Quadratic Response Functions in a Second-Order Polarization Propagator Framework †

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Quadratic Response Functions in a Second-Order Polarization Propagator Framework†

Jeppe Olsen and Poul Jørgensen*

Center for Theoretical Chemistry, Department of Chemistry, University of Aarhus, DK-8000 Århus C, Denmark

Trygve Helgaker

Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway

Jens Oddershede

Department of Chemistry, University of Southern Denmark, Campusvej 55, Odense, Denmark

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The linear and quadratic response functions have been derived for an exact state, based on an exponential parametrization of the time evolution consisting of products of exponentials for orbital rotations and for higher-order excitations. Truncating the linear response function such that the response function itself and its pole structure is correct to second order in Møller−Plesset perturbation theory, we arrive at the second-order polarization propagator approximation (SOPPA). Previous derivations of SOPPA have used the superoperator formalism, making the extension of SOPPA to quadratic and higher order response functions difficult. The derivation of the quadratic response function is described in detail, allowing molecular properties such as hyperpolarizabilities, two-photon cross sections, and excited-state properties to be calculated using the SOPPA model.

I. Introduction

Hyperpolarizabilities are important for the interpretation and analysis of experiments in such different areas as nonlinear optics,[1,2] scattering theory,[3] and the theory of intermolecular interactions.[4] The accurate prediction of hyperpolarizabilities is also essential to progress in technologically important areas such as the design of optical materials. However, theoretical predictions are difficult to make, depending critically on the description of electron correlation. The history of the determination of the static hyperpolarizability of the neon atom, which we have recently reviewed,[5] is perhaps the best illustration of the difficulties that may arise in theoretical and experimental determinations of hyperpolarizabilities.

The simplest model of electron correlation is provided by second-order Møller−Plesset perturbation theory (MP2), which typically recovers more than 90% of the correlation energy.[6] Static molecular properties, in particular molecular equilibrium structures and other properties that depend on the total energy, have been successfully calculated using this model. By contrast, the MP2 calculation of frequency-dependent molecular properties has been much less successful. To understand the reason for this failure, we note that the MP2 model represents a two-step approach, where a Hartree−Fock calculation is carried out prior to the evaluation of the perturbation correction. Since the response functions arising from this strategy retain the pole structure of time-dependent Hartree−Fock (TDHF) theory, the description of the dispersion of frequency-dependent molecular properties is not improved relative to an uncorrelated description.[7]

To correlate the response function while retaining the pole structure uncorrelated is clearly not a sound approach to the calculation of frequency-dependent molecular properties. To achieve the same accuracy as for static properties, we must also modify the pole structure, as done in the second-order polarization propagator approach (SOPPA).[8,9] In SOPPA, the linear response function is set up as an extension to the TDHF theory, with both the response function and its pole structure correct to second order in perturbation theory.

So far, SOPPA has only been derived for linear response functions and has therefore only been used to calculate second-order molecular properties such as the frequency-dependent polarizability. In particular, the SOPPA linear response function has been obtained by expressing the response function of the exact state within the superoperator inner-projection formalism,[10] truncating the response function such that the response function and the poles are both correct to second order in perturbation theory. Since the quadratic and higher-order response functions so far have not been expressed in the superoperator formalism, SOPPA has not been extended to nonlinear response functions, thereby restricting its use to linear properties.

In this paper, we demonstrate how SOPPA also may be derived from time-dependent perturbation theory by parametrizing the time evolution of the exact state in terms of exponential operators for orbital rotations and for higher-order excitations. Truncation of the exact linear response function in such a manner that the response function and its pole structure are both correct to second order in Møller−Plesset perturbation theory then gives SOPPA. This approach may straightforwardly be extended to quadratic and higher-order response functions. The derivation of the quadratic response function and its residues is described, making it possible to calculate properties such as frequency-dependent hyperpolarizability, two-photon transition matrix elements,[11] and excited-state properties[11] within the SOPPA framework.

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Response functions have previously been derived for self-consistent field (SCF) and a multiconfigurational SCF (MCSCF) states.[11] More recently, they have also been determined for a coupled-cluster state.[12] Truncating the cluster operator at the singles and doubles level, we obtain the coupled-cluster singles-and-doubles (CCSD) response functions. Further truncation of the double amplitudes equations to lowest order in Møller−Plesset perturbation theory gives the CC2 response functions.[13] Indeed, CC2 theory may be viewed as an alternative to SOPPA, where the response functions and their poles are determined to second order in perturbation theory. However, a difference between the SOPPA and CC2 models is that when the doubles are neglected, SOPPA reduces to the response function for SCF wave functions, whereas CC2 reduces to coupled-cluster singles (CCS) theory. This difference originates from the explicit inclusion of de excitation operators in the SOPPA approach.

II. Response Theory for a State Determined by Perturbation Theory

A. Parametrization of the Unperturbed Reference State. We consider a closed-shell molecular system described by a time-independent Hamiltonian H_0, which we separate into a zero-order Hamiltonian F (the Fock operator) and a perturbation operator W (the fluctuation potential):

$$H_0 = F + W \tag{1}$$

Next, we turn on adiabatically a Hermitian perturbation

$$V(t) = \int_{-\infty}^{\infty} \mathrm{d}\omega\, V(\omega) \exp(-i\omega + \epsilon)t \tag{2}$$

where the positive infinitesimal ϵ ensures that $V(-\infty)$ is zero. From the Hermiticity of $V(t)$, it follows that

$$V(\omega)^\dagger = V(-\omega) \tag{3}$$

At $t = -\infty$, the system is in the state

$$\begin{aligned} |0\rangle &= N(1 + \mathbf{c}_1\tau_1^\dagger + \mathbf{c}_2\tau_2^\dagger + \cdots)|\mathrm{HF}\rangle \\ &= N(1 + \mathbf{c}_1|\mathbf{x}_1\rangle\langle\mathrm{HF}| + \mathbf{c}_2|\mathbf{x}_2\rangle\langle\mathrm{HF}| + \cdots)|\mathrm{HF}\rangle \end{aligned} \tag{4}$$

where the $\tau_i^\dagger$ are column vectors containing all single, double, and higher excitation operators, respectively, from the Hartree−Fock state $|\mathrm{HF}\rangle$:

$$\tau_1^\dagger = (a_A^\dagger a_I) \tag{5a}$$

$$\tau_2^\dagger = (a_A^\dagger a_I a_B^\dagger a_J), \quad (AI) \geq (BJ) \tag{5b}$$

whereas the $\mathbf{c}_i$ are row vectors containing the expansion coefficients of these states. We here use indexes *I, J, K, L* for occupied Hartree−Fock spin−orbitals and *A, B, C, D* for unoccupied spin−orbitals, while *P, Q, R, S* are used for general (unspecified) spin−orbitals. The states $|\mathbf{x}_i\rangle$ are defined as

$$|\mathbf{x}_i\rangle = \tau_i^\dagger|\mathrm{HF}\rangle, \quad i = 1, 2,... \tag{6}$$

With the operators defined as in eq 5, parts a and b, these states constitute an orthonormal set

$$\langle\mathrm{HF}|\tau_{xi}\,\tau_{yj}^\dagger|\mathrm{HF}\rangle = \delta_{xy}\delta_{ij} \tag{7}$$

(here $\tau_{xi}^\dagger$ denotes element x of $\tau_i^\dagger$), so that the normalization constant becomes

$$N = \left(1 + \sum_i \mathbf{c}_i\mathbf{c}_i^\dagger\right)^{-1/2} \tag{8}$$

The expansion coefficients $\mathbf{c}_i$ may be determined from Møller−Plesset perturbation theory by solving the equations

$$\langle 0|[\Lambda^{(0)\dagger}, H_0]|0\rangle = \langle 0|[\Lambda^{(0)\dagger}, F + W]|0\rangle = 0 \tag{9}$$

to different orders in the fluctuation potential, where $\Lambda^{(0)\dagger}$ refers to the state excitation operators collected in a column vector:

$$\Lambda^{(0)\dagger} = \begin{pmatrix} |\mathbf{x}_1\rangle\langle\mathrm{HF}| \\ |\mathbf{x}_2\rangle\langle\mathrm{HF}| \\ \vdots \end{pmatrix} \tag{10}$$

Note that the normalization constant N may be removed from eq 9. We will in the following use the form without the normalization factor which leads to the same equations as obtained using standard intermediate normalization. Thus, expanding the coefficients $\mathbf{c}_i$ in powers of the fluctuation potential

$$\mathbf{c}_i = \mathbf{c}_i^{(0)} + \mathbf{c}_i^{(1)} + \mathbf{c}_i^{(2)} + \cdots \tag{11}$$

and inserting eq 4 into eq 9, we obtain to second order the following set of equations

$$\langle\mathrm{HF}|[\Lambda^{(0)\dagger}, F]\,\mathrm{HF}\rangle = 0 \tag{12a}$$

$$\sum_i [(\mathbf{c}_i^{(1)})^\dagger\langle\mathbf{x}_i|[\Lambda^{(0)\dagger}, F]|\mathrm{HF}\rangle + \mathbf{c}_i^{(1)}\langle\mathrm{HF}|[\Lambda^{(0)\dagger}, F]|\mathbf{x}_i\rangle] + \langle\mathrm{HF}|[\Lambda^{(0)\dagger}, W]|\mathrm{HF}\rangle = 0 \tag{12b}$$

$$\sum_i [(\mathbf{c}_i^{(2)})^\dagger\langle\mathbf{x}_i|[\Lambda^{(0)\dagger}, F]|\mathrm{HF}\rangle + \mathbf{c}_i^{(2)}\langle\mathrm{HF}|[\Lambda^{(0)\dagger}, F]|\mathbf{x}_i\rangle] + \sum_i [(\mathbf{c}_i^{(1)})^\dagger\langle\mathbf{x}_i|[\Lambda^{(1)\dagger}, W]|\mathrm{HF}\rangle + \mathbf{c}_i^{(1)}\langle\mathrm{HF}|[\Lambda^{(1)\dagger}, W]|\mathbf{x}_i\rangle] + \sum_{i,j} (\mathbf{c}_i^{(1)})^\dagger\mathbf{c}_j^{(1)}\langle\mathbf{x}_i|[\Lambda^{(0)\dagger}, W]|\mathbf{x}_j\rangle = 0 \tag{12c}$$

Equation 12a shows that

$$\mathbf{c}_i^{(0)} = 0 \tag{13}$$

From eq 12b, we see that only doubly excited states $|\mathbf{x}_2\rangle = \tau_2^\dagger|\mathrm{HF}\rangle$ give nonzero first-order contributions to $\mathbf{c}_2^{(1)}$ and that these contributions are identical to those obtained in a conventional derivation. Similarly, eq 12c shows that $\mathbf{c}_i^{(2)}$ with $i = 1$, 2, 3, 4 give nonzero second-order contributions.

B. Parametrization of the Time Development of the Reference State. The time development of the reference state is parametrized in terms of exponential operators for orbital rotations and higher excitations working on the unperturbed reference state:

$$|\tilde{0}(t)\rangle = \exp(\mathrm{i}\kappa(t))\exp(\mathrm{i}S(t))|0\rangle \tag{14}$$

Here the Hermitian operator $\kappa(t)$ generates a unitary transformation of the orbitals and contains a set of time-dependent orbital amplitudes

$$\kappa(t) = \sum_{AI} [\kappa_{\mathrm{AI}}(t)a_A^\dagger a_\mathrm{I} + \kappa_{IA}^*(t)a_I^\dagger a_\mathrm{A}] = \sum_\mu [\kappa_\mu(t)Q_\mu^\dagger + \kappa_\mu^*(t)Q_\mu] \tag{15}$$

Likewise, the Hermitian operator $S(t)$ generates a unitary transformation in the configuration space and contains a set of time-dependent configuration amplitudes:

$$S(t) = \sum_{x \notin \mathbf{x}_1} [S_x(t)|x\rangle\langle \mathrm{HF}| + S_x^*(t)|\mathrm{HF}\rangle\langle x|] = \sum_{x \notin \mathbf{x}_1} [S_x(t)Q_x^\dagger + S_x^*(t)Q_x] \quad (16)$$

where the summation is over all states x except the single-excited states contained in $\mathbf{x}_1$.

The time dependence of the orbital and configuration parameters $\kappa_{ai}(t)$ and $S_x(t)$ is introduced in order to describe the time evolution of the exact state in the presence of the perturbation operator $V(t)$ in eq 2. Compared to the standard parametrization of the time evolution of an exact state previously used in ref 11, eq 4 includes orbital rotations instead of state excitations between $|\mathrm{HF}\rangle$ and single-excited determinants.The replacement of single excitations with orbital rotations is is also used in Brückner coupled cluster theory.[14] We here use it in a slightly different way: instead of using orbital rotations to eliminate the single excitations from the wave function, we use the orbital rotations to eliminate the time dependence of the single excitations. As will be discussed later, the present use of κ and S without single excitations has the advantage that S vanishes in the absence of the fluctuation potential. Another difference between the present and previous forms of S is the present use of state-transfer operators $|\mathrm{HF}\rangle\langle x|$,$|x\rangle\langle \mathrm{HF}|$ working on the state $|0\rangle$ whereas the previous approach used state-transfer operators of the form $|0\rangle\langle N|$,$|N\rangle\langle 0|$ where $|N\rangle$ is an basis for the orthogonal complement to $|0\rangle$. The two forms of the state-transfer operators spans the same space except for a phase-factor. The present form will ease the perturbation expansion of S as it is expressed directly in terms of the Hartree−Fock determinant and double and higher excitations. We note that, for a complete description of the time development of the reference state, a phase factor should be included in eq 14. However, since we consider the determination of response functions and not the wave function as such, this phase factor can be ignored.[11]

C. The Linear and Quadratic Response Functions. To determine the linear and quadratic response functions, we begin by considering the time dependence of the expectation value $\langle\tilde{0}|A|\tilde{0}\rangle$ of a one-electron operator A, noting that, for our purposes, we need only expand the wave function $|\tilde{0}\rangle$ of eq 14 to second order in the external perturbation:

$$\kappa = \kappa^{(1)}(t) + \kappa^{(2)}(t) + \cdots \quad (17a)$$

$$S = S^{(1)}(t) + S^{(2)}(t) + \cdots \quad (17b)$$

We have here used that $\kappa^{(0)}$ and $S^{(0)}$ vanish, as will be demonstrated later. Substitution of these expansions into eq 14 yields to second order

$$\langle\tilde{0}|A|\tilde{0}\rangle = \langle 0|A|0\rangle - i\langle 0|[\kappa^{(1)}(t) + S^{(1)}(t), A]|0\rangle - \frac{1}{2}\langle 0|[\kappa^{(1)}(t), [\kappa^{(1)}(t), A]]|0\rangle - \frac{1}{2}\langle 0|[S^{(1)}(t),[S^{(1)}(t), A]]|0\rangle - \langle 0|[S^{(1)}(t), [\kappa^{(1)}(t), A]]|0\rangle - i\langle 0|[\kappa^{(2)}(t) + S^{(2)}(t), A]|0\rangle \quad (18)$$

Since the response functions are defined in the frequency rather than the time domain, we now introduce wave function corrections in the frequency space. By analogy with eq 2, we write

$$\kappa^{(1)}(t) = \int_{-\infty}^{\infty} \mathrm{d}\omega\, \kappa^{(1)}(\omega) \exp(-i\omega + \epsilon)t \quad (19a)$$

$$\kappa^{(2)}(t) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{d}\omega_1\, \mathrm{d}\omega_2\, \kappa^{(2)}(\omega_1,\omega_2) \exp(-i(\omega_1 + \omega_2) + 2\epsilon)t \quad (19b)$$

$$S^{(1)}(t) = \int_{-\infty}^{\infty} \mathrm{d}\omega\, S^{(1)}(\omega) \exp(-i\omega + \epsilon)t \quad (19c)$$

$$S^{(2)}(t) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{d}\omega_1\, \mathrm{d}\omega_2\, S^{(2)}(\omega_1,\omega_2) \exp(-i(\omega_1 + \omega_2) + 2\epsilon)t \quad (19d)$$

where we require the second-order corrections to be symmetric in the frequencies:

$$\kappa^{(2)}(\omega_1,\omega_2) = \kappa^{(2)}(\omega_2,\omega_1) \quad (20a)$$

$$S^{(2)}(\omega_1,\omega_2) = S^{(2)}(\omega_2,\omega_1) \quad (20b)$$

Inserting the frequency-expansions of the wave function corrections of eq 19 into eq 18, we obtain

$$\begin{aligned}\langle\tilde{0}|A|\tilde{0}\rangle = \langle 0|A|0\rangle &- i\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{d}\omega\, \langle 0|[\kappa^{(1)}(\omega) + S^{(1)}(\omega), A]|0\rangle \exp(-i\omega + \epsilon)t \\ &- \frac{1}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{d}\omega_1\, \mathrm{d}\omega_2\, \langle 0|[\kappa^{(1)}(\omega_1),[\kappa^{(1)}(\omega_2), A]]|0\rangle \\ &\exp(-i(\omega_1 + \omega_2) + 2\epsilon)t - \frac{1}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{d}\omega_1\, \mathrm{d}\omega_2\, \langle 0|[S^{(1)}(\omega_1), \\ &[S^{(1)}(\omega_2), A]]|0\rangle \exp(-i(\omega_1 + \omega_2) + 2\epsilon)t - \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{d}\omega_1\, \mathrm{d}\omega_2 \\ &\langle 0|[S^{(1)}(\omega_1),[\kappa^{(1)}(\omega_2), A]]|0\rangle \exp(-i(\omega_1 + \omega_2) + 2\epsilon)t - \\ &i\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{d}\omega_1\, \mathrm{d}\omega_2\, \langle 0|[\kappa^{(2)}(\omega_1,\omega_2) + S^{(2)}(\omega_1,\omega_2), A]|0\rangle \\ &\exp(-i(\omega_1 + \omega_2) + 2\epsilon)t \quad (21)\end{aligned}$$

Comparing eq 21 with the formal expansion of an expectation value in terms of response functions

$$\begin{aligned}\langle\tilde{0}|A|\tilde{0}\rangle = \langle 0|A|0\rangle &\int_{-\infty}^{\infty} \mathrm{d}\omega\, \langle\langle A;V(\omega)\rangle\rangle_\omega \exp(-i\omega + \epsilon)t + \\ &\frac{1}{2}\int\int_{-\infty}^{\infty} \mathrm{d}\omega_1\, \mathrm{d}\omega_2\, \langle\langle A;V(\omega_1), V(\omega_2)\rangle\rangle_{\omega_1,\omega_2} \\ &\exp(-i(\omega_1 + \omega_2) + 2\epsilon)t \quad (22)\end{aligned}$$

we may identify the linear response function

$$\langle\langle A;V(\omega)\rangle\rangle_\omega = -i\langle 0|[(\kappa^{(1)}(\omega) + S^{(1)}(\omega), A]|0\rangle \quad (23)$$

and the quadratic response function

$$\begin{aligned}\langle\langle A;V(\omega_1), V(\omega_2)\rangle\rangle_{\omega_1,\omega_2} = &-P_{12}\langle 0|[\kappa^{(1)}(\omega_1),[\kappa^{(1)}(\omega_2), A]]|0\rangle - P_{12}\langle 0|[S^{(1)}(\omega_1), \\ &[S^{(1)}(\omega_2), A]]|0\rangle - 2P_{12}\langle 0|[S^{(1)}(\omega_1),[\kappa^{(1)}(\omega_2), A]]|0\rangle - \\ &2i\langle 0|[\kappa^{(2)}(\omega_1,\omega_2) + S^{(2)}(\omega_1,\omega_2), A]|0\rangle \quad (24)\end{aligned}$$

where P_{12} averages over the two permutations of the frequencies ω_1 and ω_2:

$$P_{12}\langle 0|[S^{(1)}(\omega_1),[\kappa^{(1)}(\omega_2), A]]|0\rangle = \frac{1}{2}\langle 0|[S^{(1)}(\omega_1), [\kappa^{(1)}(\omega_2), r]]|0\rangle + \frac{1}{2}\langle 0|[S^{(1)}(\omega_2),[\kappa^{(1)}(\omega_1), A]]|0\rangle \quad (25)$$

In eq 24, we have thus explicitly ensured symmetry between index 1 and 2 in accordance with the required permutation symmetry of the quadratic response function

$$\langle\langle A;V(\omega_1), V(\omega_2)\rangle\rangle_{\omega_1,\omega_2} = \langle\langle A;V(\omega_3), V(\omega_1)\rangle\rangle_{\omega_2,\omega_1} \quad (26)$$

We have thus identified the terms of the order expansions in the external perturbation of S and κ that are needed for the linear and quadratic response functions. In the next section, we consider what terms to include in the expansions of the time-independent and time-dependent wave functions to obtain the response functions (including their pole structures) correctly to second order in the fluctuation potential.

III. Form and Solution of the Time-Dependent Equations

A. Equations for the Time Development of the Reference State. The time development of $|\tilde{0}(t)\rangle$ is determined by requiring Ehrenfest's theorem to be fulfilled for the operators in eqs 15 and 16, which describe the time evolution of $|\tilde{0}(t)\rangle$. It is convenient to collect these operators in a vector (here in row form):

$$\Lambda = (\tau_1^\dagger, |\mathbf{x}_2\rangle\langle \mathrm{HF}|, |\mathbf{x}_3\rangle\langle \mathrm{HF}|, ..., \tau_1, |\mathrm{HF}\rangle\langle \mathbf{x}_2|, |\mathrm{HF}\rangle\langle \mathbf{x}_3| ...)$$
$$= (\mathbf{Q}_\mu^\dagger, \mathbf{Q}_x^\dagger, \mathbf{Q}_\mu, \mathbf{Q}_x) \quad (27)$$

where $\mathbf{Q}_\mu^\dagger$ are the single orbital-excitation operators and $\mathbf{Q}_x^\dagger$ the double and higher state excitation operators. In the presence of the time-dependent perturbation, we introduce the transformed operator basis

$$\tilde{\Lambda}^\dagger = \begin{pmatrix} \tilde{\mathbf{Q}}_\mu \\ \tilde{\mathbf{Q}}_x \\ \tilde{\mathbf{Q}}_\mu^\dagger \\ \tilde{\mathbf{Q}}_x^\dagger \end{pmatrix} \quad (28)$$

where

$$\tilde{\mathbf{Q}}_\mu = \exp(i\kappa(t))\mathbf{Q}_\mu\exp(-i\kappa(t)) \quad (29)$$

and similarly for $\tilde{\mathbf{Q}}_x$, $\tilde{\mathbf{Q}}_\mu^\dagger$, and $\tilde{\mathbf{Q}}_x^\dagger$. Use of the transformed basis in eq 29 corresponds to the use of orbitals at time t:

$$\tilde{a}_p^\dagger(t) = \exp(i\kappa(t))a_p^\dagger\exp(-i\kappa(t)) \quad (30)$$

The time evolution of $|\tilde{0}(t)\rangle$ may now be determined using Ehrenfest's theorem for the transformed operators of $\tilde{\Lambda}^\dagger$ in eq 28:

$$\frac{d}{dt}\langle\tilde{0}(t)|\,\tilde{\mathbf{Q}}_\mu|\,\tilde{0}(t)\rangle - \left\langle\tilde{0}(t)\left|\left(\frac{\partial}{\partial t}\tilde{\mathbf{Q}}_\mu\right)\right|\,\tilde{0}(t)\right\rangle = -i(\langle\tilde{0}(t)|[\tilde{\mathbf{Q}}_\mu, H_0 + V(t)]|\,\tilde{0}(t)\rangle - \langle 0|[\mathbf{Q}_\mu, H_0]|0\rangle) \quad (31a)$$

$$\frac{d}{dt}\langle\tilde{0}(t)|\tilde{\mathbf{Q}}_x|\,\tilde{0}(t)\rangle - \left\langle\tilde{0}(t)\left|\left(\frac{\partial}{\partial t}\tilde{\mathbf{Q}}_x\right)\right|\tilde{0}(t)\right\rangle = -i\langle\tilde{0}(t)|[\tilde{\mathbf{Q}}_x, H_0 + V(t)]|\tilde{0}(t)\rangle \quad (31b)$$

and similarly for their adjoints. The term $\langle 0|[\mathbf{Q}_\mu, H_0]|0\rangle$ in Ehrenfest's theorem for $\tilde{\mathbf{Q}}_\mu$ has been introduced to ensure that $\kappa_{ai}(t)$ vanishes in the absence of the time-dependent perturbation, in agreement with the absence of a zero-order term in the expansion of κ in eq 17. We likewise note that the $S_x(t)$ parameters vanish in the absence of the perturbation as eq 31b for the state-transfer operators entering $S(t)$ reduces to eq 9 in the absence of an time-dependent perturbation.

B. Expansion of the Time-Dependent Equations in the External Perturbation. We now expand eq 31 in orders of the external perturbation, restricting ourselves to terms that are linear and quadratic in the amplitudes. Inserting eq 17 into eq 31 and collecting the terms linear in the perturbation, we obtain the first-order time-dependent equations

$$i\langle 0|[\Lambda^\dagger, \dot{S}^{(1)} + \dot{\kappa}^{(1)}]|0\rangle = -i\langle 0|[\Lambda^\dagger, V(t)]|0\rangle + \langle 0|[[\Lambda^\dagger, H_0], S^{(1)}]|0\rangle + \langle 0|[\Lambda^\dagger,[H_0,\kappa^{(1)}]]|0\rangle \quad (32)$$

Next, collecting second-order terms, we obtain the second-order time-dependent equations

$$\begin{aligned} i\langle 0|[\Lambda^\dagger, \dot{S}^{(2)} + \dot{\kappa}^{(2)}]|0\rangle &- \frac{1}{2}\langle 0|[[\Lambda^\dagger, \dot{S}^{(1)}], S^{(1)}]|0\rangle \\ &- \frac{1}{2}\langle 0|[[\Lambda^\dagger, S^{(1)}], \dot{S}^{(1)}]|0\rangle - \frac{1}{2}\langle 0|[\Lambda^\dagger,[\dot{\kappa}^{(1)},\kappa^{(1)}]]|0\rangle \\ &- \langle 0|[[\Lambda^\dagger, \dot{\kappa}^{(1)}], S^{(1)}]|0\rangle = \langle 0|[[\Lambda^\dagger, H_0], S^{(2)}]|0\rangle \\ &+ \langle 0|[\Lambda^\dagger,[H_0,\kappa^{(2)}]]|0\rangle + \langle 0|[[\Lambda^\dagger, V(t)], S^{(1)}]|0\rangle \\ &+ \frac{i}{2}\langle 0|[[[\Lambda^\dagger, H_0], S^{(1)}], S^{(1)}]|0\rangle + \langle 0|[\Lambda^\dagger,[V(t),\kappa^{(1)}]]|0\rangle \\ &+ i\langle 0|[[\Lambda^\dagger,[H_0,\kappa^{(1)}]], S^{(1)}]|0\rangle + \frac{i}{2}\langle 0|[\Lambda^\dagger,[[H_0,\kappa_1],\kappa_1]]|0\rangle \end{aligned} \quad (33)$$

To obtain eq 33, we used the Jacobi identity[6]

$$[A,[B, C]] + [B,[C, A]] + [C,[A, B]] = 0 \quad (34)$$

to rewrite

$$-\frac{1}{2}\langle 0|[[\Lambda^\dagger, \kappa^{(1)}],\dot{\kappa}^{(1)}]|0\rangle + \frac{1}{2}\langle 0|[[\Lambda^\dagger,\kappa^{(1)}], \dot{\kappa}^{(1)}]|0\rangle = -\frac{1}{2}\langle 0|[\Lambda^\dagger,[\dot{\kappa}^{(1)},\kappa^{(1)}]]|0\rangle \quad (35)$$

The first- and second-order equations have identical forms for the orbital and state operators Q_μ and Q_x. By construction, the zero-order equations are trivially satisfied, with $\kappa = S = 0$ corresponding to $|\tilde{0}\rangle = |0\rangle$.

C. The First-Order Equations. To solve the time-dependent equations eqs 32 and 33, we use the frequency expansions of the wave function corrections of eq 19 and of the external perturbation eq 2. For the first-order equations, we obtain from eq 32

$$\begin{aligned} \int_{-\infty}^{\infty} d\omega\, \exp(-i\omega + \epsilon)t(\omega\langle 0|[\Lambda^\dagger, S^{(1)}(\omega) + \kappa^{(1)}(\omega)]|0\rangle \\ - \langle 0|[[\Lambda^\dagger, H_0], S^{(1)}(\omega)]|0\rangle - \langle 0|[\Lambda^\dagger,[H_0,\kappa^{(1)}(\omega)]]|0\rangle|) = \\ \int_{-\infty}^{\infty} d\omega\, \exp(-i\omega + \epsilon)t(-i\langle 0|[\Lambda^\dagger, V(\omega)]|0\rangle) \end{aligned} \quad (36)$$

which gives the first-order response equations

$$\omega\langle 0|[\Lambda^\dagger, S^{(1)}(\omega) + \kappa^{(1)}(\omega)]|0\rangle - \langle 0|[[\Lambda^\dagger, H_0], S^{(1)}(\omega)]|0\rangle - \langle 0|[\Lambda^\dagger,[H_0,\kappa^{(1)}(\omega)]]|0\rangle) = -i\langle 0|[\Lambda^\dagger, V(\omega)]|0\rangle \quad (37)$$

The terms involving the zero-order Hamiltonian may be written in terms of the matrix

$$\mathbf{E}^{[2]} = \begin{pmatrix} \langle 0|[Q_\mu,[H_0, Q_\nu^\dagger]]|0\rangle & \langle 0|[[Q_\mu, H_0], Q_y^\dagger]|0\rangle & \langle 0|[Q_\mu,[H_0, Q_\nu]]|0\rangle & \langle 0|[[Q_\mu, H_0], Q_y]|0\rangle \\ \langle 0|[Q_x,[H_0, Q_\nu^\dagger]]|0\rangle & \langle 0|[[Q_x, H_0], Q_y^\dagger]|0\rangle & \langle 0|[Q_x,[H_0, Q_\nu]]|0\rangle & \langle 0|[[Q_x, H_0], Q_y]|0\rangle \\ \langle 0|[Q_\mu^\dagger,[H_0, Q_\nu^\dagger]]|0\rangle & \langle 0|[[Q_\mu^\dagger, H_0], Q_y^\dagger]|0\rangle & \langle 0|[Q_\mu^\dagger,[H_0, Q_\nu]]|0\rangle & \langle 0|[[Q_\mu^\dagger, H_0], Q_y]|0\rangle \\ \langle 0|[Q_x^\dagger,[H_0, Q_\nu^\dagger]]|0\rangle & \langle 0|[[Q_x^\dagger, H_0], Q_y^\dagger]|0\rangle & \langle 0|[Q_x^\dagger,[H_0, Q_\nu]]|0\rangle & \langle 0|[[Q_x^\dagger, H_0], Q_y]|0\rangle \end{pmatrix} \tag{38}$$

The diagonal blocks $\langle 0|[Q_\mu,[H_0, Q_\nu^\dagger]]|0\rangle$ and $\langle 0|[Q_\mu^\dagger,[H_0, Q_\nu]]|0\rangle$ in eq 38 are not symmetric when $|0\rangle$ is defined by means of a finite perturbation expansion. To see this, we use the Jacobi identity eq 34 to evaluate the difference between a matrix element and its transposed element:

$$\langle 0|[Q_\mu,[H_0, Q_\nu^\dagger]]|0\rangle - \langle 0|[Q_\nu,[H_0, Q_\mu^\dagger]]|0\rangle = \langle 0|[H_0,[Q_\mu, Q_\nu^\dagger]]|0\rangle \tag{39}$$

The reference state $|0\rangle$ is determined by solving $\langle 0|[\Lambda^{(0)\dagger}, H_0]|0\rangle = 0$ to a given order in the fluctuation potential; see eq 12. Thus, if $|0\rangle$ is obtained to order n, the matrix elements $\langle 0|[H_0,[Q_\mu, Q_\nu^\dagger]]|0\rangle$ is of order $n + 1$. Since we here need $|0\rangle$ only to second order, we can replace the asymmetric form of $\mathbf{E}^{[2]}$ in eq 38 by the following symmetric form by introducing third-order changes

$$\mathbf{E}^{[2]} = \begin{pmatrix} \langle 0|[Q_\mu, H_0, Q_\nu^\dagger]|0\rangle & \langle 0|[[Q_\mu, H_0], Q_y^\dagger]|0\rangle & \langle 0|[Q_\mu,[H_0, Q_\nu]]|0\rangle & \langle 0|[[Q_\mu, H_0], Q_y]|0\rangle \\ \langle 0|[Q_x,[H_0, Q_\nu^\dagger]]|0\rangle & \langle 0|[[Q_x, H_0], Q_y^\dagger]|0\rangle & \langle 0|[Q_x,[H_0, Q_\nu]]|0\rangle & \langle 0|[[Q_x, H_0], Q_y]|0\rangle \\ \langle 0|[Q_\mu^\dagger,[H_0, Q_\nu^\dagger]]|0\rangle & \langle 0|[[Q_\mu^\dagger, H_0], Q_y^\dagger]|0\rangle & \langle 0|[Q_\mu^\dagger, H_0, Q_\nu]|0\rangle & \langle 0|[[Q_\mu^\dagger, H_0], Q_y]|0\rangle \\ \langle 0|[Q_x^\dagger,[H_0, Q_\nu^\dagger]]|0\rangle & \langle 0|[[Q_x^\dagger, H_0], Q_y^\dagger]|0\rangle & \langle 0|[Q_x^\dagger,[H_0, Q_\nu]]|0\rangle & \langle 0|[[Q_x^\dagger, H_0], Q_y]|0\rangle \end{pmatrix} \tag{40}$$

where $[A, B, C]$ is the symmetric double commutator

$$[A, B, C] = \frac{1}{2}([[A, B], C] + [A,[B, C]]) \tag{41}$$

The remaining diagonal blocks of $\mathbf{E}^{[2]}$, $\langle 0|[[Q_x, H_0], Q_y^\dagger]|0\rangle$ and $0|[[Q_x^\dagger, H_0], Q_y]|0\rangle$, do not need to be symmetrized, as shown later.

To represent the remaining parts of the first-order equations eq 37 in matrix form, we introduce the symmetric metric matrix

$$\mathbf{S}^{[2]} = \begin{pmatrix} \langle 0|[Q_\mu, Q_\nu^\dagger]|0\rangle & \langle 0|[Q_\mu, Q_y^\dagger]|0\rangle & \langle 0|[Q_\mu, Q_\nu]|0\rangle & \langle 0|[Q_\mu, Q_y]|0\rangle \\ \langle 0|[Q_x, Q_\nu^\dagger]|0\rangle & \langle 0|[Q_x, Q_y^\dagger]|0\rangle & \langle 0|[Q_x, Q_\nu]|0\rangle & \langle 0|[Q_x, Q_y]|0\rangle \\ \langle 0|[Q_\mu^\dagger, Q_\nu^\dagger]|0\rangle & \langle 0|[Q_\mu^\dagger, Q_y^\dagger]|0\rangle & \langle 0|[Q_\mu^\dagger, Q_\nu]|0\rangle & \langle 0|[Q_\mu^\dagger, Q_y]|0\rangle \\ \langle 0|[Q_x^\dagger, Q_\nu^\dagger]|0\rangle & \langle 0|[Q_x^\dagger, Q_y^\dagger]|0\rangle & \langle 0|[Q_x^\dagger, Q_\nu]|0\rangle & \langle 0|[Q_x^\dagger, Q_y]|0\rangle \end{pmatrix} \tag{42}$$

and the vectors

$$\mathbf{V}^{[1]}(\omega) = \begin{pmatrix} \langle 0|[Q_\mu, V(\omega)]|0\rangle \\ \langle 0|[Q_x, V(\omega)]|0\rangle \\ \langle 0|[Q_\mu^\dagger, V(\omega)]|0\rangle \\ \langle 0|[Q_x^\dagger, V(\omega)]|0\rangle \end{pmatrix}, \alpha^{(i)} = \begin{pmatrix} \kappa^{(i)} \\ S_x^{(i)} \\ \kappa^{(i)*} \\ S_x^{(i)*} \end{pmatrix} \tag{43}$$

We can now write the first-order response equations eq 37 in the form

$$(\mathbf{E}^{[2]} - \omega\mathbf{S}^{[2]})\alpha^{(1)} = i\mathbf{V}^{[1]}(\omega) \tag{44}$$

We shall discuss the expansion of the matrices $\mathbf{S}^{[2]}$, $\mathbf{E}^{[2]}$, and $\mathbf{V}^{[1]}(\omega)$ in orders of the fluctuation potential later.

D. The Second-Order Equations. Inserting the frequency expansions of the first- and second-order wave function corrections from eq 19 into eq 33 and using the definitions of $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$ from eqs 40 and 42, we obtain

$$\begin{aligned}(\omega_1 + \omega_2)(\mathbf{S}^{[2]} - \mathbf{E}^{[2]})\,\alpha^{(2)}(\omega_1,\omega_2) = P_{12}\Big[&-\frac{i}{2}\omega_1(\langle 0|[[\Lambda^\dagger, S^{(1)}(\omega_1)], S^{(1)}(\omega_2)]|0\rangle + \langle 0|[[\Lambda^\dagger, S^{(1)}(\omega_2)], S^{(1)}(\omega_1)]|0\rangle) - \frac{i}{2}\omega_1\langle 0|[\Lambda^\dagger, \\ &[\kappa^{(1)}(\omega_1),\kappa^{(1)}(\omega_2)]]|0\rangle - i\omega_1\langle 0|[[\Lambda^\dagger,\kappa^{(1)}(\omega_1)], S^{(1)}(\omega_2)]|0\rangle + \langle 0|[[\Lambda^\dagger, V(\omega_1)], S^{(1)}(\omega_2)]|0\rangle + \frac{i}{2}\langle 0|[[[\Lambda^\dagger, H_0], S^{(1)}(\omega_1)], \\ &S^{(1)}(\omega_2)]|0\rangle + \langle 0|[\Lambda^\dagger,[V(\omega_1),\kappa^{(1)}(\omega_2)]]|0\rangle + i\langle 0|[[\Lambda^\dagger,[H_0,\kappa^{(1)}(\omega_1)]], S^{(1)}(\omega_2)]|0\rangle + \frac{i}{2}\langle 0|[\Lambda^\dagger,[[H_0,\kappa^{(1)}(\omega_1)],\kappa^{(1)}(\omega_2)]]|\,0\rangle\Big]\end{aligned} \tag{45}$$

To express the second-order equations more compactly, we introduce the three-index supermatrices $\mathbf{S}^{[3]}$ and $\mathbf{E}^{[3]}$, operationally defined in the following manner

$$\sum_{jk} S^{[3]}_{ijk}\,\alpha^{(1)}_j\,\alpha^{(2)}_k =$$
$$\frac{1}{2}\left(\langle 0|[[\Lambda_i^\dagger,\sum_x (S_x^{(1)}\,Q_x^\dagger + S_x^{(1)*}Q_x)],\sum_y (S_y^{(2)}\,Q_y^\dagger + S_y^{(2)*}Q_y)]|0\rangle + \frac{1}{2}\langle 0|[[\Lambda_i^\dagger,\sum_x (S_x^{(2)}\,Q_x^\dagger + S_x^{(2)*}Q_x)],\sum_y (S_y^{(1)}\,Q_y^\dagger + S_y^{(1)*}Q_y)]|0\rangle\right) +$$
$$\frac{1}{2}\langle 0|[\Lambda_i^\dagger,[\sum_\mu (\kappa_\mu^{(1)}\,Q_\mu^\dagger + \kappa^{(1)*}Q_\mu),\sum_\nu (\kappa_\nu^{(2)}\,Q_\nu^\dagger + \kappa^{(2)*}Q_\nu)]]|0\rangle + \langle 0|[[\Lambda_i^\dagger,\sum_\mu (\kappa_\mu^{(1)}\,Q_\mu^\dagger + \kappa^{(1)*}Q_\mu)],\sum_y (S_y^{(2)}\,Q_y^\dagger + S_y{}^{(2)*}Q_y)]|0\rangle \quad (46)$$

$$\sum_{jk} E^{[3]}_{ijk}\,\alpha^{(1)}_j\,\alpha^{(2)}_k =$$
$$\frac{1}{2}\langle 0|[[[\Lambda_i^\dagger, H_0],\sum_x (S_x^{(1)}\,Q_x^\dagger + S_x^{(1)*}Q_x)],\sum_y (S_y^{(2)}\,Q_y^\dagger + S_y^{(2)*}Q_y)]|0\rangle + \langle 0|[[\Lambda_i^\dagger,[H_0,\sum_\mu (\kappa_\mu^{(1)}\,Q_\mu^\dagger + \kappa^{(1)*}Q_\mu)]],\sum_x (S_x^{(2)}\,Q_x^\dagger +$$
$$S_x^{(2)*}Q_x)]|\,0\rangle + \frac{1}{2}\langle 0|[\Lambda_i^\dagger,[[H_0,\sum_\mu (\kappa_\mu^{(1)}\,Q_\mu^\dagger + \kappa^{(1)*}Q_\mu)],\sum_\nu (\kappa_\nu^{(2)}\,Q_\nu^\dagger + \kappa^{(2)*}Q_\nu)]]|\,0\rangle \quad (47)$$

We furthermore introduce $\mathbf{V}^{\omega[2]}$, obtained from $\mathbf{E}^{[2]}$ in eq 40 by replacing H_0 with V^ω. The second-order equations can now be written as

$$[(\omega_1+\omega_2)\mathbf{S}^{[2]} - \mathbf{E}^{[2]}]\,\alpha^{(2)}(\omega_1,\omega_2) = -P_{12}[(i\omega_1\mathbf{S}^{[3]} - i\mathbf{E}^{[3]})\,\alpha^{(1)}(\omega_1)\,\alpha^{(1)}(\omega_2) - \mathbf{V}^{[2]}(\omega_1)\,\alpha^{(1)}(\omega_2)] \quad (48)$$

The contractions of vectors with $\mathbf{E}^{[3]}$ and $\mathbf{S}^{[3]}$ is discussed in greater detail later.

IV. Response Functions and Their Residues

A. The Linear and Quadratic Response Functions. The linear response function is obtained by inserting the first-order correction as obtained in eq 44 in the expression for the linear response function eq 23. Renaming the perturbation operator $V(\omega)$ to B and introducing

$$A_j^{[1]} = -\langle 0|[\Lambda_j, A]|0\rangle \quad (49a)$$

$$B_j^{[1]} = \langle 0|[\Lambda_j^\dagger, B]|0\rangle \quad (49b)$$

we obtain

$$\langle\langle A;B\rangle\rangle_\omega = -\mathbf{A}^{[1]}(\mathbf{E}^{[2]} - \omega\mathbf{S}^{[2]})^{-1}\mathbf{B}^{[1]} \quad (50)$$

The linear response function may thus be calculated by solving one set of linear equations at each frequency.[11]

The quadratic response function is likewise obtained by inserting the first- and second-order corrections eqs 44 and 48 into the expression for the quadratic response function eq 24. We next rename $V(\omega_1)$ and $V(\omega_2)$ to B and C, respectively, introduce the vector $\mathbf{C}^{[1]}$ by analogy with $\mathbf{B}^{[1]}$ of eq 49b, and finally generate $\mathbf{B}^{[2]}$ and $\mathbf{C}^{[2]}$ from the original definition of $\mathbf{E}^{[2]}$ in eq 38 by replacing H_0 with B and C, respectively. Introducing the matrix

$$\mathbf{A}^{[2]} = -\frac{1}{2}\begin{pmatrix} \langle 0|[Q_\mu,[A,Q_\nu^\dagger]]|0\rangle & \langle 0|[[Q_\mu,A],Q_y^\dagger]|0\rangle & \langle 0|[Q_\mu,[A,Q_\nu]]|0\rangle & \langle 0|[[Q_\mu,A],Q_y]|0\rangle \\ \langle 0|[Q_x,[A,Q_\nu^\dagger]]|0\rangle & \langle 0|[[Q_x,A],Q_y^\dagger]|0\rangle & \langle 0|[Q_x,[A,Q_\nu]]|0\rangle & \langle 0|[[Q_x,A],Q_y]|0\rangle \\ \langle 0|[Q_\mu^\dagger,[A,Q_\nu^\dagger]]|0\rangle & \langle 0|[[Q_\mu^\dagger,A],Q_y^\dagger]|0\rangle & \langle 0|[Q_\mu^\dagger,[A,Q_\nu]]|0\rangle & \langle 0|[[Q_\mu^\dagger,A],Q_y]|0\rangle \\ \langle 0|[Q_x^\dagger,[A,Q_\nu^\dagger]]|0\rangle & \langle 0|[[Q_x^\dagger,A],Q_y^\dagger]|0\rangle & \langle 0|[Q_x^\dagger,[A,Q_\nu]]|0\rangle & \langle 0|[[Q_x^\dagger,A],Q_y]|0\rangle \end{pmatrix} \quad (51)$$

we find that the quadratic response function may be written in the form

$$\langle\langle A;B,C\rangle\rangle_{\omega_1,\omega_2} = \sum_{ijkl} B_i^{[1]}(\mathbf{E}^{[2]} - \omega_1\mathbf{S}^{[2]})^{-1}_{ij}(A_{jk}^{[2]} + A_{kj}^{[2]})(\mathbf{E}^{[2]} - \omega_1\mathbf{S}^{[2]})^{-1}_{kl}\,C_l^{[1]} + \sum_{ijkl} A_i^{[1]}(\mathbf{E}^{[2]} - (\omega_1+\omega_2)\mathbf{S}^{[2]})^{-1}_{ij}\,B_{jk}^{[2]}(\mathbf{E}^{[2]} -$$
$$\omega_2\mathbf{S}^{[2]})^{-1}_{kl}\,C_l^{[1]} + \sum_{ijkl} A_i^{[1]}(\mathbf{E}^{[2]} - (\omega_1+\omega_2)\mathbf{S}^{[2]})^{-1}_{ij}\,C_{jk}^{[2]}(\mathbf{E}^{[2]} - \omega_1\mathbf{S}^{[2]})^{-1}_{kl}\,B_l^{[1]} - \sum_{ijklmn} A_i^{[1]}(\mathbf{E}^{[2]} - (\omega_1+\omega_2)\mathbf{S}^{[2]})^{-1}_{ij}(E_{jkl}^{[3]} + E_{jlk}^{[3]} -$$
$$\omega_1 S_{jkl}^{[3]} - \omega_2 S_{jlk}^{[3]}) \times (\mathbf{E}^{[2]} - \omega_1\mathbf{S}^{[2]})^{-1}_{km}\,B_m^{[1]}(\mathbf{E}^{[2]} - \omega_2\mathbf{S}^{[2]})^{-1}_{ln}\,C_n^{[1]} \quad (52)$$

For a given pair of frequencies ω_1 and ω_2, the quadratic response function may thus be evaluated by solving three sets of first-order equations:

$$\mathbf{N}^a(\omega_1+\omega_2) = (\mathbf{E}^{[2]} - (\omega_1+\omega_2)\mathbf{S}^{[2]})^{-1}\mathbf{A}^{[1]\mathbf{T}} \quad (53a)$$

$$\mathbf{N}^b(\omega_1) = (\mathbf{E}^{[2]} - \omega_1\mathbf{S}^{[2]})^{-1}\mathbf{B}^{[1]} \quad (53b)$$

$$\mathbf{N}^c(\omega_2) = (\mathbf{E}^{[2]} - \omega_2\mathbf{S}^{[2]})^{-1}\mathbf{C}^{[1]} \quad (53c)$$

which allow us to write the quadratic response function as

$$\langle\langle A;B,C\rangle\rangle_{\omega_1,\omega_2} = \sum_{ij} N_i^b(\omega_1)(A_{ij}^{[2]} + A_{ji}^{[2]})N_j^c(\omega_2) + \sum_{ij} N_i^a(\omega_1+\omega_2)B_{ij}^{[2]}\, N_j^c(\omega_2) + \sum_{ij} N_i^a(\omega_1+\omega_2)C_{ij}^{[2]}\, N_j^b(\omega_1) - \sum_{ijk} N_i^a(\omega_1+\omega_2)(E_{ijk}^{[3]} + E_{ikj}^{[3]} - \omega_1 S_{ijk}^{[3]} - \omega_2 S_{ikj}^{[3]})N_j^b(\omega_1)N_k^c(\omega_2) \quad (54)$$

Note that only first-order equations are needed to calculate the quadratic response function for a given set of given frequencies. For variational wave functions such as SCF and MCSCF wave functions, it has previously been established that the first-order correction to the wave function is sufficient to determine the quadratic response function.[11]

B. Excitation Energies and Residues of the Quadratic Response Functions. The linear and quadratic response functions obtained above have the same structure as those previously obtained for SCF and MCSCF wave functions, differing only in the detailed form of the various vectors and matrices. We can thus straightforwardly take over the identifications of residues previously made in SCF and MCSCF theories.[11] However, before discussing these identification, we shall briefly comment on the excitation energies obtained in the present approach.

Motivated by the occurrence of the exact excitation energies as the poles of the exact linear response function, the excitation energies are in the present approach obtained as the poles of the linear response function eq 50, by solving the symmetric generalized eigenvalue problem

$$\mathbf{E}^{[2]}\mathbf{X}_i = \omega_i \mathbf{S}^{[2]}\mathbf{X}_i \quad (55)$$

Because of the paired structure of $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$ in eqs 40 and 42, with the appearance of deexcitation as well as excitation operators, the eigensolutions are also paired. Thus, if the vector

$$\mathbf{X} = \begin{pmatrix} Z_\mu \\ Z_x \\ Y_\mu \\ Y_x \end{pmatrix} \quad (56)$$

is an eigenvector for the generalized eigenvalue problem eq 55 with eigenvalue ω_i, then the paired structure of $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$ ensures that the related vector

$$\mathbf{X}^{\mathrm{P}} = \begin{pmatrix} Y_\mu \\ Y_x \\ Z_\mu \\ Z_x \end{pmatrix} \quad (57)$$

is an eigenvector of the generalized eigenvalue problem with eigenvalue $-\omega_i$. This paired structure of the solutions of the linear response function is well established and has been utilized to set up an efficient iterative method for solving the eigenvalue problem.[15]

Since the residues of the second-order linear response function have already been analyzed in detail,[16] we focus here on the residues of the quadratic response function. As previously discussed in SCF and MCSCF theories,[11] the transition moment of an operator A between two excited states f and g may be obtained by solving first the linear response equations eq 55 to generate the excitation energies ω_f and ω_g and the eigenvectors $\mathbf{X}_f$ and $\mathbf{X}_g$, followed by the solution of the linear equations

$$\mathbf{N}^a(\omega_f - \omega_g) = [\mathbf{E}^{[2]} - (\omega_f - \omega_g)\mathbf{S}^{[2]}]^{-1}\mathbf{A}^{[1]\mathrm{T}} \quad (58)$$

and the identification of the transition moment as

$$\langle g|A|f\rangle = \delta_{fg}\langle 0|A|0\rangle - \sum_{ij} X_{ig}^P(A_{ij}^{[2]} + A_{ji}^{[2]})X_{jf} + \sum_{ijk} N_i^a(\omega_f - \omega_g)(E_{ijk}^{[3]} + E_{ikj}^{[3]} + \omega_g S_{ijk}^{[3]} - \omega_f S_{ikj}^{[3]})X_{jg}^P X_{kf} \quad (59)$$

An important application of quadratic response theory is the calculation of two-photon transition moments. Whereas the two-photon transition moment was traditionally considered a property connected with the cubic response function, it was shown in ref 11 that it may also be extracted as a single residue from the quadratic response function. The two-photon transition moment between states 0 and f for the operators A and B at frequency ω_1 may be obtained by first solving eq 55 to obtain ω_f and $\mathbf{X}_f$, followed by the solution of two sets of linear equations:

$$\mathbf{N}^a(\omega_f - \omega_1) = (\mathbf{E}^{[2]} - (\omega_f - \omega_1)\mathbf{S}^{[2]})^{-1}\mathbf{A}^{[1]\mathrm{T}} \quad (60a)$$

$$\mathbf{N}^b(-\omega_1) = (\mathbf{E}^{[2]} + \omega_1\mathbf{S}^{[2]})^{-1}\mathbf{B}^{[1]} \quad (60b)$$

The two-photon transition matrix element is then obtained as

$$\Gamma_{0\to f}^{AB}(\omega_1) = -\sum_{ij} N_i^a(\omega_f - \omega_1)B_{ij}^{[2]}X_{kf} - \sum_{ij} N_i^b(-\omega_1)(A_{ij}^{[2]} + A_{ji}^{[2]})X_{jf} + \sum_{ijk}(E_{ijk}^{[3]} + E_{ikj}^{[3]} + \omega_1 S_{ijk}^{[3]} - \omega_f S_{ikj}^{[3]})N_i^a(\omega_f - \omega_1)\, N_j^b(-\omega_1)X_{kf} \quad (61)$$

V. Determination of the Response Matrices

In the preceding discussion, we introduced a number of matrices—in particular, $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$. However, only their general index structure was presented; their detailed form was not examined. In this section, we discuss these matrices in detail, analyzing which terms in the expansion of $|0\rangle$ are required for the construction of the matrices. We begin by discussing what operators in κ and S must be included to calculate the response functions to second order in the fluctuation potential. Next, we derive the form of the various blocks of the matrices. This information is then used in the following section to set up algorithms for the direct contraction of response matrices with one or several vectors.

A. Expansion of *S* in the Fluctuation Potential. In the absence of the fluctuation potential, only a single determinant is needed to describe the unperturbed and perturbed states so S in eq 14 vanishes in this limit. The S parameters are thus at least of first order in the fluctuation potential, unlike the κ parameters in eq 14, which contain zero-order terms. On the other hand, no terms in S of second order in the fluctuation potential are needed to calculate the expectation value of a one-electron operator eq 18 to second order. This is easy to show—remembering that S by definition only contains double and higher excitations. Consider, for example, the term in eq 18 of the form $\langle 0|[S, A]|0\rangle$. Any second-order term in S must necessarily occur together with the zero-order term $|\mathrm{HF}\rangle$ of the wave function $|0\rangle$. However, terms such as $\langle \mathrm{HF}|[S, A]|\mathrm{HF}\rangle$ vanish trivially since A gives zero matrix elements between the Hartree−Fock and states higher than single excitations. The same argument holds for the other terms that contain a single S operator and one or several κ operators. In the term that contains two S operators, only the terms in S that are linear in the fluctuation potential give contributions that are at most

quadratic in the fluctuation potential. In short, to determine the linear, quadratic, and higher order response to an external perturbation, it is only necessary to include terms in S that are linear in the fluctuation potential.

Let us next consider what excitation ranks should be included in S. Remember first that single excitations are excluded by definition in S. Whereas the corrections to the Hartree−Fock wave function from triple and higher excitations are of second or higher orders in the fluctuation potential, this is not necessarily true for the corrections due to the external perturbation. However, a closer analysis reveals that only double excitations are required to determine the response functions and the pole structure correct to second order in the fluctuation potential.[8] We conclude that only double excitations should be included in S and that S is at least first order in the fluctuation potential.

B. The Structure of $\mathbf{S}^{[2]}$, $\mathbf{E}^{[2]}$, and $\mathbf{V}^{[1]}(\omega)$. We now discuss the terms that should be included to obtain the excitation energies and transition moments of single-excitation-dominated excitations to second order in the fluctuation potential. Let us consider the various blocks of $\mathbf{S}^{[2]}$ and $\mathbf{E}^{[2]}$. The blocks where both indexes refer to orbital excitations must be obtained to second order in the fluctuation potential. Since S is of at least first order in the fluctuation potential, the remaining blocks may be calculated to lower orders. Thus, the blocks of $\mathbf{S}^{[2]}$ and $\mathbf{E}^{[2]}$ that couple orbital and state rotations need only to be obtained to first order, whereas the blocks where both indexes refer to transfer operators are needed to zero order.

Let us first consider $\mathbf{S}^{[2]}$ as defined in eq 42. As this matrix is manifestly symmetric, we need only consider the blocks on or below the diagonal. In the $\langle 0|[Q_\mu, Q_\nu^\dagger]|0\rangle$ block, we notice that $[Q_\mu, Q_\nu^\dagger]$ is an operator of zero excitation rank,[6] so only terms of identical bra and ket excitation ranks give nonzero contributions. We therefore have

$$\langle 0|[Q_\mu, Q_\nu^\dagger]|0\rangle = \langle HF|[Q_\mu, Q_\nu^\dagger]|HF\rangle(1 - \mathbf{c}_2^{(1)}\,\mathbf{c}_2^{(1)\dagger}) + \mathbf{c}_2^{(1)\dagger}\langle \mathbf{x}_2|[Q_\mu, Q_\nu^\dagger]|\mathbf{x}_2\rangle\mathbf{c}_2^{(1)} \quad (62a)$$

$$\langle 0|[Q_\mu^\dagger, Q_\nu]|0\rangle = -\langle 0|[Q_\nu, Q_\mu^\dagger]|0\rangle \quad (62b)$$

As all excitation operators commute among themselves as do all deexcitation operators, the remaining orbital blocks vanish:

$$\langle 0|[Q_\mu, Q_\nu]|0\rangle = 0 \quad (63a)$$

$$\langle 0|[Q_\mu^\dagger, Q_\nu^\dagger]|0\rangle = 0 \quad (63b)$$

The blocks that couple orbital operators with state operators need only be obtained to first order in the fluctuation potential. Since only double excitations contribute to first order, we find that these coupling blocks vanish to first order:

$$\langle 0|[Q_\mu, Q_x^\dagger]|0\rangle = \langle 0|Q_\mu|x\rangle\langle HF|0\rangle - \langle 0|x\rangle\langle HF|Q_\mu|0\rangle = 0 \quad (64a)$$

$$\langle 0|[Q_\mu^\dagger, Q_x^\dagger]|0\rangle = \langle 0|Q_\mu^\dagger|x\rangle\langle HF|0\rangle - \langle 0|x\rangle\langle HF|Q_\mu^\dagger|0\rangle = 0 \quad (64b)$$

$$\langle 0|[Q_\mu^\dagger, Q_x]|0\rangle = -\langle 0|[Q_\mu, Q_x^\dagger]|0\rangle^* = 0 \quad (64c)$$

$$\langle 0|[Q_\mu, Q_x]|0\rangle = -\langle 0|[Q_\mu^\dagger, Q_x^\dagger]|0\rangle = 0 \quad (64d)$$

Finally, the blocks that involve two state operators should only be obtained to zero order. Whereas matrix elements between two excitation operators or between two deexcitation operators vanish, those that involve both excitations and deexcitations do not vanish:

$$\langle 0|[Q_x, Q_y]|0\rangle = \langle 0|[Q_x^\dagger, Q_y^\dagger]|0\rangle = 0 \quad (65a)$$

$$\langle 0|[Q_x, Q_y^\dagger]|0\rangle = -\langle 0|[Q_x^\dagger, Q_y]|0\rangle = \delta_{xy} \quad (65b)$$

Let us next examine the blocks of the symmetric form of $\mathbf{E}^{[2]}$ of eq 40. The Hamiltonian H_0 is partitioned as in eq 1 into the Fock operator of excitation rank $s = 0$ and the fluctuation potential with excitation ranks $-2 \le s \le 2$. Since $[Q_\mu, F, Q_\nu^\dagger]$ has rank zero and since $[Q_\mu, W, Q_\nu^\dagger]$ contains terms with excitation ranks $-2 \le s \le 2$, we obtain

$$\langle 0|[Q_\mu, H_0, Q_\nu^\dagger]|0\rangle = \langle 0|[Q_\mu, F, Q_\nu^\dagger]|0\rangle + \langle 0|[Q_\mu, W, Q_\nu^\dagger]|0\rangle = \langle HF|[Q_\mu, F, Q_\nu^\dagger]|HF\rangle(1 - \mathbf{c}_2^{(1)}\,\mathbf{c}_2^{(1)\dagger}) + \langle HF|[Q_\mu, W, Q_\nu^\dagger]|HF\rangle + \mathbf{c}_2^{(1)\dagger}\langle \mathbf{x}_2|[Q_\mu, F, Q_\nu^\dagger]|\mathbf{x}_2\rangle\mathbf{c}_2^{(1)} + \mathbf{c}_2^{(1)\dagger}\langle \mathbf{x}_2|[Q_\mu, W, Q_\nu^\dagger]|HF\rangle + \langle HF|[Q_\mu, W, Q_\nu^\dagger]|\mathbf{x}_2\rangle\mathbf{c}_2^{(1)} \quad (66a)$$

$$\langle 0|[Q_\mu^\dagger, H_0, Q_\nu]|0\rangle = \langle 0|[Q_\mu, H_0, Q_\nu^\dagger]|0\rangle^* \quad (66b)$$

For the block containing two orbital excitations $\langle 0|[Q_\mu^\dagger,[H_0, Q_\nu^\dagger]]|0\rangle$, the contributions from the Fock operator vanishes as $[F, Q_\nu^\dagger]$ is an excitation operator and therefore commutes with $Q_\mu^\dagger$. As $[Q_\mu^\dagger,[W, Q_\nu^\dagger]]$ has terms with excitation ranks $0 \le s \le 2$, we obtain

$$\langle 0|[Q_\mu^\dagger,[H_0, Q_\nu^\dagger]]|0\rangle = \langle 0|[Q_\mu^\dagger,[W, Q_\nu^\dagger]]|0\rangle = \langle \mathrm{HF}|[Q_\mu^\dagger,[W, Q_\nu^\dagger]]|\mathrm{HF}\rangle + \mathbf{c}_2^{(1)\dagger}\langle \mathbf{x}_2|[Q_\mu^\dagger,[W, Q_\nu^\dagger]]|\mathrm{HF}\rangle \quad (67a)$$

$$\langle 0|[Q_\mu,[H_0, Q_\nu]]|0\rangle = \langle 0|[Q_\mu^\dagger,[H_0, Q_\nu^\dagger]]|0\rangle^* \quad (67b)$$

The mixed blocks, containing one orbital operator and one state operator, should be calculated to first order in the fluctuation potential. From rank considerations, we find

$$\langle 0|[[Q_\mu^\dagger, H_0], Q_x^\dagger]|0\rangle = \langle 0|[[Q_\mu, H_0], Q_x]|0\rangle = 0 \quad (68a)$$

$$\langle 0|[[Q_\mu, H_0], Q_x^\dagger]|0\rangle = \langle \mathrm{HF}|[Q_\mu, W]|x\rangle \quad (68b)$$

$$\langle 0|[[Q_\mu^\dagger, H_0], Q_x]|0\rangle = \langle 0|[[Q_\mu, H_0], Q_x^\dagger]|0\rangle^* \quad (68c)$$

Finally, the blocks involving only state operators need only be evaluated to zero order. Whereas the blocks containing only excitation operators or only deexcitation operators vanish to zero order, the remaining blocks are nonzero:

$$\langle 0|[[Q_x, H_0], Q_y]|0\rangle = \langle 0|[[Q_x^\dagger, H_0], Q_y^\dagger]|0\rangle = 0 \quad (69a)$$

$$\langle 0|[[Q_x, H_0], Q_y^\dagger]|0\rangle = \langle x|F|y\rangle - \delta_{xy}\langle \mathrm{HF}|F|\mathrm{HF}\rangle \quad (69b)$$

$$\langle 0|[[Q_x^\dagger, H_0], Q_y]|0\rangle = \langle 0|[[Q_x, H_0], Q_y^\dagger]|0\rangle^* \quad (69c)$$

Clearly, these blocks are symmetric to the required order.

Turning our attention to $\mathbf{V}^{[1]}$ in eq 43, we note that the elements involving orbital operators should be calculated to second order in the fluctuation potential, whereas those that involve state operators should be calculated to first order. Since $V(\omega)$ is a one-electron operator, the commutator $[Q_\mu, V(\omega)]$ has contributions of excitation ranks -1 and 0. We therefore obtain

$$\langle 0|[Q_\mu, V(\omega)]|0\rangle = \langle \mathrm{HF}|[Q_\mu, V(\omega)]|\mathrm{HF}\rangle(1 - \mathbf{c}_2^{(1)}\,\mathbf{c}_2^{(1)\dagger}) + \mathbf{c}_2^{(1)\dagger}\langle \mathbf{x}_2|[Q_\mu, V(\omega)]|\mathbf{x}_2\rangle\mathbf{c}_2^{(1)} + \langle \mathrm{HF}|[Q_\mu, V(\omega)]|\mathbf{x}_1\rangle\mathbf{c}_1^{(2)} \quad (70a)$$

$$\langle 0|[Q_\mu^\dagger, V(\omega)]|0\rangle = -\langle 0|[Q_\mu, V(-\omega)]|0\rangle^* \quad (70b)$$

The elements involving state operators are given by

$$\langle 0|[Q_x, V(\omega)]|0\rangle = \langle x|V(\omega)|\mathbf{x}_2\rangle\mathbf{c}_2^{(1)} - \langle \mathrm{HF}|V(\omega)|\mathrm{HF}\rangle c_{x2}^{(1)} \quad (71a)$$

$$\langle 0|[Q_x^\dagger, V(\omega)]|0\rangle = -\langle 0|[Q_x, V(-\omega)]|0\rangle^* \quad (71b)$$

It is interesting to note that all above matrices are identical to those obtained using the SOPPA superoperator algebra.[8]

C. The Structure of $\mathbf{E}^{[3]}$, $\mathbf{S}^{[3]}$, and $\mathbf{V}^{[2]}(\omega)$. The three-index quantities $\mathbf{S}^{[3]}$ and $\mathbf{E}^{[3]}$ both contain $4^3 = 64$ blocks. Since their elements are obtained in the same manner as those of $\mathbf{S}^{[2]}$ and $\mathbf{E}^{[2]}$, we only give the final expressions here. In general, a matrix element containing I state operators is only required to order $2 - I$ in the fluctuation potential. With this restriction, most of the blocks of $\mathbf{S}^{[3]}$ and $\mathbf{E}^{[3]}$ vanish. For the unique nonvanishing blocks of $\mathbf{S}^{[3]}$, we obtain

$$\langle 0|[Q_\mu,[Q_\nu^\dagger, Q_\omega]]|0\rangle = \langle \mathrm{HF}|[Q_\mu,[Q_\nu^\dagger, Q_\omega]]|\mathbf{x}_1\rangle\mathbf{c}_1^{(2)} \quad (72a)$$

$$\langle 0|[[Q_\mu, Q_\nu^\dagger], Q_x^\dagger]|0\rangle = \mathbf{c}_2^{(1)\dagger}\langle \mathbf{x}_2|[Q_\mu, Q_\nu^\dagger]|x\rangle - c_{x2}^{(1)}\langle \mathrm{HF}|[Q_\mu, Q_\nu^\dagger]|\mathrm{HF}\rangle \quad (72b)$$

Likewise, the unique nonvanishing blocks of $\mathbf{E}^{[3]}$ are given by

$$\langle 0|[Q_\mu,[[H_0, Q_\nu^\dagger], Q_\omega^\dagger]]|0\rangle = \langle \mathrm{HF}|[Q_\mu,[[W, Q_\nu^\dagger], Q_\omega^\dagger]]|\mathrm{HF}\rangle \quad (73a)$$

$$\langle 0|[Q_\mu,[[H_0, Q_\nu^\dagger], Q_\omega]]|0\rangle = \langle \mathrm{HF}|[Q_\mu,[[F, Q_\nu^\dagger], Q_\omega]]|\mathbf{x}_1\rangle\mathbf{c}_1^{(2)} + \langle \mathrm{HF}|[Q_\mu,[[W, Q_\nu^\dagger], Q_\omega]]|\mathrm{HF}\rangle + \langle \mathrm{HF}|[Q_\mu,[[W, Q_\nu^\dagger], Q_\omega]]|\mathbf{x}_2\rangle\mathbf{c}_2^{(1)} \quad (73b)$$

$$\langle 0|[Q_\mu,[[H_0, Q_\nu], Q_\omega^\dagger]]|0\rangle = \langle \mathrm{HF}|[Q_\mu,[[F, Q_\nu], Q_\omega^\dagger]]|\mathbf{x}_1\rangle\mathbf{c}_1^{(2)} + \langle \mathrm{HF}|[Q_\mu,[[W, Q_\nu], Q_\omega^\dagger]]|\mathrm{HF}\rangle + \langle \mathrm{HF}|[Q_\mu,[[W, Q_\nu], Q_\omega^\dagger]]|\mathbf{x}_2\rangle\mathbf{c}_2^{(1)} \quad (73c)$$

$$\langle 0|[Q_\mu,[[H_0, Q_\nu], Q_\omega]]|0\rangle = \langle \mathrm{HF}|[Q_\mu,[[W, Q_\nu], Q_\omega]]|\mathbf{x}_2\rangle\mathbf{c}_2^{(1)} \quad (73d)$$

$$\langle 0|[[Q_\mu,[H_0, Q_\nu^\dagger]], Q_x^\dagger]|0\rangle = \langle HF|[Q_\mu,[W, Q_\nu^\dagger]]|x\rangle + \mathbf{c}_2^{(1)\dagger}\langle \mathbf{x}_2|[Q_\mu,[F, Q_\nu^\dagger]]|x\rangle - c_{x2}^{(1)}\langle \mathrm{HF}|[Q_\mu,[F, Q_\nu^\dagger]]|\mathrm{HF}\rangle \quad (73e)$$

$$\langle 0|[[Q_\mu,[H_0, Q_\nu^\dagger]], Q_x]|0\rangle = \langle HF|[Q_\mu,[F, Q_\nu^\dagger]]|\mathrm{HF}\rangle c_{x2}^{(1)} - \langle x|[[Q_\mu,[F, Q_\nu^\dagger]]|\mathbf{x}_2\rangle\mathbf{c}^{(1)} - \langle x|[Q_\mu,[W, Q_\nu^\dagger]]|\mathrm{HF}\rangle \quad (73f)$$

$$\langle 0|[[Q_\mu,[H_0, Q_\nu]], Q_x^\dagger]|0\rangle = \langle \mathrm{HF}|[Q_\mu,[W, Q_\nu]]|x\rangle \quad (73g)$$

$$\langle 0|[[Q_\mu,[H_0, Q_\nu]], Q_x]|0\rangle = -\langle x|[Q_\mu,[W, Q_\nu]]|\mathrm{HF}\rangle \quad (73h)$$

Finally, $\mathbf{V}^{[2]}(\omega)$ has the following unique nonvanishing elements

$$\langle 0|[[Q_\mu, V(\omega)], Q_\nu^\dagger]|0\rangle = \langle HF|[[Q_\mu, V], Q_\nu^\dagger]|\mathrm{HF}\rangle (1 - \mathbf{c}^{(1)}\mathbf{c}^{(1)\dagger}) + \mathbf{c}_2^{(1)\dagger}\langle \mathbf{x}_2|[[Q_\mu, V(\omega)], Q_\nu^\dagger]|\mathbf{x}_2\rangle\mathbf{c}_2^{(1)} + \mathbf{c}_1^{(2)\dagger}\langle \mathbf{x}_1|[[Q_\mu, V(\omega)], Q_\nu^\dagger]|\mathrm{HF}\rangle \quad (74a)$$

$$\langle 0|[[Q_\mu, V(\omega)], Q_\nu]|0\rangle = \langle \mathrm{HF}|[[Q_\mu, V(\omega)], Q_\nu]|\mathbf{x}_1\rangle\mathbf{c}_1^{(2)} \quad (74b)$$

$$\langle 0|[[Q_\mu, V(\omega)], Q_x^\dagger]|0\rangle = \mathbf{c}_2^{(1)\dagger}\langle \mathbf{x}_2|[Q_\mu, V(\omega)]|x\rangle - c_{x2}^{(1)}\langle \mathrm{HF}|[Q_\mu, V(\omega)]|HF\rangle \quad (74c)$$

$$\langle 0|[[Q_\mu, V(\omega)], Q_x]|0\rangle = \langle HF|[Q_\mu, V(\omega)]|\mathrm{HF}\rangle c_{x2}^{(1)} - \langle x|[Q_\mu, V(\omega)]|\mathbf{x}_2\rangle\mathbf{c}_2^{(1)} \quad (74d)$$

$$\langle 0|[[Q_x, V(\omega)], Q_y^\dagger]|0\rangle = \langle x|V(\omega)|y\rangle - \delta_{xy}\langle \mathrm{HF}|V(\omega)|HF\rangle \quad (74e)$$

VI. Computational Aspects

The indexes of the various matrices discussed in the preceding sections have the dimension of twice the number of single and double excitations. As the matrices contain two or three such indexes, they cannot be explicitly constructed and stored. Moreover, the matrices are not needed as such. When iterative methods are used to solve the generalized eigenvalue problem of eq 55 and linear equations such as eq 60b, only products of $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$ with vectors are required. Algorithms for the direct generation of such products have previously been described.[9] They not only eliminate the need for the explicit storage of $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$, but they also have a lower scaling than the explicit construction of $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$. With these direct methods, the evaluation of excitation energies and linear response functions has the same scaling as the standard MP2 energy calculation.

Consider, for example, the contribution to that part of $(\mathbf{E}^{[2]}\mathbf{X})_\mu$ where the free index μ refers to an orbital deexcitation from the orbital part of $\mathbf{X}$. Using eq 40, we obtain

$$(\mathbf{E}^{[2]}\mathbf{X}_{\mathrm{orb}})_\mu = \langle 0|[Q_\mu, H_0,\sum_\nu Z_\nu Q_\nu^\dagger]|0\rangle + \langle 0|[Q_\mu,[H_0,\sum_\nu Y_\nu Q_\nu]]|0\rangle \quad (75)$$

where in $\mathbf{X}_{\mathrm{orb}}$, the elements Z_x and Y_x in eq 56 are zero. From the identifications in eqs 66a and 67a and from the Jacobi identity eq 34, we obtain

$$\begin{aligned}(\mathbf{E}^{[2]}\mathbf{X}_\mu)_\mu = {}& \langle \mathrm{HF}|[Q_\mu,[H_0 - \mathbf{c}_2^{(1)}\,\mathbf{c}_2^{(1)\dagger}F,\sum_\nu(Z_\nu Q_\nu^\dagger + Y_\nu Q_\nu)]]|\mathrm{HF}\rangle - \frac{1}{2}\langle \mathrm{HF}|[H_0 - \mathbf{c}_2^{(1)}\,\mathbf{c}_2^{(1)\dagger}F,[Q_\mu,\sum_\nu(Z_\nu Q_\nu^\dagger + Y_\nu Q_\nu)]]|\mathrm{HF}\rangle + \mathbf{c}_2^{(1)\dagger}\langle \mathbf{x}_2|[Q_\mu,[F,\sum_\nu(Z_\nu Q_\nu^\dagger + Y_\nu Q_\nu)]]|\mathbf{x}_2\rangle\mathbf{c}_2^{(1)} - \\ & \frac{1}{2}\mathbf{c}_2^{(1)\dagger}\langle \mathbf{x}_2|[F,[Q_\mu,\sum_\nu(Z_\nu Q_\nu^\dagger + Y_\nu Q_\nu)]]|\mathbf{x}_2\rangle\mathbf{c}_2^{(1)} + \mathbf{c}_2^{(1)\dagger}\langle \mathbf{x}_2|[Q_\mu, \\ & [H_0,\sum_\nu(Z_\nu Q_\nu^\dagger + Y_\nu Q_\nu)]]|\mathrm{HF}\rangle - \frac{1}{2}\mathbf{c}_2^{(1)\dagger}\langle \mathbf{x}_2|[H_0,[Q_\mu,\sum_\nu(Z_\nu Q_\nu^\dagger + Y_\nu Q_\nu)]]|\mathrm{HF}\rangle + \langle \mathrm{HF}|[Q_\mu,[H_0,\sum_\nu(Z_\nu Q_\nu^\dagger + Y_\nu Q_\nu)]]|\mathbf{x}_2\rangle\mathbf{c}_2^{(1)} \\ & - \frac{1}{2}\langle \mathrm{HF}|[H_0,[Q_\mu,\sum_\nu(Z_\nu Q_\nu^\dagger + Y_\nu Q_\nu)]]|\mathbf{x}_2\rangle\mathbf{c}_2^{(1)} \quad (76)\end{aligned}$$

To simplify the expression and, in particular to eliminate the explicit reference to the fluctuation potential, a number of

vanishing terms have been added to obtain eq 76. Introducing the orbital operator

$$O = \sum_{\nu}(Z_{\nu}Q_{\nu}^{\dagger} + Y_{\nu}Q_{\nu}) \tag{77}$$

and the effective Hamiltonian and Fock operator

$$H_0(X) = [H_0, \sum_{\nu}(Z_{\nu}Q_{\nu}^{\dagger} + Y_{\nu}Q_{\nu}^{\dagger})] \tag{78a}$$

$$F(X) = [F, \sum_{\nu}(Z_{\nu}Q_{\nu}^{\dagger} + Y_{\nu}Q_{\nu}^{\dagger})] \tag{78b}$$

the contraction in eq 76 may be written as

$$\begin{aligned}(\mathbf{E}^{[2]}\mathbf{X}_{\mu})_{\mu} = {}& \langle \mathrm{HF}|[Q_{\mu}, H_0(X) - \mathbf{c}_2^{(1)}\mathbf{c}_2^{(1)\dagger}F(X)]|\mathrm{HF}\rangle \\ & - \frac{1}{2}\langle \mathrm{HF}|[H_0 - \mathbf{c}_2^{(1)}\mathbf{c}_2^{(1)\dagger}F, [Q_{\mu}, O]]|\mathrm{HF}\rangle \\ & + \mathbf{c}_2^{(1)\dagger}\langle \mathbf{x}_2|[Q_{\mu}, F(X))]|\mathbf{x}_2\rangle\mathbf{c}_2^{(1)} - \frac{1}{2}\mathbf{c}_2^{(1)\dagger}\langle \mathbf{x}_2|[F, [Q_{\mu}, O]]|\mathbf{x}_2\rangle\mathbf{c}_2^{(1)} \\ & + \mathbf{c}_2^{(1)\dagger}\langle \mathbf{x}_2|[Q_{\mu}, H_0(X)]|\mathrm{HF}\rangle - \frac{1}{2}\mathbf{c}_2^{(1)\dagger}\langle \mathbf{x}_2|[H_0, [Q_{\mu}, O]]|\mathrm{HF}\rangle \\ & + \langle \mathrm{HF}|[Q_{\mu}, H_0(X)|\mathbf{x}_2\rangle\mathbf{c}_2^{(1)} - \frac{1}{2}\langle \mathrm{HF}|[H_0, [Q_{\mu}, O]]|\mathbf{x}_2\rangle\mathbf{c}_2^{(1)}\end{aligned} \tag{79}$$

All contributions to this product may be obtained by procedures that scale at most like the fifth power in system size. For a more detailed description of the algorithms for such direct products of $\mathbf{E}^{[2]}$ times a vector, see ref 9.

We now briefly sketch how the developed method can be extended to treat contributions from the three-index supermatrices $\mathbf{E}^{[3]}$ and $\mathbf{S}^{[3]}$. Contracted with two vectors, these supermatrices occur in the expression for the quadratic response function eq 54 and its residues—see, for example, eq 59. Let us see how the orbital-deexcitation part of $\mathbf{E}^{[3]}$ contracted with two orbital vectors may be constructed. In eq 73, the four blocks containing one deexcitation orbital operator and two general orbital operators are given. Introducing the transformed Hamiltonians for two vectors X^1 and X^2 in the notation of eq 56

$$\begin{aligned}H_0(X^1, X^2) = {}& \\ & [[H_0, \sum_{\nu}(Z_{\nu}^1 Q_{\nu}^{\dagger} + Y_{\nu}^1 Q_{\nu}^{\dagger})], \sum_{\omega}(Z_{\omega}^2 Q_{\omega}^{\dagger} + Y_{\omega}^2 Q_{\omega}^{\dagger})]\end{aligned} \tag{80a}$$

$$\begin{aligned}F(X^1, X^2) = {}& \\ & [[F, \sum_{\nu}(Z_{\nu}^1 Q_{\nu}^{\dagger} + Y_{\nu}^1 Q_{\nu}^{\dagger})], \sum_{\omega}(Z_{\omega}^2 Q_{\omega}^{\dagger} + Y_{\omega}^2 Q_{\omega}^{\dagger})]\end{aligned} \tag{80b}$$

we obtain

$$\begin{aligned}\sum_{\nu\omega}E_{\mu\nu\omega}^{[3]}X_{\nu}^1 X_{\omega}^2 = {}& \langle \mathrm{HF}|[Q_{\mu}, H_0(X_1, X_2)]|\mathrm{HF}\rangle + \langle \mathrm{HF}|[Q_{\mu}, H_0 \\ & (X_1, X_2)]|\mathbf{x}_2\rangle\mathbf{c}_2^{(1)} + \langle \mathrm{HF}|[Q_{\mu}, H_0(X_1, X_2)]|\mathbf{x}_1\rangle\mathbf{c}_1^{(2)}\end{aligned} \tag{81}$$

The terms in eq 81 may again be calculated with procedures that scale at most like the fifth power in system size. Similar schemes can be devised for the remaining terms in the contraction of $\mathbf{E}^{[3]}$ with two vectors, all of which scale as the fifth power in system size or less.

VII. Conclusion

We have determined linear and quadratic response functions including their pole structure and residues to second order in the fluctuation potential. The time-independent reference wave function is determined using the standard Møller−Plesset perturbation expansion. The time-dependent wave function is obtained by applying, to the time-independent wave function, exponential operators for orbital rotations and for double and higher excitations. The time development of the wave function is determined from Ehrenfest equations for the state-excitation operators and modified Ehrenfest equations for the orbital rotations. The modification was made to ensure that the wave function reduces to the time-independent reference wave function when the time-dependent perturbation vanishes.

The response functions and their pole structures may be determined to arbitrary order in the fluctuation potential. Because of the computational success of the second-order linear response methods[17] and the slow convergence or divergence of the Møller−Plesset perturbation series,[6] we restrict our study to second order. We furthermore restrict the treatment so it is only for one-electron operators that the response functions including their poles and residues should be correct through second order. With these restrictions, the perturbation expansion is well-defined and we have developed explicit expressions for all involved matrices. The linear response function obtained in this way is identical to the second-order polarization propagator approximation (SOPPA) obtained 3 decades ago using superoperator algebra. A connection between perturbation-based methods using time-dependent expansions and the generalized Ehrenfest equations with methods using superoperator algebra has thereby been established.

We have furthermore sketched the computational procedures for the linear and quadratic response functions. By the use of direct techniques—that is, direct contractions of matrices with one vector and three-index supermatrices with two vectors—all quantities can be calculated with at computational cost that scales at most as the fifth power in system size.

It is pertinent to compare the current approach to the previously developed CC2 method,[13] which also allows the calculation of linear and nonlinear response properties and their poles at the level of second-order Møller−Plesset perturbation theory. Whereas the present method uses symmetric matrices in the determination of the excitation energies in eq 55, the CC2 method uses an inherently asymmetric Jacobian matrix. The presence of an asymmetric Jacobian leads to a number of complications in CC2, including different left- and right-hand side eigenvectors. These complications are avoided in the present formalism.

The two methods differ also in the choice of operator manifold. In the CC2 method, only single and double excitations are included, whereas the present approach includes orbital- and state-excitation operators as well as the corresponding deexcitation operators. When the second-order contributions are discarded, the present approach therefore reduces to the standard time-dependent Hartree−Fock method, whereas the CC2 method reduces to the coupled-cluster singles (CCS) method. The presence of both excitations and deexcitations in the present approach leads to a more symmetric approach, where the eigenvalues of Eq.. (55) occur in pairs with opposite sign and with twice the number of parameters that occur in CC2. The computational costs of the present approach and CC2 are comparable—there is only a single set of eigenvectors in the present approach, but their length is twice the length of the eigenvectors in CC2.

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