbf{B}t^A(\omega_A)+\mathbf{A}^A] \\
&\qquad \times E^{iB}(\omega_i,\omega_B))M^C_{i\rightarrow 0}. \qquad (66)
\end{aligned}$$

The expression in parentheses is the right hand side vector $\xi^{iAB}(\omega_i,\omega_A,\omega_B)$ for the second-order response equations for the right excited state vectors. One identifies in accordance with Eq. (62):

$$M^{AB}_{f\leftarrow i}(\omega_B)=\overline{E}^f(-\omega_f)\xi^{iAB}(\omega_i,\omega_A,\omega_B). \qquad (67)$$

Thus, we obtain also for the two-photon transition moments between two excited states the same expressions from the residues of the left and the right ground–excited state transition moments.

The expression for the difference between the excited state and ground state linear response functions is obtained by taking $i=f$ and applying the appropriate symmetrization:

$$\begin{aligned}
&\langle\langle A;B\rangle\rangle^{(f)}_{\omega_B}-\langle\langle A;B\rangle\rangle^{(0)}_{\omega_B} \\
&\quad = \tfrac{1}{2}\hat{C}^{\pm\omega}\hat{P}^{AB}(\overline{E}^f(-\omega_f)[\tfrac{1}{2}\mathbf{C}t^A(\omega_A)+\mathbf{B}^A]t^B(\omega_B)E^f(\omega_f) \\
&\qquad + \overline{E}^{fB}(-\omega_f,\omega_B)\xi^{fA}(\omega_f,\omega_A) \\
&\qquad + \tfrac{1}{2}\overline{N}^{ff}(-\omega_f,\omega_f)\xi^{AB}(\omega_A,\omega_B)), \qquad (68)
\end{aligned}$$

where $\omega_A=-\omega_B$. The operator $\hat{C}^{\pm\omega}$ symmetrizes with respect to an overall sign inversion of the frequencies of the external fields and simultaneous complex conjugation. Note that it does not affect the frequencies associated with the excited state.

The first-order responses of the left and right excited state vectors $\overline{E}^{fX}(-\omega_f,\omega_X)$ and $E^{fX}(\omega_f,\omega_X)$ are obtained as solutions of the response equations (28) and (29). Because the excitation energy ω_f is subtracted from the diagonal of the Jacobian matrix in these equations, the responses of the excited state vectors become singular in the static limit, where ω_X equals zero. These singularities are physical in the expressions for the multiphoton transition moments, but are unphysical artifacts in the expressions for the excited state response functions. These so-called secular divergencies[28,32] of the static limit of response functions originate from terms which cancel mutually and can be removed by mathematical manipulations. Defining the projection operator to the orthogonal complement of state f,

$$Q^f_{\mu\nu}=\delta_{\mu\nu}-E^f_\mu(\omega_f)\overline{E}^f_\nu(-\omega_f)=[\mathbf{1}-\mathbf{R}^f]_{\mu\nu}, \qquad (69)$$

the terms which contain the secular divergencies in Eq. (68) can be rewritten as:

$$\hat{P}^{AB}\overline{E}^{fB}(-\omega_f,\omega_B)\xi^{fA}(\omega_f,\omega_A)$$
$$=\hat{P}^{AB}\overline{\xi}^{fB}(-\omega_f,\omega_B)(\mathbf{A}-(\omega_f+\omega_B)\mathbf{1})^{-1}\xi^{fA}(\omega_f,\omega_A), \tag{70}$$

$$=\hat{P}^{AB}\{(\overline{\xi}^{fB}(-\omega_f,\omega_B)E^f(\omega_f))\omega_B^{-1}(\overline{E}^f(-\omega_f)\xi^{fA}(\omega_f,\omega_A))$$
$$+\overline{\xi}^{fB}(-\omega_f,\omega_B)\mathbf{Q}^f(\mathbf{A}-(\omega_f+\omega_B)\mathbf{1})^{-1}$$
$$\times\mathbf{Q}^f\xi^{fA}(\omega_f,\omega_A)\}. \tag{71}$$

The secular divergencies originate from the first term on the right hand side. If the permutation operator $\hat{P}^{AB}$ is applied, the contributions from this term cancel each other because $\omega_A=-\omega_B$. The second term on the right hand side of Eq. (71) has a finite static limit. Thus, we obtain a form of the excited state response function which is numerical stable in the static limit as:

$$\langle\langle A;B\rangle\rangle_{\omega_B}^{(f)}-\langle\langle A;B\rangle\rangle_{\omega_B}^{(0)}$$
$$=\tfrac{1}{2}\hat{C}^{\pm\omega}\hat{P}^{AB}(\overline{E}^f(-\omega_f)[\tfrac{1}{2}\mathbf{C}t^A(\omega_A)+\mathbf{B}^A]$$
$$\times t^B(\omega_B)E^f(\omega_f)+\overline{\xi}^{fB}(-\omega_f,\omega_B)$$
$$\times\mathbf{Q}^f(\mathbf{A}-(\omega_f+\omega_B)\mathbf{1})^{-1}\mathbf{Q}^f\xi^{fA}(\omega_f,\omega_A)$$
$$+\tfrac{1}{2}\overline{N}^{ff}(-\omega_f,\omega_f)\xi^{AB}(\omega_A,\omega_B)). \tag{72}$$

IV. A TRANSITION MOMENT LAGRANGIAN FOR TRANSITIONS BETWEEN TWO EXCITED STATES

Equations (57), (61) and (62) suggest that in coupled cluster response theory multiphoton transition moments between two excited states can be calculated in analogy to Eqs. (16) and (17) as:

$$M_{f\leftarrow i}^{X_1\ldots X_n}(\omega_2,\ldots,\omega_n)=\overline{\xi}^{fX_1\ldots X_n}(-\omega_f,\omega_1,\ldots,\omega_n)E^i(\omega_i), \tag{73}$$

and

$$M_{f\leftarrow i}^{X_1\ldots X_n}(\omega_2,\ldots,\omega_n)=\overline{E}^f(-\omega_f)\xi^{iX_1\ldots X_n}(\omega_i,\omega_1,\ldots,\omega_n), \tag{74}$$

where $\omega_1=\omega_f-\omega_i-\omega_2\ldots-\omega_n$. Equations (73) and (74) obviously hold in first and second order as shown in Sec. III. Induction may be used to prove that they also hold for arbitrary order. The details are given in the Appendix.

It remains to prove that the two expressions lead in every order to the same expressions for excited state–excited state transition moments and excited state response functions. The equivalence of Eqs. (73) and (74) is verified in the following by demonstrating that both expressions can be rewritten as derivatives of the same functional. In Ref. 21 we showed how the projection formulas (16) and (17) for the ground–excited state transition moments can be reformulated as derivatives of variational time-averaged functionals. To derive a similar functional for the transition moments between two excited states, we start from Eq. (73). Without changing the result for $M_{i\leftarrow f}^{X_1\ldots X_n}$ we can add to the right hand side of Eq. (73) lower-order response equations for the left excited state vectors, multiplied by right excited state response vectors:

$$0=[\overline{\xi}^{iX_1\ldots X_m}(-\omega_i,\omega_1,\ldots,\omega_m)+\overline{E}^{iX_1\ldots X_m}(-\omega_i,\omega_1,\ldots,\omega_m)$$
$$\times(\mathbf{A}+(\omega_1+\ldots+\omega_m-\omega_i)\mathbf{1})^{-1}]$$
$$\times E^{fX_{m+1}\ldots X_n}(\omega_f,\omega_{m+1},\ldots,\omega_n). \tag{75}$$

We may further add the eigenvector equations for $\overline{E}^i$ and E^f multiplied by the excited state response vectors of order n,

$$\lim_{\omega_1+\ldots+\omega_n\rightarrow\omega_i-\omega_f}\overline{E}^{iX_1\ldots X_n}(-\omega_i,\omega_1,\ldots,\omega_n)(\mathbf{A}-\omega_f\mathbf{1})^{-1}$$
$$\times E^f(\omega_f)=0, \tag{76}$$

$$\lim_{\omega_1+\ldots+\omega_n\rightarrow\omega_i-\omega_f}\overline{E}^i(-\omega_i)(\mathbf{A}-\omega_i\mathbf{1})^{-1}$$
$$\times E^{fX_1\ldots X_n}(\omega_f,\omega_1,\ldots,\omega_n)=0, \tag{77}$$

where we impose the limes in order to guarantee that the equality still holds, when the sum of the frequencies approaches the excitation energy difference $\omega_i-\omega_f$. Using Eqs. (75)–(77), we can rewrite the expression for the multiphoton transition moments between two excited states as

$$M_{i\leftarrow f}^{X_1\ldots X_n}(\omega_2,\ldots,\omega_n)$$
$$=\lim_{\omega_1+\ldots+\omega_n\rightarrow\omega_i-\omega_f}\hat{P}^{X_1\ldots X_n}\sum_{m=0}^{n}\frac{1}{m!(n-m)!}$$
$$\times[\overline{\xi}^{iX_1\ldots X_m}(-\omega_i,\omega_1,\ldots,\omega_m)$$
$$+\overline{E}^{iX_1\ldots X_m}(\mathbf{A}+(\omega_1\ldots+\omega_m-\omega_i)\mathbf{1})]$$
$$\times E^{fX_{m+1}\ldots X_n}(\omega_f,\omega_{m+1},\ldots,\omega_n). \tag{78}$$

Employing the variational conditions for the left excited state response vectors, the term braces can be formulated as a derivative:

$$\overline{\xi}^{iX_1\ldots X_m}(-\omega_i,\omega_1,\ldots,\omega_m)+\overline{E}^{iX_1\ldots X_m}(-\omega_i,\omega_1,\ldots,\omega_m)$$
$$\times(\mathbf{A}+(\omega_1\ldots+\omega_m-\omega_i)\mathbf{1})$$
$$=\left(\frac{d^m\{\overline{E}^i(t,\epsilon)(\mathbf{A}(t,\epsilon)+(\omega_1\ldots+\omega_m-\omega_i)\mathbf{1})\}}{d\epsilon_1(\omega_1)\ldots d\epsilon_m(\omega_m)}\right)_0. \tag{79}$$

Since the responses of right excited state vectors are the derivatives of $E(t,\epsilon)$ with respect to some field strengths,

$$E^{fX_{m+1}\ldots X_n}(\omega_f,\omega_{m+1},\ldots,\omega_n)$$
$$=\left(\frac{d^{(n-m)}E^f(t,\epsilon)}{d\epsilon_{m+1}(\omega_{m+1})\ldots d\epsilon_n(\omega_n)}\right)_0, \tag{80}$$

Eq. (78) becomes a special case of the binomial formula and $M_{i\leftarrow f}^{X_1\ldots X_n}(\omega_2,\ldots,\omega_n)$ can be formulated as derivative of a functional:

$$M_{i\leftarrow f}^{X_1\ldots X_n}(\omega_2,\ldots,\omega_n) = \left(\frac{d^n}{d\epsilon_1(\omega_1)\ldots d\epsilon_n(\omega_n)} \left\{ \lim_{\rho\to 0} e^{\rho t}\overline{E^i}(t,\epsilon) \times \left(\mathbf{A}(t,\epsilon)+i\frac{d}{dt}\right)E^f(t,\epsilon)\right\}_T \right)_{\epsilon_i=0}. \quad (81)$$

With $\{\ \}_T$ we denote time-averaging as in Eq. (6). The expression in braces in Eq. (81) can be interpreted as an excited state–excited state transition moment functional:

$$\mathscr{T}^{if}(t,\epsilon) = \lim_{\rho\to 0} e^{\rho t}\overline{E^i}(t,\epsilon)\left(\mathbf{A}(t,\epsilon)-i\frac{d}{dt}\right)E^f(t,\epsilon). \quad (82)$$

Alternatively, one may start from Eq. (74) for the transition moments between two excited states and add to the right hand side of Eq. (74) lower-order response equations for the right excited state vectors multiplied by left excited state response vectors and again the eigenvector equations for $\overline{E^i}$ and E^f multiplied by the nth-order excited state response vectors, Eqs. (76) and (77). This leads to the same transition moment functional:

$$M_{i\leftarrow f}^{X_1\ldots X_n}(\omega_2,\ldots,\omega_n) = \lim_{\omega_1+\ldots+\omega_n\to\omega_i-\omega_f} \hat{P}^{X_1\ldots X_n}\sum_{m=0}^{n} \frac{1}{m!(n-m)!}\left(\frac{d^{(n-m)}\overline{E^i}(t,\epsilon)}{d\epsilon_{m+1}(\omega_{m+1})\ldots d\epsilon_n(\omega_n)}\right)_0 \times\left(\frac{d^m\{(\mathbf{A}(t,\epsilon)-(\omega_f+\omega_1\ldots+\omega_m)\mathbf{1})E^f(t,\epsilon)\}}{d\epsilon_1(\omega_1)\ldots d\epsilon_m(\omega_m)}\right)_0 \quad (83)$$

$$= \left(\frac{d^n}{d\epsilon_1(\omega_1)\ldots d\epsilon_n(\omega_n)} \left\{ \lim_{\rho\to 0} e^{\rho t}\overline{E^i}(t,\epsilon)\left(\mathbf{A}(t,\epsilon)-i\frac{d}{dt}\right)E^f(t,\epsilon)\right\}_T \right)_0. \quad (84)$$

This proves that the two formulations (73) and (74) for the transition moments between two excited states are indeed equivalent for arbitrary order n.

We observe, that the time-average of the functional $\mathscr{T}^{if}$ is variational in the Fourier components of the left and right excited state vectors, but not in the ground state cluster amplitudes. To obtain a Lagrangian which may be required to be stationary in all its variables we complement $\mathscr{T}^{if}$ with the time-dependent coupled cluster equations as constraints:

$$L^{if}(t,\epsilon) = \lim_{\rho\to 0} e^{\rho t}\overline{E^i}(t,\epsilon)\left(\mathbf{A}(t,\epsilon)-i\frac{d}{dt}\right)E^f(t,\epsilon) + \overline{N^{if}}(t,\epsilon)\left(e(t,\epsilon)-i\frac{d}{dt}t(t,\epsilon)\right). \quad (85)$$

From the derivatives of $\{L^{if}\}_T$ one obtains expressions for the left and right transition moments between two excited states which are equivalent to those derived from the second residues of the ground state response functions or from the first residues of the ground–excited state transition moments. The variational formulation through a transition moment Lagrangian makes the implementation of $2n+1$ and $2n+2$ rules straightforward: The calculation of $(2n+1)$-photon transition moments requires only the solution of the response equations up order n for the variables of t, $\overline{E^i}$, E^f and $\overline{N^{if}}$. For the Lagrangian multipliers $\overline{N^{if}}$ and either for the left or for the right excited state vectors also the stronger $2n+2$ rule can be applied. The singular terms which during the derivation of the transition moment functional were added to $M_{i\leftarrow f}^{X_1\ldots X_n}$ have no effect for the applicability of the transition moment Lagrangian, since these terms are proportional to $\overline{E^{iX_1\ldots X_n}}$ and $\overline{E^{fX_1\ldots X_n}}$ and automatically eliminated from the expressions when the $2n+1$ and $2n+2$ rules are applied.

From the variational condition for the time-average of the transition moment Lagrangian,

$$\delta\{L^{if}(t,\epsilon)\}_T = 0, \quad (86)$$

one obtains per construction for the ground state cluster amplitudes and for the left and right excited state vectors the same response equations as obtained from the ground state quasienergy Lagrangian and the ground–excited state transition moment Lagrangians. The only new response equations which arise are those for the Lagrangian multipliers $\overline{N^{if}}$. They are obtained from the condition that $\{L^{if}\}_T$ is stationary in the cluster amplitudes t.

Because we used a phase-isolated parametrization of the coupled cluster ground state wave functions, the intermediates $t(t,\epsilon)$, $\overline{E^i}(t,\epsilon)$, $E^f(t,\epsilon)$ and $\overline{N^{if}}(t,\epsilon)$ of the transition moment Lagrangian are phase-isolated with respect to the ground state quasienergy-dependent phase-factor. They are not phase-isolated with respect to phase-factors that depend on the quasienergy differences between the ground and the excited states. Thus, the transition moment Lagrangian does not become a quasienergy Lagrangian for $i=f$. The Lagrangian $L^{ff}(t,\epsilon)$ could be used to derive excited state response functions, but the resulting expressions would as a consequence of the incomplete phase-isolation contain the same secular divergent terms as the expressions obtained from the residues. In Sec. VII we will derive an excited state quasienergy Lagrangian with a parametrization that is completely phase-isolated for the excited state and leads there-

fore to expressions which are numerical stable in the static limit.

V. MULTIPHOTON TRANSITION MOMENTS AS DERIVATIVES OF THE TRANSITION MOMENT LAGRANGIAN

The variational transition moment Lagrangian renders it possible to derive multiphoton transition moments in a straightforward and simple way as derivatives, without the roundabout way via second residues of the ground state response functions:

$$M^{X_1\ldots X_n}_{i\leftarrow f}(\omega_2,\ldots,\omega_n)=\left(\frac{d^n\{L^{if}\}_T}{d\epsilon_1(\omega_1)\ldots d\epsilon_n(\omega_n)}\right)_0. \tag{87}$$

To exemplify the usage of the last equation, we derive in the following the coupled cluster response theory expressions for one- through three-photon transition moments between two excited states. According to the $2n+2$ rule we need for these transition moments the zeroth- and the first-order Lagrangian multipliers $\overline{N}^{if}(-\omega_i,\omega_f)$ and $\overline{N}^{if}(-\omega_i,\omega_f,\omega_A)$. From the stationary condition of $\{L^{if}\}_T$ in the Fourier components of the cluster amplitudes we obtain the equations:

$$\overline{N}^{if}(-\omega_i,\omega_f)(\mathbf{A}+(\omega_f-\omega_i)\mathbf{1})=-\overline{E}^{i}(-\omega_i)\mathbf{B}E^f(\omega_f), \tag{88}$$

and

$$\begin{aligned}\overline{N}^{ifA}&(-\omega_i,\omega_f,\omega_A)(\mathbf{A}+(\omega_f-\omega_i+\omega_A)\mathbf{1})\\&=-\overline{n}^{ifA}(-\omega_i,\omega_f,\omega_A),\end{aligned} \tag{89}$$

with

$$\begin{aligned}\overline{n}^{ifA}&(-\omega_i,\omega_f,\omega_A)\\&=\overline{E}^{i}(-\omega_i)(\mathbf{C}t^A(\omega_A)+\mathbf{B}^A)E^f(\omega_f)\\&\quad+\overline{E}^{iA}(-\omega_i,\omega_A)\mathbf{B}E^f(\omega_f)+\overline{E}^{i}(-\omega_i)\\&\quad\times\mathbf{B}E^{fA}(\omega_f,\omega_A)+\overline{N}^{if}(-\omega_i,\omega_f)(\mathbf{B}t^A(\omega_A)+\mathbf{A}^A).\end{aligned} \tag{90}$$

From the first derivative of the time-averaged transition moment functional we get the expression for one-photon transion moment. If we apply the $2n+1$ and $2n+2$ rules, we obtain the one-photon transition moment immediately in the formulation of Eq. (55),

$$\begin{aligned}M^{A}_{i\leftarrow f}&=\left(\frac{d\{L^{if}\}_T}{d\epsilon_A(\omega_i-\omega_f)}\right)_0\\&=\overline{E}^{i}(-\omega_i)\mathbf{A}^AE^f(\omega_f)+\overline{N}^{if}(-\omega_i,\omega_f)\xi^A,\end{aligned} \tag{91}$$

which from the residue of the ground–excited state transition moments was only found after some algebraic manipulations. The two-photon transition moment between two excited states is obtained from the second derivative of the transition moment Lagrangian as:

$$\begin{aligned}M^{AB}_{i\leftarrow f}(\omega_B)&=\left(\frac{d^2\{L^{if}\}_T}{d\epsilon_A(\omega_A)d\epsilon_B(\omega_B)}\right)_0 \qquad (92)\\&=\hat{P}^{AB}\{\overline{E}^{i}(-\omega_i)[\mathbf{B}t^A(\omega_A)+\mathbf{A}^A]E^{fB}(\omega_f,\omega_B)\\&\quad+\overline{E}^{i}(-\omega_i)[\tfrac{1}{2}\mathbf{C}t^A(\omega_A)t^B(\omega_B)+\mathbf{B}^At^B(\omega_B)]\\&\quad\times E^f(\omega_f)+\overline{N}^{if}(-\omega_i,\omega_f)\\&\quad\times[\tfrac{1}{2}\mathbf{B}t^A(\omega_A)t^B(\omega_B)+\mathbf{A}^At^B(\omega_B)]\},\qquad (93)\end{aligned}$$

with $\omega_A=\omega_i-\omega_f-\omega_B$. Equation (93) is equivalent to the expression in Eq. (63), derived in Sec. III using the interchange rule. Employing the $2n+1$ and $2n+2$ rules one obtains for the three-photon transition moments between excited states:

$$M^{ABC}_{i\leftarrow f}(\omega_B,\omega_C)=\left(\frac{d^3\{L^{if}\}_T}{d\epsilon_A(\omega_A)d\epsilon_B(\omega_B)d\epsilon_C(\omega_C)}\right)_0, \tag{94}$$

$$\begin{aligned}&=\hat{P}^{ABC}\{\overline{E}^{iA}\xi^{fBC}+N^{ifA}\xi^{BC}+\tfrac{1}{6}\overline{E}^{i}\mathbf{D}t^At^Bt^CE^f\\&\quad+\overline{E}^{i}[\tfrac{1}{2}\mathbf{C}t^At^B+\mathbf{B}^At^B]E^{fC}\\&\quad+\overline{N}^{if}[\tfrac{1}{6}\mathbf{C}t^At^Bt^C+\tfrac{1}{2}\mathbf{B}^Bt^At^C]\},\end{aligned} \tag{95}$$

where we for notational convenience omitted the frequency arguments on the right hand side, implying that $\overline{E}^{i}=\overline{E}^{i}(-\omega_i)$, $\overline{N}^{if}=\overline{N}^{if}(-\omega_i,\omega_f)$, $t^A=t^A(\omega_A)$, etc. and that $\omega_A=\omega_i-\omega_f-\omega_B-\omega_C$.

VI. A REGULARIZED PERTURBATION EXPANSION FOR THE EXCITED STATE VECTORS

The left and right excited state response vectors $\overline{E}^{fX_1\ldots X_n}$ and $E^{fX_1\ldots X_n}$, determined by the variational conditions for the transition moment Lagrangians, are the coefficient of a Fourier and perturbation expansion of the time-dependent vectors $\overline{E}^{f}(t,\epsilon)$ and $E^f(t,\epsilon)$. These vectors provide a parameterization of the time-dependent bra and ket wave functions for the excited state f in the biorthogonal space spanned by the similarity transformed left projection manifold

$$\langle \mathrm{HF}|\hat{\tau}^{\dagger}_{\mu}\exp(-\hat{T}(t,\epsilon))\exp\left(i\int_{t_0}^{t}\mathscr{W}(t',\epsilon)dt'\right),$$

and by the single, double, etc. excitations out of the coupled cluster state,

$$\hat{\tau}_{\mu}|\mathrm{CC}(t,\epsilon)\rangle=\exp\left(-i\int_{t_0}^{t}\mathscr{W}(t',\epsilon)dt'\right)\exp(\hat{T}(t,\epsilon))\,\hat{\tau}_{\mu}|\mathrm{HF}\rangle. \tag{96}$$

The coupled cluster state and the bra states of the left projection manifold include an oscillating phase-factor depending on the so-called level shift or time-dependent quasienergy $\mathscr{W}(t,\epsilon)$ for the ground state which was defined in Eq. (2). Because this phase-factor is incorporated in the biorthogonal basis, the vectors $\overline{E}^{f}(t,\epsilon)$ and $E^f(t,\epsilon)$ are phase-isolated with respect to the ground state quasienergy. They are, however, not phase-isolated with respect to the quasienergy of the excited state f. As discussed in detail by Lang-

hoff *et al.*,[28] a wave function ansatz which is not completely phase-isolated leads in time-dependent perturbation expansions to so-called secular terms which diverge in the static limit. These divergencies can be avoided by factoring out the quasienergy-dependent phase factor and expanding the wave function and the quasienergy separately in orders of the perturbation strength.

For the excited state vectors $\overline{E^f}(t,\epsilon)$ and $E^f(t,\epsilon)$ such an ansatz can be realized by isolating the quasienergy difference between the ground state and the excited state f:

$$E^f(t,\epsilon)=\tilde{E}^f(t,\epsilon)\exp\left(-i\int_{t_0}^{t}\Delta\dot{\mathscr{W}}_{0f}(t',\epsilon)dt'\right), \tag{97}$$

$$\overline{E^f}(t,\epsilon)=\tilde{\bar{E}}^f(t,\epsilon)\exp\left(+i\int_{t_0}^{t}\Delta\dot{\mathscr{W}}_{0f}(t',\epsilon)dt'\right), \tag{98}$$

where the explicit form of $\Delta\dot{\mathscr{W}}_{0f}(t,\epsilon)$ will be determined below. The vectors $\tilde{E}^f(t,\epsilon)$ and $\tilde{\bar{E}}^f(t,\epsilon)$ can now be parametrized such that secular terms which describe an overall time-dependent phase-factor are excluded. From the biorthogonality condition,

$$\tilde{\bar{E}}^f(t,\epsilon)\tilde{E}^f(t,\epsilon)=\overline{E^f}(t,\epsilon)E^f(t,\epsilon)=\overline{E^f}(-\omega_f)E^f(\omega_f)=1, \tag{99}$$

it follows that a remaining overall phase-factor in $\tilde{\bar{E}}^f(t,\epsilon)$ must be the inverse of an overall phase-factor in $\tilde{E}^f(t,\epsilon)$. Requiring in addition to Eq. (99) that

$$\overline{E^f}(-\omega_f)\tilde{E}^f(t,\epsilon)=\tilde{\bar{E}}^f(t,\epsilon)E^f(\omega_f), \tag{100}$$

forces the overall phase-factors in $\tilde{\bar{E}}^f(t,\epsilon)$ and $\tilde{E}^f(t,\epsilon)$ to be equal and thus fixes them to 1. A similar time-independent phase-factor for the nonphase-isolated parametrization and for the unperturbed vectors is fixed by the condition $E^f(\omega_f)E^f(\omega_f)=1$. In the unperturbed limit $\tilde{\bar{E}}^f(t,\epsilon)$ and $\tilde{E}^f(t,\epsilon)$ must converge to the time-independent vectors $\overline{E^f}(-\omega_f)$ and $E^f(\omega_f)$. An expansion of $\tilde{\bar{E}}^f(t,\epsilon)$ and $\tilde{E}^f(t,\epsilon)$ in the field strengths and Fourier components of the external perturbation $\hat{V}(t,\epsilon)$ which is compatible with Eq. (100) is obtained by:

$$\tilde{E}^f(t,\epsilon)=E^f(\omega_f)+\sum_{n=1}^{\infty}\frac{1}{n!}\sum_{j_1}\cdots\sum_{j_n}\tilde{E}^{fX_{j_1}\cdots X_{j_n}}(\omega_f,\omega_{j_1},\ldots,\omega_{j_n})\times\prod_{m=1}^{n}\epsilon_{j_m}(\omega_{j_m})e^{-i\omega_{j_m}t}, \tag{101}$$

$$\tilde{\bar{E}}^f(t,\epsilon)=\overline{E^f}(-\omega_f)+\sum_{n=1}^{\infty}\frac{1}{n!}\sum_{j_1}\cdots\sum_{j_n}\tilde{\bar{E}}^{fX_{j_1}\cdots X_{j_n}}(-\omega_f,\omega_{j_1},\ldots,\omega_{j_n})\times\prod_{m=1}^{n}\epsilon_{j_m}(\omega_{j_m})e^{-i\omega_{j_m}t}. \tag{102}$$

Inserting the expansion ansatzes for the left and right excited state vectors into Eqs. (99) and (100), these two equations can be combined to:

$$\begin{aligned}\overline{E^f}(-\omega_f)\tilde{E}^{fX_1\cdots X_n}(\omega_f,\omega_1,\ldots,\omega_n)&=\tilde{\bar{E}}^{fX_1\cdots X_n}(-\omega_f,\omega_1,\ldots,\omega_n)E^f(\omega_f)\\&=-\tfrac{1}{2}\hat{P}^{X_1\cdots X_n}\sum_{k=1}^{n-1}\tilde{\bar{E}}^{fX_1\cdots X_k}(-\omega_f,\omega_1,\ldots,\omega_k)\\&\quad\times\tilde{E}^{fX_{k+1}\cdots X_n}(\omega_f,\omega_{k+1},\ldots,\omega_n).\end{aligned} \tag{103}$$

The projection of the excited state response vectors onto the unperturbed reference state are thus dependend variables that can be expressed in terms of lower-order response vectors. The independent variables of the expansion in Eqs. (101) and (102) are the components of the zeroth-order vectors $E^f(\omega_f)$ and $\overline{E^f}(-\omega_f)$ (restricted by the normalization conditions) and the projection of the higher-order response vectors onto the orthogonal complement of the excited reference state f. Using the projection operator $\mathbf{Q}^f$ introduced in Eq. (69), the latter components can be defined by:

$${}^{\perp}\tilde{E}^{fX_1\cdots X_n}(\omega_f,\omega_1,\ldots,\omega_n)=\mathbf{Q}^f\tilde{E}^{fX_1\cdots X_n}(\omega_f,\omega_1,\ldots,\omega_n), \tag{104}$$

$${}^{\perp}\tilde{\bar{E}}^{fX_1\cdots X_n}(-\omega_f,\omega_1,\ldots,\omega_n)=\tilde{\bar{E}}^{fX_1\cdots X_n}(-\omega_f,\omega_1,\ldots,\omega_n)\mathbf{Q}^f. \tag{105}$$

A. Time-dependent effective Schrödinger equations and variation principles for the phase-isolated excited state vectors

Inserting the ansatz (97) and (98) into the effective Schrödinger equations for the excited state vectors, Eqs. (30) and (31), leads to effective Schrödinger equations for the phase-isolated parts:

$$(\mathbf{A}(t,\epsilon)-\Delta\dot{\mathscr{W}}_{0f}(t,\epsilon))\tilde{E}^f(t,\epsilon)=i\frac{d}{dt}\tilde{E}^f(t,\epsilon), \tag{106}$$

$$\tilde{\bar{E}}^f(t,\epsilon)(\mathbf{A}(t,\epsilon)-\Delta\dot{\mathscr{W}}_{0f}(t,\epsilon))=-i\frac{d}{dt}\tilde{\bar{E}}^f(t,\epsilon). \tag{107}$$

Projecting Eq. (106) onto $\tilde{\bar{E}}^f(t,\epsilon)$ or Eq. (107) onto $\tilde{E}^f(t,\epsilon)$ leads to the equation for the quasienergy difference between the excited state f and the ground state:

$$\Delta\dot{\mathscr{W}}_{0f}(t,\epsilon)=\left(\tilde{\bar{E}}^f(t,\epsilon)\left(\mathbf{A}(t,\epsilon)-i\frac{d}{dt}\right)\tilde{E}^f(t,\epsilon)\right), \tag{108}$$

where we used the normalization condition for the excited state vectors Eq. (99).

Alternatively to the effective Schrödinger equations, the generalized Frenkel variation principle,[21,28]

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

can be used to determine the time-evolution of the excited state vectors. In Eq. (109) the symbol δ^E denotes variations with respect to the independent variables of the excited state vectors. Inserting the phase-isolated ansatz, Eqs. (97) and (98), into Eq. (109) one obtains:

$$\delta^E\Bigg(\tilde{\bar{E}}^f(t,\epsilon)\Bigg[\mathbf{A}(t,\epsilon)-\Delta\dot{\mathscr{W}}_{0f}(t,\epsilon)-i\frac{d}{dt}\Bigg]\tilde{E}^f(t,\epsilon)\Bigg)$$
$$+i\frac{d}{dt}\Bigg(\tilde{\bar{E}}^f(t,\epsilon)\,\delta^E\tilde{E}^f(t,\epsilon)-i\tilde{\bar{E}}^f(t,\epsilon)\tilde{E}^f(t,\epsilon)$$
$$\times\delta^E\int_{t_0}^{t}\Delta\dot{\mathscr{W}}_{0f}(t',\epsilon)dt'\Bigg)=0. \tag{110}$$

Using the normalization condition (99), the phase-isolated form of the generalized Frenkel principle is obtained as:

$$\delta^E\Bigg(\tilde{\bar{E}}^f(t,\epsilon)\Bigg[\mathbf{A}(t,\epsilon)-i\frac{d}{dt}\Bigg]\tilde{E}^f(t,\epsilon)\Bigg)$$
$$+i\frac{d}{dt}(\tilde{\bar{E}}^f(t,\epsilon)\,\delta^E\tilde{E}^f(t,\epsilon))=0, \tag{111}$$

or, if Eq. (108) for the quasienergy difference $\Delta\dot{\mathscr{W}}_{0f}(t,\epsilon)$ is inserted, as:

$$\delta^E\Delta\dot{\mathscr{W}}_{0f}(t,\epsilon)+i\frac{d}{dt}(\tilde{\bar{E}}^f(t,\epsilon)\,\delta^E\tilde{E}^f(t,\epsilon))=0. \tag{112}$$

Because we consider only (quasi-)periodic perturbations which can be written as a sum over Fourier components as in Eq. (5), the time-average of Eq. (112) is sufficient to determine the time-evolution of $\tilde{\bar{E}}^f(t,\epsilon)$ and $\tilde{E}^f(t,\epsilon)$. Due to the (quasi-)periodic form of $\tilde{\bar{E}}^f(t,\epsilon)$ and $\tilde{E}^f(t,\epsilon)$ the time-average of the second term in Eq. (112) vanishes and we arrive at a variational condition for the time-averaged quasienergy difference between the excited state f and the ground state:

$$\delta^E\{\Delta\dot{\mathscr{W}}_{0f}(t,\epsilon)\}_T=0. \tag{113}$$

As in the generalized Frenkel principle for the complete time-dependent excited state vectors, Eq. (109), are the allowed variation δ^E in Eqs. (110)–(113) restricted by the normalization condition Eq. (99) and the phase condition Eq. (100). In the next paragraphs we show how the response equations for the phase-isolated excited state vectors $\tilde{\bar{E}}^f(t,\epsilon)$ and $\tilde{E}^f(t,\epsilon)$ can be determined from the effective Schrödinger equations (106) and (107). Equivalent response equations can be obtained from the variational conditions (111)–(113).

B. Response equations for the phase-isolated excited state vectors

We use the effective Schrödinger equations and Eqs. (99) and (100) to derive the first- and second-order response equations for the phase-isolated excited state vectors. The time- and field-dependent Jacobian matrix $\mathbf{A}(t,\epsilon)$ which appears in Eqs. (106) and (107) can be expanded in the Fourier components and the strengths of the external fields up to second order as:

$$\mathbf{A}(t,\epsilon)=\mathbf{A}+\sum_j\epsilon_j(\omega_j)e^{-i\omega_j t}[\mathbf{B}t^{X_j}(\omega_j)+\mathbf{A}^{X_j}]$$
$$+\sum_{jk}\frac{1}{2}\epsilon_j(\omega_j)\epsilon_k(\omega_k)e^{-i(\omega_j+\omega_k)t}$$
$$\times[\mathbf{C}t^{X_j}(\omega_j)t^{X_k}(\omega_k)+\mathbf{B}t^{X_jX_k}(\omega_j,\omega_k)$$
$$+\mathbf{B}^{X_k}t^{X_y}(\omega_j)+\mathbf{B}^{X_j}t^{X_k}(\omega_k)]+\ldots. \tag{114}$$

For the quasienergy difference $\Delta\dot{\mathscr{W}}_{0f}(t,\epsilon)$ we make the ansatz:

$$\Delta\dot{\mathscr{W}}_{0f}(t,\epsilon)=\omega_f+\sum_{n=1}^{\infty}\frac{1}{n!}\sum_{j_1}\ldots\sum_{j_n}$$
$$\Delta\dot{\mathscr{W}}_{0f}^{X_{j_1}\ldots X_{j_n}}(\omega_{j_1},\ldots,\omega_{j_n})$$
$$\times\prod_{m=1}^{n}\epsilon_{j_m}(\omega_{j_m})e^{-i\omega_{j_m}t}. \tag{115}$$

Inserting Eq. (114) and the expansion for the phase-isolated excited state vectors, Eqs. (101) and (102), into Eqs. (106) and (107) and expanding it in orders of the field strengths, one obtains in zeroth order the usual left and right eigenvalue equations for $\overline{E^f}(-\omega_f)$ and $E^f(\omega_f)$. In first order one gets the response equations:

$$(\mathbf{A}-(\omega_f+\omega_A)\mathbf{1})\tilde{E}^{fA}(\omega_f,\omega_A)$$
$$=-(\mathbf{B}t^A(\omega_A)+\mathbf{A}^A-\Delta\dot{\mathscr{W}}_{0f}^{A}(\omega_A))E^f(\omega_f), \tag{116}$$

and

$$\tilde{\bar{E}}^{fA}(-\omega_f,\omega_A)(\mathbf{A}+(\omega_A-\omega_f)\mathbf{1})$$
$$=-\overline{E^f}(-\omega_f)(\mathbf{B}t^A(\omega_A)+\mathbf{A}^A-\Delta\dot{\mathscr{W}}_{0f}^{A}(\omega_A)). \tag{117}$$

From Eq. (103) we obtain

$$\tilde{\bar{E}}^{fA}(-\omega_f,\omega_A)E^f(\omega_f)=\overline{E^f}(-\omega_f)\tilde{E}^{fA}(\omega_f,\omega_A)=0. \tag{118}$$

Thus, the first-order responses of the phase-isolated excited state vectors have no component parallel to the unperturbed excited reference state vectors, $\overline{E^f}(-\omega_f)$ and $E^f(\omega_f)$. Multiplying Eq. (116) from the left and Eq. (117) from the right with the projector to the orthogonal complement of state f, $\mathbf{Q}^f=\mathbf{1}-\mathbf{R}^f$, defined in Sec. III B, and using that $\mathbf{Q}^f$ commutes with the Jacobian, we obtain:

$$(\mathbf{A}-(\omega_f+\omega_A)\mathbf{1})\tilde{E}^{fA}(\omega_f,\omega_A)$$
$$=-\mathbf{Q}^f(\mathbf{B}t^A(\omega_A)+\mathbf{A}^A)E^f(\omega_f), \tag{119}$$

$$\tilde{\bar{E}}^{fA}(\omega_f,\omega_A)(\mathbf{A}+(\omega_A-\omega_f)\mathbf{1})$$
$$=-\overline{E^f}(-\omega_f)(\mathbf{B}t^A(\omega_A)+\mathbf{A}^A)\mathbf{Q}^f. \tag{120}$$

Due to this projection the response equations (119) and (120) are regular in the static limit $\omega_A\rightarrow 0$. Projection of the first-order response equations onto the excited reference state leads to an expression for the quasienergy derivative $\Delta\dot{\mathscr{W}}_{0f}^{A}(\omega_A)$:

$$\Delta\mathscr{W}^{A}_{0f}(\omega_A)=\overline{E}^{f}(-\omega_f)(\mathbf{B}t^{A}(\omega_A)+\mathbf{A}^{A})E^{f}(\omega_f). \quad (121)$$

The second-order response equations for the right and left excited state vectors are:

$$(\mathbf{A}-(\omega_f+\omega_A+\omega_B)\mathbf{1})\tilde{E}^{fAB}(\omega_f,\omega_A,\omega_B)=\tilde{\xi}^{fAB}(\omega_f,\omega_A,\omega_B), \quad (122)$$

$$\tilde{\bar{E}}^{fAB}(-\omega_f,\omega_A,\omega_B)(\mathbf{A}-(\omega_f+\omega_A+\omega_B)\mathbf{1})=\tilde{\bar{\xi}}^{fAB}(-\omega_f,\omega_A,\omega_B), \quad (123)$$

with

$$\begin{aligned}\tilde{\xi}^{fAB}(\omega_f,\omega_A,\omega_B)=\hat{P}^{AB}\{&(\mathbf{B}t^{A}(\omega_A)+\mathbf{A}^{A}-\Delta\mathscr{W}^{A}_{0f}(\omega_A))\\&\times\tilde{E}^{fB}(\omega_f,\omega_B)+(\tfrac{1}{2}\mathbf{C}t^{A}(\omega_A)t^{B}(\omega_B)\\&+\tfrac{1}{2}\mathbf{B}t^{AB}(\omega_A,\omega_B)+\mathbf{B}^{A}t^{B}(\omega_B))E^{f}(\omega_f)\\&-\Delta\mathscr{W}^{AB}_{0f}(\omega_A,\omega_B)E^{f}(\omega_f)\},\end{aligned} \quad (124)$$

and

$$\begin{aligned}\tilde{\xi}^{fAB}(\omega_f,\omega_A,\omega_B)=\hat{P}^{AB}\{&\tilde{\bar{E}}^{fB}(-\omega_f,\omega_B)(\mathbf{B}t^{A}(\omega_A)\\&+\mathbf{A}^{A}-W^{A}_{f}(\omega_A))+\overline{E}^{f}(-\omega_f)(\tfrac{1}{2}\mathbf{C}t^{A}(\omega_A)\\&\times t^{B}(\omega_B)+\tfrac{1}{2}\mathbf{B}t^{AB}(\omega_A,\omega_B)+\mathbf{B}^{A}t^{B}(\omega_B))\\&-\overline{E}^{f}(-\omega_f)\Delta\mathscr{W}^{AB}_{0f}(\omega_A,\omega_B)\}.\end{aligned} \quad (125)$$

From the projection onto the orthogonal complement of f we obtain regular equations for the part of the second-order response vectors which are orthogonal to the reference state.

$$(\mathbf{A}-(\omega_f+\omega_A+\omega_B)\mathbf{1})^{\perp}\tilde{E}^{fAB}(\omega_f,\omega_A,\omega_B)=-\mathbf{Q}^{f}\tilde{\xi}^{fAB}(\omega_f,\omega_A,\omega_B), \quad (126)$$

$${}^{\perp}\tilde{\bar{E}}^{fAB}(-\omega_f,\omega_A,\omega_B)(\mathbf{A}-(\omega_f+\omega_A+\omega_B)\mathbf{1})=-\tilde{\bar{\xi}}^{fAB}(-\omega_f,\omega_A,\omega_B)\mathbf{Q}^{f}. \quad (127)$$

The reference state coefficients of the second-order excited state response vectors are obtained from Eq. (103):

$$\begin{aligned}\overline{E}^{fAB}(-\omega_f,\omega_A,\omega_B)E^{f}(\omega_f)&=\overline{E}^{f}(-\omega_f)E^{fAB}(\omega_f,\omega_A,\omega_B)\\&=-\tfrac{1}{2}(\overline{E}^{fA}(-\omega_f,\omega_A)E^{fB}(\omega_f,\omega_B)\\&\quad+\overline{E}^{fB}(-\omega_f,\omega_B)E^{fA}(\omega_f,\omega_A)).\end{aligned} \quad (128)$$

Projection of the second-order response equations onto the excited reference state f gives equations from which the second-order quasienergy $\Delta\mathscr{W}^{AB}_{0f}(\omega_A,\omega_B)$ could be calculated once the second-order excited state response vectors are known.

The procedure used to solve for the second-order response vectors can be generalized to higher orders: In general the component of the nth-order response vectors orthogonal to the excited reference state are determined from the nth-order response equations projected onto orthogonal complement of state f:

$$(\mathbf{A}-(\omega_f+\omega_1+\ldots)\mathbf{1})^{\perp}E^{fX_1\cdots}(\omega_f,\omega_1,\ldots)=-\mathbf{Q}^{f}\tilde{\xi}^{fX_1\cdots}(\omega_f,\omega_1,\ldots), \quad (129)$$

$${}^{\perp}\overline{E}^{fX_1\cdots}(-\omega_f,\omega_1,\ldots)(\mathbf{A}+(-\omega_f+\omega_1+\ldots)\mathbf{1})=-\tilde{\bar{\xi}}^{fX_1\cdots}(-\omega_f,\omega_1,\ldots)\mathbf{Q}^{f}, \quad (130)$$

while the reference state coefficients are determined by Eq. (103). To calculate the right hand side vectors for the nth-order response equations the responses of the quasienergy difference are needed up to order $n-1$. They can be obtained either from the expectation value type expression (108) or from equivalent equations obtained from projecting the response equations onto the excited reference state. We note, that the $2n+1$ and $2n+2$ rules cannot be applied without modifications to the calculation of the coefficients $\Delta\mathscr{W}^{AB}_{f}(\omega_A,\omega_B)$ of the time-dependent quasienergy difference, because only the time-average $\{\Delta\mathscr{W}_{0f}(t,\epsilon)\}_T$ is subject to the variational condition (113).

Although we used for the phase-isolated and the nonphase-isolated perturbation expansions different parametrizations of the time-dependent excited state vectors, the final results for $\overline{E}^{f}(t,\epsilon)$ and $E^{f}(t,\epsilon)$ must be the same order by order in the perturbation strengths. To compare the two perturbation series, we expand the quasienergy-dependent phase-factor which has been factored off in the phase-isolated expansion. Doing so, we get for the right excited state vectors:

$$E^{f}(t,\epsilon)=E^{f}(\omega_f)e^{-i\omega_f t}+\sum_j \epsilon_j(\omega_j)\left(\tilde{E}^{fX_j}(\omega_f,\omega_j)+E^{f}(\omega_f)\frac{\Delta\mathscr{W}^{X_j}_{0f}(\omega_j)}{\omega_j}\right)e^{-i(\omega_f+\omega_j)t}+\ldots. \quad (131)$$

If we compare the last equation with the nonphase-isolated perturbation expansion for the right excited state vectors we find in first order:

$$E^{fA}(\omega_f,\omega_A)=\tilde{E}^{fA}(\omega_f,\omega_A)+E^{f}(\omega_f)\frac{\Delta\mathscr{W}^{A}_{0f}(\omega_A)}{\omega_A}. \quad (132)$$

For the left excited state vectors one finds in a similar manner:

$$\overline{E}^{f}(t,\epsilon)=\overline{E}^{f}(-\omega_f)e^{+i\omega_f t}+\sum_j \epsilon_j(\omega_j)\left(\tilde{\bar{E}}^{fX_j}(-\omega_f,\omega_j)-\overline{E}^{f}(-\omega_f)\frac{\Delta\mathscr{W}^{X_j}_{0f}(\omega_j)}{\omega_j}\right)e^{-i(\omega_j-\omega_f)t}+\ldots, \quad (133)$$

and

$$E^{fA}(-\omega_f,\omega_A)=\tilde{\bar{E}}^{fA}(-\omega_f,\omega_A)-\overline{E}^{f}(-\omega_f)\frac{\Delta\mathscr{W}^{A}_{0f}(\omega_A)}{\omega_A}. \quad (134)$$

Of course, the same relations can be derived from a comparison of the respective response equations for the phase-isolated and the nonphase-isolated perturbation expansions.

From the results of Ref. 21 and from the examples derived in Sec. III it is evident that the first and second residues of the ground state response functions and thus the expressions for multiphoton transition moments are more closely related to the irregular nonphase-isolated perturbation expansion. For excited state response functions the singularities from the left and from the right excited state vectors cancel mutually. In this case it is evidently computationally advantageous to use the regularized phase-isolated perturbation series in order to avoid numerical instabilities for small or zero frequencies.

VII. RESPONSE FUNCTIONS FOR EXCITED STATES AS DERIVATIVES OF A QUASIENERGY DIFFERENCE LAGRANGIAN

Similar to the ground state response functions, the difference between the ground state and the excited state response functions can be calculated as derivative of the real part of the time-averaged quasienergy difference:

$$\langle\langle X_1;X_2,\ldots,X_n\rangle\rangle^{(f)}_{\omega_2\ldots\omega_n}-\langle\langle X_1;X_2,\ldots,X_n\rangle\rangle^{(0)}_{\omega_2\ldots\omega_n}$$
$$=\left(\frac{d^n\{\frac{1}{2}\Delta\dot{\mathscr{W}}_{0f}(t,\epsilon)+\frac{1}{2}\Delta\dot{\mathscr{W}}_{0f}(t,\epsilon)^*\}_T}{d\epsilon_1(\omega_1)d\epsilon_2(\omega_2)\ldots d\epsilon_n(\omega_n)}\right)_0, \tag{135}$$

with $\omega_1=-\omega_2\ldots-\omega_n$. The expressions for the excited state response functions obtained from the derivative of the quasienergy difference are equivalent to those obtained from the derivatives of the transition moment functional $\mathscr{T}^{ff}(t,\epsilon)$. This conjecture can be proven as follows: From the generalized Frenkel variation principles for the *complete* and for the *phase-isolated* excited state vectors, Eqs. (109) and (111), we obtain the two equations:

$$\frac{d}{d\epsilon_j(\omega_j)}\left(\overline{E^f}(t,\epsilon)\left[\mathbf{A}(t,\epsilon)-i\frac{d}{dt}\right]E^f(t,\epsilon)\right)$$
$$+i\frac{d}{dt}\left(\overline{E^f}(t,\epsilon)\,\frac{d}{d\epsilon_j(\omega_j)}E^f(t,\epsilon)\right)$$
$$=\overline{E^f}(t,\epsilon)\frac{d\mathbf{A}(t,\epsilon)}{d\epsilon_j(\omega_j)}E^f(t,\epsilon), \tag{136}$$

$$\frac{d}{d\epsilon_j(\omega_j)}\left(\tilde{\bar{E}}^f(t,\epsilon)\left[\mathbf{A}(t,\epsilon)-i\frac{d}{dt}\right]\tilde{E}^f(t,\epsilon)\right)$$
$$+i\frac{d}{dt}\left(\tilde{\bar{E}}^f(t,\epsilon)\,\frac{d}{d\epsilon_j(\omega_j)}\,\tilde{E}^f(t,\epsilon)\right)$$
$$=\tilde{\bar{E}}^f(t,\epsilon)\,\frac{d\mathbf{A}(t,\epsilon)}{d\epsilon_j(\omega_j)}\,\tilde{E}^f(t,\epsilon), \tag{137}$$

which resemble the time-dependent Hellmann–Feynman theorem for exact states:[2,25,28]

$$\frac{d}{d\epsilon_j(\omega_j)}\langle 0(t,\epsilon)|\hat{H}(t,\epsilon)-i\frac{d}{dt}|0(t,\epsilon)\rangle$$
$$+i\frac{d}{dt}\langle 0(t,\epsilon)|\frac{d}{d\epsilon_j(\omega_j)}|0(t,\epsilon)\rangle$$
$$=\langle 0(t,\epsilon)|\frac{d\hat{H}(t,\epsilon)}{d\epsilon_j(\omega_f)}|0(t,\epsilon)\rangle. \tag{138}$$

In the parametrization (97)–(102) the time-average of the second term of the left hand side of Eq. (137) vanishes. This can be used to rewrite the derivatives of the time-averaged quasienergy difference $\{\Delta\dot{\mathscr{W}}_{0f}(t,\epsilon)\}_T$ as:

$$\frac{d^n\{\Delta\dot{\mathscr{W}}_{0f}(t,\epsilon)\}_T}{d\epsilon_1(\omega_1)\ldots d\epsilon_n(\omega_n)}$$
$$=\left\{\frac{d^{n-1}}{d\epsilon_2(\omega_2)\ldots d\epsilon_n(\omega_n)}\left[\frac{d}{d\epsilon_1(\omega_1)}\right.\right.$$
$$\times\left(\tilde{\bar{E}}^f(t,\epsilon)\left[\mathbf{A}(t,\epsilon)-i\frac{d}{dt}\right]\tilde{E}^f(t,\epsilon)\right)$$
$$\left.\left.+i\frac{d}{dt}\left(\tilde{\bar{E}}^f(t,\epsilon)\,\frac{d}{d\epsilon_1(\omega_1)}\,\tilde{E}^f(t,\epsilon)\right)\right]\right\}_T, \tag{139}$$

$$=\left\{\frac{d^{n-1}}{d\epsilon_2(\omega_2)\ldots d\epsilon_n(\omega_n)}\left(\tilde{\bar{E}}^f(t,\epsilon)\,\frac{d\mathbf{A}(t,\epsilon)}{d\epsilon_1(\omega_1)}\,\tilde{E}^f(t,\epsilon)\right)\right\}_T, \tag{140}$$

$$=\left\{\frac{d^{n-1}}{d\epsilon_2(\omega_2)\ldots d\epsilon_n(\omega_n)}\right.$$
$$\left.\times\lim_{\rho\to 0}\,e^{\rho t}\left(\overline{E^f}(t,\epsilon)\,\frac{d\mathbf{A}(t,\epsilon)}{d\epsilon_1(\omega_1)}E^f(t,\epsilon)\right)\right\}_T. \tag{141}$$

In Eq. (141) the limes was imposed because divergent secular terms appear in the nonphase-isolated excited state vectors. In the parametrization (22)–(23) for the complete excited state vectors the time-average of the second term of the left hand side of Eq. (136) vanishes and thus one obtains, that the derivatives of the time-averaged quasienergy difference $\{\Delta\dot{\mathscr{W}}_{0f}(t,\epsilon)\}_T$ are equal to the derivatives of the time-averaged transition moment functional $\{\mathscr{T}^{ff}(t,\epsilon)\}_T$ given in Eq. (82):

$$\frac{d^n\{\Delta\dot{\mathscr{W}}_{0f}(t,\epsilon)\}_T}{d\epsilon_1(\omega_1)\ldots d\epsilon_n(\omega_n)}$$
$$=\left\{\frac{d^n}{d\epsilon_1(\omega_1)\ldots d\epsilon_n(\omega_n)}\right.$$
$$\left.\times\lim_{\rho\to 0}\,e^{\rho t}\left(\overline{E^f}(t,\epsilon)\left[\mathbf{A}(t,\epsilon)-i\frac{d}{dt}\right]E^f(t,\epsilon)\right)\right\}_T, \tag{142}$$

$$=\frac{d^n\{\dot{\mathscr{T}}^{ff}(t,\epsilon)\}_T}{d\epsilon_1(\omega_1)\ldots d\epsilon_n(\omega_n)}. \tag{143}$$

The last equation proves that expressions for excited state response functions derived from the derivatives of the

quasienergy difference in Eq. (135) are formally equivalent to the expressions identified from the second residues of the ground state response functions.

As shown in the last section, the time-average of $\Delta\bar{\mathscr{W}}_{0f}(t,\epsilon)$ is stationary in the Fourier components of the left and right excited state vectors. To obtain a quasienergy difference Lagrangian in which the time-average can be required to be stationary in all its independent variables, we must add to $\Delta\bar{\mathscr{W}}_{0f}(t,\epsilon)$ the constraints for the ground state cluster amplitudes, multiplied by excited state Lagrangian multipliers (cf. Eq. (85)):

$$\Delta L^f(t,\epsilon)=\Delta\bar{\mathscr{W}}_{0f}(t,\epsilon)+\tilde{\bar{N}}^f(t,\epsilon)\left(e(t,\epsilon)-i\frac{d}{dt}T(t,\epsilon)\right). \tag{144}$$

The variational condition for the time-average of $\Delta L^f(t,\epsilon)$,

$$\delta\{\Delta L^f(t,\epsilon)\}_T=0, \tag{145}$$

gives per construction for $\tilde{\bar{E}}^f(t,\epsilon)$ and $\tilde{E}^f(t,\epsilon)$ the same response equations as the generalized Frenkel variational principle, Eq. (111), or the effective Schrödinger equations (106) and (107) used in Sec. VI. For the cluster amplitudes $t(t,\epsilon)$ the same response equations are obtained as from the ground state quasienergy Lagrangian. For the excited states Lagrangian multipliers Eq. (145) leads to response equations which are formally equivalent to those obtained from the transition moment Lagrangian for the Fourier components of $\bar{N}^{ff}(t,\epsilon)$, but all secular divergent terms are eliminated from the right hand side vectors. No difference appears in zeroth-order,

$$\tilde{\bar{N}}^f\mathbf{A}=-\bar{E}^f(-\omega_f)\mathbf{B}E^f(\omega_f), \tag{146}$$

but in the first-order equations,

$$\tilde{\bar{N}}^{fA}(\omega_A)(\mathbf{A}+\omega_A\mathbf{1})=-\tilde{\bar{n}}^{fA}(\omega_A), \tag{147}$$

$$\begin{aligned}\tilde{\bar{n}}^{fA}(\omega_A)=&\bar{E}^f(-\omega_f)(\mathbf{C}t^A(\omega_A)+\mathbf{B}^A)E^f(\omega_f)\\&+\tilde{\bar{E}}^{fA}(-\omega_f,\omega_A)\mathbf{B}E^f(\omega_f)+\bar{E}^f(-\omega_f)\\&\times\mathbf{B}\tilde{\bar{E}}^{fA}(\omega_f,\omega_A)+\tilde{\bar{N}}^f(\mathbf{B}t^A(\omega_A)+\mathbf{A}^A),\end{aligned} \tag{148}$$

the secular terms, present in Eqs. (89) and (90), are eliminated.

Since all zeroth-order intermediates in the phase-isolated parametrization are identical to the zeroth-order intermediates in the nonphase-isolated parametrization, we get from the excited state quasienergy difference Lagrangian exactly the same expression for first-order properties as we identified from the residues in Eq. (56). For the difference between the excited state and the ground state linear response functions we obtain from the second derivative of $\Delta L^f(t,\epsilon)$:

$$\begin{aligned}&\langle\langle A;B\rangle\rangle^{(f)}_{\omega_B}-\langle\langle A;B\rangle\rangle^{(0)}_{\omega_B}\\&=\tfrac{1}{2}\hat{C}^{\pm\omega}\hat{P}^{AB}\{\bar{E}^f(-\omega_f)(\mathbf{B}t^B(\omega_B)+\mathbf{A}^B)\tilde{E}^{fA}(\omega_f,\omega_A)\\&\quad+\bar{E}^f(-\omega_f)(\tfrac{1}{2}\mathbf{C}t^A(\omega_A)t^B(\omega_B)+\mathbf{B}^At^B(\omega_B))E^f(\omega_f)\\&\quad+\tilde{\bar{N}}^f(\tfrac{1}{2}\mathbf{B}t^A(\omega_A)t^B(\omega_B)+\mathbf{A}^At^B(\omega_B))\},\end{aligned} \tag{149}$$

with $\omega_A=-\omega_B$. The first term on the right hand side of Eq. (149) can be rewritten as:

$$\begin{aligned}&\bar{E}^f(-\omega_f)(\mathbf{B}t^B(\omega_B)+\mathbf{A}^B)\tilde{E}^{fA}(\omega_f,\omega_A)\\&=\bar{\xi}^{fB}(-\omega_f,\omega_B)\mathbf{Q}^f(\mathbf{A}-(\omega_f+\omega_A)\mathbf{1})^{-1}\mathbf{Q}^f\xi^{fA}(\omega_f,\omega_A).\end{aligned} \tag{150}$$

Thus, Eq. (149) is equivalent to Eq. (72), obtained in Sec. III after eliminating ''by hand'' the secular divergent terms. Using the $2n+1$ and $2n+2$ rules we get for the difference between the quadratic response functions for the excited state f and the ground state:

$$\begin{aligned}\langle\langle A;B,C\rangle\rangle^{(f)}_{\omega_B,\omega_C}-\langle\langle A;B,C\rangle\rangle^{(0)}_{\omega_B,\omega_C}=&\tfrac{1}{2}\hat{C}^{\pm\omega}\hat{P}^{ABC}\{\tfrac{1}{6}\bar{E}^f(-\omega_f)\mathbf{D}t^A(\omega_A)t^B(\omega_B)t^C(\omega_C)E^f(\omega_f)+\bar{E}^f(-\omega_f)(\tfrac{1}{2}\mathbf{C}t^A(\omega_A)t^B(\omega_B)\\&+\mathbf{B}^At^B(\omega_B))\tilde{E}^{fC}(\omega_f,\omega_C)+\tilde{\bar{E}}^{fC}(-\omega_f,\omega_C)(\tfrac{1}{2}\mathbf{C}t^A(\omega_A)t^B(\omega_B)+\mathbf{B}^At^B(\omega_B))E^f(\omega_f)\\&+\tilde{\bar{E}}^{fC}(-\omega_f,\omega_C)(\mathbf{B}t^A(\omega_A)+\mathbf{A}^A)\tilde{E}^{fB}(\omega_f,\omega_B)+\tilde{\bar{N}}^{fC}(\omega_C)(\tfrac{1}{2}\mathbf{B}t^A(\omega_A)t^B(\omega_B)\\&+\mathbf{A}^At^B(\omega_B))+\tilde{\bar{N}}^f(\tfrac{1}{6}\mathbf{C}t^A(\omega_A)t^B(\omega_B)t^C(\omega_C)+\tfrac{1}{2}\mathbf{B}^At^B(\omega_B)t^C(\omega_C))-\bar{E}^f(-\omega_f)\\&\times(\mathbf{B}t^A(\omega_A)+\mathbf{A}^A)E^f(\omega_f)(\tilde{\bar{E}}^{fC}(-\omega_f,\omega_C)\tilde{E}^{fB}(\omega_f,\omega_B))\}.\end{aligned} \tag{151}$$

From the derivatives of the excited state quasienergy difference Lagrangian one obtains the differences between the excited state and the ground state response functions. To get the complete excited state response functions the ground state response functions are also needed and the respective response equations for the ground state Lagrangian multipliers must be solved. If one is only interested in the excited state response properties but not in the ground state properties, the calculation of the ground state response function and the solution for ground state Lagrangian multipliers can be avoided using a Lagrangian for the excited state quasienergy, i.e., a Lagrangian consisting of the sum of the quasienergy difference and the ground state quasienergy and the constraints for the ground state cluster amplitudes multiplied by Lagrangian multipliers. A time-independent Lagrangian of this form has recently been proposed by Christiansen *et al.*[25]

for calculation of static excited state properties and geometrical derivatives. A Lagrangian for the excited state quasienergy applicable for the calculation of frequency-dependent excited state properties is obtained by:

$$L^f(t,\epsilon) = L(t,\epsilon) + \Delta L^f(t,\epsilon)$$
$$= \langle \mathrm{HF}|\hat{H}(t,\epsilon)\exp(\hat{T}(t,\epsilon))|\mathrm{HF}\rangle + \tilde{\bar{E}}^f(t,\epsilon)\mathbf{A}(t,\epsilon)$$
$$\times \tilde{E}^f(t,\epsilon) + \overline{t^f}(t,\epsilon)\left(e(t,\epsilon) - i\frac{d}{dt}t(t,\epsilon)\right). \quad (152)$$

The essential difference of this approach and the quasienergy difference Lagrangian derived in the foregoing paragraphs is that the ground state Lagrangian multipliers and the multipliers for the excited state quasienergy difference Lagrangian are combined to one set of Lagrangian multipliers:

$$\overline{t^f}(t,\epsilon) = \overline{t}(t,\epsilon) + \tilde{\bar{N}}^f(t,\epsilon). \quad (153)$$

We note that in the static limit the quasienergy becomes identical to the time-independent energy. The calculation of excited states (higher-order) properties as derivatives of the Lagrangians (144) or (152) becomes then equivalent to calculate them as derivatives of the time-independent energy of the excited state, where, however, the molecular orbitals are not allowed to relax in the external fields.

VIII. CONCLUSIONS

We have analyzed the structure of the second residues of the ground state response functions and the first residues of the left and the right multiphoton transition moments for ground to excited state transitions as obtained in coupled cluster response theory and compared them with the expressions obtained in exact state response theory. All three types of residues give in coupled cluster response theory equivalent results for multiphoton transition moments between two excited states and for excited states response functions. We showed that the coupled cluster expressions for n-photon transition moments between two excited states can be written as the projections of the right hand side vectors for the nth-order response equations for one of the excited states onto the zeroth-order vector for the other state. We utilized this formulation to derive a variational transition moment Lagrangian from which computational efficient expressions in accordance with $2n+1$ and $2n+2$ rules can be obtained as derivatives.

For excited state response functions the expressions identified from the residues of the ground state response functions contain secular divergencies; i.e., unphysical terms which diverge in the static limit and which cancel mutually. The appearance of the secular terms is related to an implicit phase factor in the excited state vectors which depends on the quasienergy difference between the excited state and the ground state. We demonstrated that the secular divergencies can be removed by choosing a completely phase-isolated parametrization for the excited state vectors and devised a Lagrangian for the quasienergy difference between the excited state and the ground state, from which numerical stable expressions for the excited state response functions can be obtained as derivatives. These expressions are formally equivalent to those obtained from the residues of the ground state response functions, but contain no secular divergencies. Using the excited state quasienergy Lagrangian, we derived the working expressions for the coupled cluster excited state linear and quadratic response functions. Based on the equations derived in Secs. VI and VII we have implemented the coupled cluster excited state linear response function for the coupled cluster models CCS, CC2 and CCSD. Details of the implementation and numerical examples will be reported in a forthcoming publication.[33] From the excited state linear response function one obtains f.x. dynamic polarizabilities for excited states; the key quantity in the description and understanding of the Stark effect, solvatochromatic shifts of excitation energies and of electrochromic properties.

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APPENDIX: PROOF OF EQUATIONS (73) AND (74)

To prove that Eqs. (73) and (74) hold for arbitrary order we analyze the general structure of the residues of the coupled cluster ground–excited state transition moments. We start from Eq. (16) for the left transition moments. To find the first residues of the right hand side vectors $\overline{\xi}^{X_1\ldots X_{n+1}}(\omega_1,\ldots,\omega_n)$ for the limit $\omega_{n+1}\rightarrow -\omega_i$, we first note that the resolvent $\mathbf{R}(-\omega_{n+1})$ enters in this vector via the first-order multipliers $\overline{t}^{X_{n+1}}(\omega_{n+1})$, either by the direct contributions of $\overline{t}^{X_{n+1}}(\omega_{n+1})$ to $\overline{\xi}^{X_1\ldots X_{n+1}}(\omega_1,\ldots,\omega_{n+1})$ or indirectly by the contributions of $\overline{t}^{X_{n+1}}(\omega_{n+1})$ to higher-order multipliers $\overline{t}^{X_{n+1}X_{k_1}\ldots X_{k_m}}(\omega_{n+1},\omega_{k_1},\ldots,\omega_{k_m})$ with $m<n$.[21] Thus the residue of $\overline{\xi}^{X_1\ldots X_{n+1}}(\omega_1,\ldots,\omega_{n+1})$ for $\omega_{n+1}\rightarrow -\omega_i$ can be obtained by

(1) skipping in $\overline{\xi}^{X_1\ldots X_{n+1}}(\omega_1,\ldots,\omega_{n+1})$ all terms in which the operator-frequency pair (X_{n+1},ω_{n+1}) does not occur in a response of the lagrange multipliers $\overline{t}$, and
(2) substituting the responses of the Lagrange multipliers by their residues:

$$\lim_{\omega_{n+1}\rightarrow -\omega_i}(-\omega_{n+1}-\omega_i)\overline{t}^{X_{n+1}X_{k_1}\ldots X_{k_m}}(\omega_{n+1},\omega_{k_1},\ldots,\omega_{k_m})$$
$$= M^{X_{n+1}}_{0\leftarrow i}\overline{R}^{iX_{k_1}\ldots X_{k_m}}(-\omega_i,\omega_{k_1},\ldots,\omega_{k_m}), \quad (A1)$$

where the vectors $\overline{R}^{iX_{k_1}\ldots X_{k_m}}$ are defined through the last equation.

If we do so with the expression for the $\overline{\xi}^{X_1\ldots X_n}$ vectors derived in Appendix A of Ref. 21 we find:

$$\lim_{\omega_{n+1}\rightarrow-\omega_i}(-\omega_{n+1}-\omega_i)\overline{\xi}^{X_1\ldots X_nX_{n+1}} \tag{A2}$$

$$=M_{0\leftarrow i}^{X_{n+1}}\hat{P}^{X_1\ldots X_n}\Bigg\{\frac{1}{(n-1)!}\overline{R}^{iX_2\ldots X_n}\mathbf{A}^{X_1}+\sum_{i=1}^{n-1}\frac{1}{i!(n-i)!}\overline{R}^{iX_1\ldots X_i}\mathbf{B}t^{X_{i+1}\ldots X_n}+\sum_{i=1}^{n-2}\frac{1}{i!(n-i-1)!}\overline{R}^{iX_2\ldots X_{i+1}}\mathbf{B}^{X_1}t^{X_{i+2}\ldots X_n}$$
$$+\frac{1}{2}\sum_{i=2}^{n-1}\sum_{j=1}^{i-1}\frac{1}{j!(i-j)!(n-i)!}\overline{R}^{iX_1\ldots X_j}\mathbf{C}t^{X_{j+1}\ldots X_i}t^{X_{i+1}\ldots X_n}$$
$$+\frac{1}{6}\sum_{i=3}^{n-1}\sum_{j=2}^{i-1}\sum_{k=1}^{j-1}\frac{1}{k!(j-k)!(i-j)!(n-i)!}\overline{R}^{iX_1\ldots X_k}\mathbf{D}t^{X_{k+1}\ldots X_j}t^{X_{j+1}\ldots X_i}t^{X_{i+1}\ldots X_n}\Bigg\}, \tag{A3}$$

$$=M_{0\leftarrow i}^{X_{n+1}}\overline{r}^{tX_1\ldots X_n}. \tag{A4}$$

For notational convenience we have suppressed in the last equation the frequency arguments of the response amplitude and the vectors $\overline{R}^{iX_1\ldots X_n}$. The vectors $\overline{R}^{iX_{k_1}\ldots X_{k_m}}(-\omega_i,\omega_{k_1},\ldots,\omega_{k_m})$ are the solution to a set of response equations:

$$\overline{R}^{iX_{k_1}\ldots X_{k_m}}(-\omega_i,\omega_{k_1},\ldots,\omega_{k_m})$$
$$=-(M_{0\leftarrow i}^{X_{n+1}})^{-1}\lim_{\omega_{n+1}\rightarrow-\omega_i}(-\omega_{n+1}-\omega_i)$$
$$\times\mathbf{R}(-\omega_{n+1}-\omega_{k_1}\ldots-\omega_{k_m})$$
$$\times\overline{\xi}^{X_{n+1}X_{k_1}\ldots X_{k_m}}(\omega_{n+1},\omega_{k_1},\ldots,\omega_{k_m}), \tag{A5}$$

$$=-\mathbf{R}(\omega_i-\omega_{k_1}\ldots-\omega_{k_m})\overline{r}^{tX_{k_1}\ldots X_{k_m}}(-\omega_i,\omega_{k_1},\ldots,\omega_{k_m}). \tag{A6}$$

In Eq. (46) we showed that the residues of the first-order response Lagrange multipliers $\overline{t}^C(\omega_C)$ for $\omega_C\rightarrow-\omega_i$ become the left eigenvector $\overline{E}^i(-\omega_i)$, multiplied by the transition moment $M_{0\leftarrow i}^C$. Similarly, the residue of the second-order response Lagrange multipliers $\overline{t}^{BC}(\omega_B,\omega_C)$ was shown to be equal to the first-order response $\overline{E}^{iB}(-\omega_i,\omega_B)$ of the left excited state vector, multiplied by $M_{0\leftarrow i}^C$. Thus, in zeroth and in first order the vectors $\overline{R}^{iX_1\ldots X_n}$ are equal to the left excited state vectors $\overline{E}^{iX_1\ldots X_n}$. If we compare Eq. (A3) with the expression for the right hand side for the left excited state response equations given in Appendix C of Ref. 21, it follows by induction for arbitrary order n that $\overline{R}^{iX_1\ldots X_n}=\overline{E}^{iX_1\ldots X_n}$ and $\overline{r}^{tX_1\ldots X_n}=\overline{\xi}^{iX_1\ldots X_n}$. From this result, Eq. (73) follows straightforwardly:

$$M_{i\leftarrow f}^{X_1\ldots X_n}(\omega_2,\ldots,\omega_n)$$
$$=(M_{0\leftarrow i}^{X_{n+1}})^{-1}\lim_{\omega_{n+1}\rightarrow-\omega_i}(-\omega_{n+1}-\omega_i)$$
$$\times M_{0\leftarrow f}^{X_1\ldots X_nX_{n+1}}(\omega_2,\ldots,\omega_n,\omega_{n+1}), \tag{A7}$$

$$=(M_{0\leftarrow i}^{X_{n+1}})^{-1}\lim_{\omega_{n+1}\rightarrow-\omega_i}(-\omega_{n+1}-\omega_i)$$
$$\times\overline{\xi}^{X_1\ldots X_nX_{n+1}}(\omega_1,\omega_2,\ldots,\omega_n,\omega_{n+1})E^f(\omega_f), \tag{A8}$$

$$=\overline{\xi}^{iX_1\ldots X_n}(-\omega_i,\omega_1,\omega_2,\ldots,\omega_n)E^f(\omega_f). \tag{A9}$$

In a similar manner the residue of the right hand side vectors for the cluster amplitude response equations $\xi^{X_1\ldots X_{n+1}}$ are found as

$$\lim_{\omega_{n+1}\rightarrow-\omega_i}(-\omega_{n+1}-\omega_i)\xi^{X_1\ldots X_{n+1}}(\omega_1,\ldots,\omega_{n+1})$$
$$=\xi^{iX_1\ldots X_n}(\omega_i,\omega_1,\ldots,\omega_n)M_{i\leftarrow0}^{X_{n+1}}, \tag{A10}$$

where $\xi^{iX_1\ldots X_n}$ are the right hand side vectors for the response equations for the right excited state vectors, derived in Ref. 21. Introducing this result into Eq. (38) we obtain immediately Eq. (74):

$$M_{f\leftarrow i}^{X_1\ldots X_n}(\omega_2,\ldots,\omega_n)$$
$$=(M_{i\leftarrow0}^{X_{n+1}})^{-1}\lim_{\omega_{n+1}\rightarrow\omega_i}(\omega_{n+1}-\omega_i)\overline{E}^f(-\omega_f)$$
$$\times\xi^{X_1\ldots X_nX_{n+1}}(\omega_1,\omega_2,\ldots,\omega_n,\omega_{n+1}), \tag{A11}$$

$$=\overline{E}^f(-\omega_f)\xi^{iX_1\ldots X_n}(\omega_i,\omega_1,\omega_2,\ldots,\omega_n). \tag{A12}$$

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