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Linear and nonlinear response functions for an exact state and for an MCSCF state

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We have examined the response of an exact and an MCSCF reference state to a general time-dependent field. The time development of both the exact and the MCSCF reference state have been parametrized in terms of explicit exponential time-dependent transformations. The time development has been determined by requiring the Ehrenfest theorem to be satisfied through each order in the interaction between the molecular system and the field. The response of the exact and the MCSCF reference state has been used to evaluate linear, quadratic, and cubic response functions. It has been shown how a large variety of molecular properties may be expressed in terms of these response functions. It has also been demonstrated that molecular properties containing the electric dipole operator may be expressed in equivalent forms involving the momentum operator both for the exact and the MCSCF state. The MCSCF response functions have been transformed to computationally attractive expressions which do not contain summation indices over intermediate states and which allow direct techniques to be straightforwardly applied.

I. INTRODUCTION

The polarization of a molecular system due to the interaction between the molecular system and a time-dependent electric field can be expressed in terms of a power series expansion in the field strength. The expansion coefficients of the power series determine the response functions characteristic of the electric field response. The coefficient linear in the field strength determines the linear response function and the coefficients for the squared and cubed terms determine the quadratic and cubic response functions, respectively. For small field strengths terms quadratic, cubic, etc. in the field strength may be neglected and the polarization becomes proportional to the field strength.¹ If intense laser fields are used the quadratic and higher order terms²⁻⁵ become important for determining the polarization.

The interaction between the molecular system and the electric field may be described in terms of time-dependent perturbation theory.⁶ Most textbooks¹ treat the case where an electric field of small field strength is applied to the molecular system. The textbook methodology has also been used to describe the case of intense fields.^{2,7} However, this extension is rather tedious and in our opinion a simplified treatment may be obtained if time-dependent perturbation theory is formulated in terms of an explicit exponential unitary time dependent transformation of the reference state⁹ and if the results of the perturbation treatment are expressed in terms of response functions.¹⁰⁻¹² The use of an exponential unitary transformed reference state makes the normalization condition redundant. The phase factor may then also be factored out of the response function derivation using group theoretical arguments¹³ in the beginning of the derivation.

The advantages of expressing the results of time-dependent perturbation theory in terms of response functions are widely recognized.²⁻⁵ The linear, quadratic, and cubic response functions which will be derived for an exact reference state become the frequency-dependent polarizability, hyperpolarizability, and second hyperpolarizability, respectively, and determine the polarization of the molecular system through first, second, and third order in the field strength. Residues of the response functions may be used to determine for example one- and two-photon absorption matrix elements.^{3,14}

The time-dependent perturbation theory become identical to time-independent perturbation theory in the limit of a static (i.e., time-independent) perturbation. A large group of molecular properties which refer to frequency-independent or combinations of frequency-independent and frequency-dependent perturbations can therefore be expressed in terms of response functions. One example is the derivative of the frequency-dependent polarizability with respect to a normal coordinate. This derivative is the main contributor to the intensity of Raman spectra^{4,15} and can be expressed in terms of a quadratic response function. Many more examples will be given of molecular properties that can be described in terms of response functions.

The time development of the exact reference state is determined by requiring the Ehrenfest theorem¹⁶ to be satisfied in each order in the field strength. The Ehrenfest theorem also determines the equations of motion for the response functions. These equations of motion show how molecular properties containing the electric dipole operator may be expressed in equivalent forms involving the momentum operator.¹⁷

The derivation of the exact response functions we have carried out is simple and straightforward compared to previous derivations. The response functions are expressed in a convenient and compact notation. However, the greatest advantage is that the methodology used to derive the exact response functions can be straightforwardly applied to determine response functions for approximate states. In this paper we determine the linear, quadratic, and cubic response functions for a multiconfiguration self-consistent field (MCSCF) state. The time development of the MCSCF state in the presence of the field is parametrized in terms of two exponential unitary time-dependent operators, carrying out transformations in the orbital and configuration-state-function space.¹⁸ The time dependence of the MCSCF state is determined by requiring that the Ehrenfest theorem is satisfied in each order of the field strength. The MCSCF response functions are thus determined by solving the equations for the exact response functions in a subspace spanned by the operators describing the time development of the MCSCF state. The MCSCF response functions satisfy the same equations of motion as the response functions for the exact state. This assures that molecular properties which contain the electric dipole operator can be expressed in equivalent forms containing the momentum operator.

The expressions we have derived for the MCSCF response functions contain summation indices over all intermediate states and are therefore not in general attractive to use for evaluating actual response functions. The MCSCF response functions may be transformed to computationally attractive expressions which do not contain summations over intermediate states and which are expressed in the configuration state function basis. The technique that allows these simplifications to be performed was originally described in connection with efficient evaluation of cubic contributions in MCSCF.^{19,20} The technique is also used in the direct MCSCF algorithm^{20,21} that recently has been applied in MCSCF calculations containing as many as 10^3 – 10^5 configuration state functions.²² The MCSCF response functions may be evaluated for these very large configuration state function spaces using the same direct techniques and work along this line is in progress.²³

The MCSCF linear response function has previously been derived by Yeager and Jørgensen²⁴ and by Dalgaard¹⁸ and very promising linear response function results for excitation energies, transition moments, and frequency-dependent polarizabilities have been determined using small configuration spaces.^{24,25} The so-called random phase (RPA) or time-dependent Hartree–Fock (TDHF) approximation represents the linear response function for a single configuration self-consistent field (SCF) reference state.¹² The quadratic response function has been determined previously²⁶ for an SCF state using the methodology we will use. Accurate linear response function calculations have also been carried out by approximating the exact linear response function with the one obtained by keeping all terms through second order in the fluctuation potential.^{12,27,28}

In Sec. II we derive the linear, quadratic, and cubic response functions for an exact state. Section III gives examples of molecular properties that can be expressed in terms of linear, quadratic, and cubic response functions. Section IV discusses when approximate calculations of molecular properties containing the electric dipole operator can be expressed in equivalent forms containing the momentum operator. The MCSCF linear, quadratic, and cubic response functions are derived in Sec. V, and sec. VI demonstrates how the MCSCF response functions may be rewritten to computationally tractable forms which allow direct techniques to be used. The last section contains some concluding remarks.

II. RESPONSE THEORY FOR AN EXACT STATE

In this section we examine the interaction between a molecular system and a general time-dependent field in order to determine the linear, quadratic, and cubic response functions for the molecular system. We first parametrize the time development of the exact reference state in terms of an explicit unitary exponential transformation within the set of eigenstates of the molecular system. The time development is then determined by requiring the Ehrenfest theorem satisfied through each order in the interaction between the molecular system and the field. The linear, quadratic, and cubic response functions are then determined from the time development of the average value of an operator A .

A. The perturbation operator

Consider a molecular system with a time-independent Hamiltonian H_0 . When a general field $W(t)$ is applied to the molecular system the system will interact with the field.¹⁰ The interaction operator may be denoted V^t . We assume that $W(t)$ vanishes at $t = -\infty$. The interaction operator V^t then also vanishes at $t = -\infty$ and can be expressed as¹⁰

$$V^t = \int_{-\infty}^{\infty} d\omega V^\omega \exp(-i\omega + \epsilon)t. \quad (2.1)$$

ϵ is a positive infinitesimal that ensures $V^{-\infty}$ is zero. From the Hermiticity of V^t it follows that

$$(V^\omega)^+ = V^{(-\omega)}. \quad (2.2)$$

The frequency distribution in Eq. (2.1) reduces in most applications to a sum of interaction operators at specific frequencies. In Sec. III A we give examples of interaction operators representing various fields.

We assume that at $t = -\infty$ the molecular system is in an exact eigenstate $|0\rangle$ of H_0 :

$$H_0|0\rangle = E_0|0\rangle \quad (2.3)$$

and that $\{E_n\}$ and $\{|n\rangle\}$ denote the residual set of exact eigenvalues and eigenstates, respectively, of the noninteracting system

$$H_0|n\rangle = E_n|n\rangle. \quad (2.4)$$

B. Parametrization of the exact reference state

The time development of $|0\rangle$ may be described in terms of a unitary transformation¹⁸ of $|0\rangle$ within the set of eigenstates $\{|0\rangle, |n\rangle\}$. The time developed state $|\bar{0}\rangle$ is thus automatically normalized. The unitary transformed state is defined as

$$|\bar{0}\rangle = \exp[iP(t)]|0\rangle. \quad (2.5)$$

The operator $P(t)$ is

$$P(t) = \sum_n (P_n|n\rangle\langle 0| + P_n^*|0\rangle\langle n|) + (P_0 + P_0^*)|0\rangle\langle 0|, \quad (2.6)$$

where P_n are the time-dependent expansion coefficients. The real $\{P_n^R\}$ and imaginary $\{P_n^I\}$ part of $\{P_n\}$:

$$P_n = P_n^R + iP_n^I \quad (2.7)$$

constitute a linear-independent set of expansion coefficients. Only the real part P_0^R of P_0 contributes to P . When these parameters are inserted in $P(t)$ of Eq. (2.6) $P(t)$ may be divided into two terms

$$P(t) = {}^aP + {}^bP, \quad (2.8)$$

where

$${}^aP = \sum_n P_n^R(|n\rangle\langle 0| + |0\rangle\langle n|) + iP_n^I(|n\rangle\langle 0| - |0\rangle\langle n|), \quad (2.9)$$

$${}^bP = 2P_0^R|0\rangle\langle 0|. \quad (2.10)$$

The operator $|0\rangle\langle 0|$ is a generator of the subgroup of the unitary transformations described by $\exp[iP(t)]$ which create a phase change of $|0\rangle$. The unitary transformation of $|0\rangle$ in Eq. (2.5) may therefore be parametrized as

$$\begin{aligned} |\bar{0}\rangle &= \exp(i{}^aP)\exp(i{}^bP)|0\rangle \\ &= \exp(i{}^aP)|0\rangle\exp(i2P_0^R). \end{aligned} \quad (2.11)$$

The exponential operator $\exp(i{}^bP)$ thus introduces a time-dependent phase factor $\exp(i2P_0^R)$ in the transformed wave function.

The parameter set $\{P_n, P_n^*\}$ of aP is related to the set $\{P_n^R, P_n^I\}$ through a nonsingular transformation. $\{P_n, P_n^*\}$ may therefore be used as a linear-independent set of expansion coefficient. The operator aP may then be written as

$${}^aP = \sum_n (P_n|n\rangle\langle 0| + P_n^*|0\rangle\langle n|). \quad (2.12)$$

We occasionally use the notation

$$\begin{pmatrix} \Lambda_n \\ \Lambda_{-n} \end{pmatrix} = \begin{pmatrix} |n\rangle\langle 0| \\ |0\rangle\langle n| \end{pmatrix}; \quad (n > 0) \quad (2.13)$$

and write Eq. (2.12) as

$$\begin{aligned} {}^aP &= \sum_{n>0} (P_n\Lambda_n + P_n^*\Lambda_{-n}) \\ &= \sum_{n>0} (P_n\Lambda_n + P_{-n}\Lambda_{-n}), \end{aligned} \quad (2.14)$$

where we have defined

$$P_{-n} = P_n^* \quad (n > 0). \quad (2.15)$$

The operator aP becomes in this notation

$${}^aP = \sum_n P_n\Lambda_n, \quad (2.16)$$

where the summation is over both positive and negative indices n and where 0 is excluded. Summation indices which refer to both positive and negative indices will in the rest of this paper always be assumed not to include 0.

C. Parametrization of the time development of the reference state

The time dependence of the parameters P_{n0} may be determined by applying the Ehrenfest theorem¹⁶ to all the operators Λ_n of Eq. (2.13). Let Λ denote an element of $\{\Lambda_n\}$. Since Λ does not contain an explicit time dependence, Ehrenfest's theorem becomes

$$\langle \bar{0}|\Lambda|\dot{\bar{0}}\rangle + \langle \dot{\bar{0}}|\Lambda|\bar{0}\rangle = -i\langle \bar{0}|\Lambda, H_0 + V^I|\bar{0}\rangle. \quad (2.17)$$

Inserting Eq. (2.11) into Eq. (2.17) gives

$$\langle \bar{0}|\Lambda|\dot{\bar{0}}\rangle + \langle \dot{\bar{0}}|\Lambda|\bar{0}\rangle = -i\langle \bar{0}|\Lambda, H_0 + V^I|\bar{0}\rangle, \quad (2.18)$$

where

$$|\dot{\bar{0}}\rangle = \exp(i{}^aP)|0\rangle. \quad (2.19)$$

In Eq. (2.18) all reference to the phase factor has disappeared. The Ehrenfest theorem therefore cannot be used to determine P_0^R . The explicit form of P_0^R may be determined by imposing the condition²⁹

$$\langle \bar{0}|\left(i\frac{d}{dt} - H_0 - V^I\right)|\bar{0}\rangle = 0 \quad (2.20)$$

on the time development of the reference state. P_0^R then must satisfy the linear differential equation

$$2\frac{dP_0^R}{dt} = \langle 0|\exp(-i{}^aP)\left(i\frac{d}{dt} - H_0 - V^I\right)\exp(i{}^aP)|0\rangle. \quad (2.21)$$

We will not discuss the determination of P_0^R in more detail as P_0^R does not enter in the calculation of the response functions.

The parameter set in the operator aP may be determined from Eq. (2.18). The unitary transformed state $|\bar{0}\rangle$ in Eq. (2.19) may be expanded the exponential operator be written as

$$|\bar{0}\rangle = |0\rangle\cos x + i\sum_{n>0}|n\rangle\frac{P_n}{x}\sin x, \quad (2.22)$$

where

$$x = \left[\sum_{n>0}|P_n|^2\right]^{1/2}. \quad (2.23)$$

Equation (2.18) may be solved through each order in the perturbation V^I . In Eq. (2.18) the state $|\bar{0}\rangle$ has an implicit dependence on V^I in the parameters orders of P_n . The parameters P_n can be expanded in the perturbation

$$P_n = P_n^{(1)} + P_n^{(2)} + \dots, \quad (2.24)$$

where $P_n^{(0)}$ vanishes since $|0\rangle$ is an eigenstate of H_0 . We concentrate on determining $P_n^{(i)}$, $i = 1, 2, 3$. The coefficients $P_n^{(i)}$, $i = 1, 2, 3 \dots$ satisfy the boundary condition

$$\lim_{t \rightarrow -\infty} P_n^{(i)}(t) = 0, \quad i = 1, 2, 3, \dots \quad (2.25)$$

as the perturbation is turned on adiabatically. A power series of $|\tilde{0}\rangle$ may be determined

$$|\tilde{0}\rangle = |0^{(0)}\rangle + |0^{(1)}\rangle + |0^{(2)}\rangle + |0^{(3)}\rangle + \dots \quad (2.26)$$

by inserting Eq. (2.24) into Eq. (2.22). The individual terms of Eq. (2.26) become

$$|\tilde{0}^{(0)}\rangle = |0\rangle, \quad (2.27)$$

$$|\tilde{0}^{(1)}\rangle = i \sum_{n>0} |n\rangle P_n^{(1)}, \quad (2.28)$$

$$|\tilde{0}^{(2)}\rangle = -\frac{1}{2}|0\rangle \sum_{j>0} P_j^{(1)} P_j^{*(1)} + i \sum_{n>0} |n\rangle P_n^{(2)}, \quad (2.29)$$

$$|\tilde{0}^{(3)}\rangle = -\frac{1}{2}|0\rangle \sum_{j>0} (P_j^{(2)} P_j^{*(1)} + P_j^{(1)} P_j^{*(2)}) + i \sum_{n>0} |n\rangle (P_n^{(3)} - \frac{1}{6} P_n^{(1)} \sum_{j>0} P_j^{(1)} P_j^{*(1)}). \quad (2.30)$$

D. Differential equations for the time development of the reference state

In this subsection we will determine the three lowest order equations derived from the Ehrenfest's theorem by inserting Eqs. (2.26)–(2.30) into Eq. (2.18). The zeroth-order equation vanishes as $|0\rangle$ is an eigenstate of H_0 . The first-order equation may be written as

$$\sum_{n>0} (i\langle 0|\Lambda|n\rangle \dot{P}_n^{(1)} - i\langle n|\Lambda|0\rangle \dot{P}_n^{*(1)} - \langle 0|[\Lambda, H_0]|n\rangle P_n^{(1)} + \langle n|[\Lambda, H_0]|0\rangle P_n^{*(1)}) = -i\langle 0|[\Lambda, V^t]|0\rangle. \quad (2.31)$$

The second-order equation is determined to be

$$\sum_{n>0} (i\langle 0|\Lambda|n\rangle \dot{P}_n^{(2)} - i\langle n|\Lambda|0\rangle \dot{P}_n^{*(2)} - \langle 0|[\Lambda, H_0]|n\rangle P_n^{(2)} + \langle n|[\Lambda, H_0]|0\rangle P_n^{*(2)}) = \sum_{n>0} (\langle 0|[\Lambda, V^t]|n\rangle P_n^{(1)} - \langle n|[\Lambda, V^t]|0\rangle P_n^{*(1)}), \quad (2.32)$$

where we have used that $\{|0\rangle, |n\rangle\}$ are eigenstates of H_0 and that terms of the form $\langle 0|\Lambda|0\rangle$ and $\langle n|\Lambda|m\rangle$, $n, m \neq 0$ are zero because Λ is a state transfer operator [see Eq. (2.13)]. The third-order equation is determined in a similar manner to be

$$\sum_{n>0} (i\langle 0|\Lambda|n\rangle \dot{D}_n^{(3)} - i\langle n|\Lambda|0\rangle \dot{D}_n^{*(3)} - \langle 0|[\Lambda, H_0]|n\rangle D_n^{(3)} + \langle n|[\Lambda, H_0]|0\rangle D_n^{*(3)}) = \sum_{n>0} (\langle 0|[\Lambda, V^t]|n\rangle P_n^{(2)} - \langle n|[\Lambda, V^t]|0\rangle P_n^{*(2)}) - i \sum_{n,j>0} \langle n|[\Lambda, V^t]|j\rangle P_n^{*(1)} P_j^{(1)} + i\langle 0|[\Lambda, V^t]|0\rangle \sum_{j>0} P_j^{(1)} P_j^{*(1)}, \quad (2.33)$$

where we have introduced the short hand notation

$$D_n^{(3)} = P_n^{(3)} - \frac{2}{3} P_n^{(1)} \sum_{j>0} P_j^{(1)} P_j^{*(1)}. \quad (2.34)$$

The parameters $D_n^{(3)}$ represent the third-order terms in an expansion of an expectation value. The last term in $D_n^{(3)}$ in Eq. (2.34) ensures normalization through third order. The operator Λ appearing in Eqs. (2.31)–(2.33) may have both positive and negative indices. The differential equations resulting from the positive and negative index are complex conjugated of each other and can be combined into one differential equation that is valid for both positive and negative indices. This will be illustrated by carrying out a detailed derivation of the set of differential equations which determines the first order expansion coefficients in Eq. (2.31). Initially we insert $|0\rangle\langle k|$ as the operator Λ in the first-order equation

$$i\dot{P}_k^{(1)} - (E_k - E_0)P_k^{(1)} = -i\langle k|V^t|0\rangle. \quad (2.35)$$

If $|k\rangle\langle 0|$ is inserted into Eq. (2.31) we obtain

$$-i\dot{P}_k^{*(1)} - (E_k - E_0)P_k^{*(1)} = i\langle 0|V^t|k\rangle. \quad (2.36)$$

Equations (2.35) and (2.36) are the complex conjugated of each other. Since they furthermore are separate we need to solve either Eq. (2.35) for $P_k^{(1)}$ or Eq. (2.36) for $P_k^{*(1)}$. However, for convenience in the later development we combine Eqs. (2.35) and (2.36) into a single equation and solve this equation. Using the nomenclature of Eqs. (2.15) and (2.16) we obtain

$$i \operatorname{sgn}(k) \dot{P}_k^{(1)} - \omega_k P_k^{(1)} = -iV_k^t, \quad (2.37)$$

where k denotes both a positive and a negative index. We have in Eq. (2.37) introduced the notation

$$V_k^t = \begin{pmatrix} \langle k|V^t|0\rangle \\ -\langle 0|V^t|-k\rangle \end{pmatrix}; \quad \begin{pmatrix} k > 0 \\ k < 0 \end{pmatrix} \quad (2.38)$$

and

$$\omega_k = \omega_{-k} = E_k - E_0, \quad (2.39)$$

and defined the function $\operatorname{sgn}(k)$ which equals one for positive k index and minus one for negative k index.

The set of linear inhomogeneous differential equations for determining the second-order expansion coefficients may be obtained from Eq. (2.32) in a similar way using Eqs. (2.39) and (2.15):

$$i \operatorname{sgn}(k) \dot{P}_k^{(2)} - \omega_k P_k^{(2)} = \sum_n V_{k-n}^t P_n^{(1)}, \quad (2.40)$$

where

$$V_{kn}^t = \begin{pmatrix} 0 & \langle k|V^t|-n\rangle - \delta_{k-n}\langle 0|V^t|0\rangle \\ \langle n|V^t|-k\rangle - \delta_{-kn}\langle 0|V^t|0\rangle & 0 \end{pmatrix}; \quad \begin{pmatrix} k, n > 0 & k > 0, n < 0 \\ k < 0, n > 0 & k, n < 0 \end{pmatrix}. \quad (2.41)$$

$P_k^{(1)}$ has to be determined prior to evaluating $P_k^{(2)}$ from Eq. (2.40).

The third-order equation is obtained in a similar way from Eq. (2.33) using Eqs. (2.15), (2.38)–(2.39), and (2.41):

$$i \operatorname{sgn}(k) \dot{D}_k^{(3)} - \omega_k D_k = \sum_n [V_{k-n}^i P_n^{(2)} + i\theta(kn) V_n^i P_{-n}^{(1)} P_k^{(1)}] + i V_k^i \sum_{n>0} P_n^{(1)} P_{-n}^{(1)}. \quad (2.42)$$

In Eq. (2.42) we have introduced the Heaviside step function $\theta(kn)$ which is equal to one if the signs of k and n are equal and zero if the signs of k and n differ. $P_k^{(1)}$ and $P_k^{(2)}$ must be determined from Eqs. (2.37) and (2.40), respectively, prior to evaluating $D_k^{(3)}$. From $D_k^{(3)}$ we may straightforwardly evaluate $P_k^{(3)}$ [see Eq. (2.34)]. However, $D_k^{(3)}$ appears as an entity in the cubic response function that will be derived in Secs. II F and II G and explicit expressions for $P_k^{(3)}$ will for that reason not be evaluated.

E. Time dependence of the reference state

Both the first-, second-, and third-order expansion coefficients are determined from linear inhomogeneous differential equations³⁰ of the type [see Eqs. (2.37), (2.40), and (2.42)]

$$i \operatorname{sgn}(k) \frac{df(t)}{dt} - \omega_k f(t) = g(t), \quad (2.43)$$

where $g(t)$ is a known function of t . The solution to Eq. (2.43) with the boundary condition

$$\lim_{t \rightarrow -\infty} f(t) = 0 \quad (2.44)$$

is

$$f(t) = -i \operatorname{sgn}(k) \exp[-i\omega_k \operatorname{sgn}(k)t] \int_{-\infty}^t d\tau \times \exp[i\omega_k \operatorname{sgn}(k)\tau] g(\tau). \quad (2.45)$$

Using Eq. (2.45) for $P_k^{(1)}$ of Eq. (2.37) gives

$$P_k^{(1)} = -i \operatorname{sgn}(k) \exp[-i\omega_k \operatorname{sgn}(k)t] \int_{-\infty}^t d\tau \times \exp[i\omega_k \operatorname{sgn}(k)\tau] (-i) \int_{-\infty}^{\infty} d\omega_1 V_k^{\omega_1} \times \exp(-i\omega_1 + \epsilon)\tau, \quad (2.46)$$

where we have used the definition of V^i in Eq. (2.1) and where $V_k^{\omega_1}$ is defined as in Eq. (2.38) with V^{ω_1} replacing V^i . In Eq. (2.46) and in the following we use $\omega_1, \omega_2, \omega_3, \omega_b, \omega_c,$ and ω_d to denote general frequency variables. These variables should not be confused with the excitation energies $\omega_e, \omega_f, \omega_j, \omega_l, \omega_m,$ and ω_n which are defined in Eq. (2.39). The integration over τ gives

$$P_k^{(1)} = -i \int_{-\infty}^{\infty} d\omega_1 \exp[(-i\omega_1 + \epsilon)t] \times \frac{\operatorname{sgn}(k) V_k^{\omega_1}}{\omega_1 - \operatorname{sgn}(k)\omega_k + i\epsilon}, \quad (2.47)$$

thus determining the linear expansion coefficients.

The quadratic expansion coefficients are determined from Eq. (2.40) in a similar manner:

$$P_k^{(2)} = -i \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \exp[(-i\omega_1 - i\omega_2 + 2\epsilon)t] \sum_n \frac{V_{k-n}^{\omega_1} V_n^{\omega_2}}{[\omega_1 + \omega_2 - \operatorname{sgn}(k)\omega_k + 2i\epsilon][\omega_2 - \operatorname{sgn}(n)\omega_n + i\epsilon]}. \quad (2.48)$$

The third-order coefficient becomes

$$D_k^{(3)} = i \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \int_{-\infty}^{\infty} d\omega_3 \exp[(-i\omega_1 - i\omega_2 - i\omega_3 + 3\epsilon)t] \frac{\operatorname{sgn}(k)}{\omega_1 + \omega_2 + \omega_3 - \operatorname{sgn}(k)\omega_k + 3i\epsilon} \times \left(\sum_n \left[-\sum_m \frac{V_{k-n}^{\omega_1} V_{n-m}^{\omega_2} V_m^{\omega_3}}{[\omega_2 + \omega_3 - \operatorname{sgn}(n)\omega_n + 2i\epsilon][\omega_3 - \operatorname{sgn}(m)\omega_m + i\epsilon]} + \frac{\theta(kn) V_n^{\omega_1} V_{-n}^{\omega_2} V_k^{\omega_3}}{[\omega_2 + \operatorname{sgn}(n)\omega_n + i\epsilon][\omega_3 - \operatorname{sgn}(k)\omega_k + i\epsilon]} \right] + \sum_{n>0} \frac{V_k^{\omega_1} V_n^{\omega_2} V_{-n}^{\omega_3}}{[\omega_2 - \operatorname{sgn}(n)\omega_n + i\epsilon][\omega_3 + \operatorname{sgn}(n)\omega_n + i\epsilon]} \right). \quad (2.49)$$

We have now derived explicit expressions for the expansion coefficients which determine the first-, second-, and third-order time development of the reference state. In the next section we use these expressions to determine the linear, quadratic, and cubic response functions.

F. Time development of the average value of an operator A

We now examine the time development of the average value of an operator A . We assume that A is time-independent in the Schrödinger picture. Since the time development of $|0\rangle$ is described in terms of a unitary

transformed state $|\tilde{0}\rangle$ the time development of the average value of A is

$$A_{Av}(t) = \langle \tilde{0} | A | \tilde{0} \rangle. \quad (2.50)$$

The average value of A may be formally expanded as¹⁰

$$A_{Av}(t) = \langle 0 | A | 0 \rangle + \int_{-\infty}^{\infty} d\omega_1 \exp[(-i\omega_1 + \epsilon)t] \langle \langle A; V^{\omega_1} \rangle \rangle_{\omega_1+i\epsilon} + \frac{1}{2} \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \times \exp[(-i\omega_1 - i\omega_2 + 2\epsilon)t]$$

$$\begin{aligned} & \langle\langle A; V^{\omega_1}, V^{\omega_2} \rangle\rangle_{\omega_1+i\epsilon, \omega_2+i\epsilon} + \frac{1}{6} \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \\ & \times \int_{-\infty}^{\infty} d\omega_3 \exp[(-i\omega_1 - i\omega_2 - i\omega_3 + 3\epsilon)t] \\ & \langle\langle A; V^{\omega_1}, V^{\omega_2}, V^{\omega_3} \rangle\rangle_{\omega_1+i\epsilon, \omega_2+i\epsilon, \omega_3+i\epsilon} + \dots, \end{aligned} \quad (2.51)$$

where

$$\langle\langle A; V^{\omega_1} \rangle\rangle_{\omega_1+i\epsilon}, \quad (2.52)$$

$$\langle\langle A; V^{\omega_1}, V^{\omega_2} \rangle\rangle_{\omega_1+i\epsilon, \omega_2+i\epsilon}, \quad (2.53)$$

$$\langle\langle A; V^{\omega_1}, V^{\omega_2}, V^{\omega_3} \rangle\rangle_{\omega_1+i\epsilon, \omega_2+i\epsilon, \omega_3+i\epsilon} \quad (2.54)$$

denote the linear, quadratic, and cubic response functions, respectively.

When A denotes the electric dipole operator the response functions provide us with a Fourier decomposition of the time development of the dipole moment and give information on the absorption and emission of photons. For example, the quadratic response function $\langle\langle A; V^{\omega_1}, V^{\omega_2} \rangle\rangle_{\omega_1+i\epsilon, \omega_2+i\epsilon}$ provides information on the process where one photon of frequency ω_1 and one of frequency ω_2 are absorbed and one of frequency $\omega_1 + \omega_2$ is emitted.

In the rest of this section we will determine explicit representations for these response functions. To do this we insert the power series expansion of $|\tilde{0}\rangle$ of Eqs. (2.28)–(2.30) and (2.47)–(2.49) into Eq. (2.50):

$$\begin{aligned} A_{Av}(t) &= \langle 0|A|0\rangle + \langle 0^{(1)}|A|0\rangle \\ &+ \langle 0|A|0^{(1)}\rangle + \langle 0^{(2)}|A|0\rangle \\ &+ \langle 0^{(1)}|A|0^{(1)}\rangle + \langle 0|A|0^{(2)}\rangle \\ &+ \langle 0^{(3)}|A|0\rangle + \langle 0^{(2)}|A|0^{(1)}\rangle \\ &+ \langle 0^{(1)}|A|0^{(2)}\rangle + \langle 0|A|0^{(3)}\rangle + \dots \\ &= \langle 0|A|0\rangle - i \sum_n A_{-n} P_n^{(1)} - i \sum_n A_{-n} P_n^{(2)} \\ &+ \sum_{n,j>0} P_{-j}^{(1)} A_{j-n} P_n^{(1)} - i \sum_k A_{-k} D_k^{(3)} \\ &+ \sum_{k,j>0} P_{-k}^{(2)} A_{k-n} P_n^{(1)} \\ &+ \sum_{k,j>0} P_{-k}^{(1)} A_{k-n} P_n^{(2)} + \dots \end{aligned} \quad (2.55)$$

To obtain the last equality we used Eq. (2.15) and the matrix definitions of Eqs. (2.38) and (2.41). $D^{(3)}$ is defined in Eq. (2.34).

G. The linear, quadratic, and cubic response functions

The linear response function may be determined from the second term in Eq. (2.55). The third and fourth terms determine the quadratic response function and the fifth through seventh terms determine the cubic response function.

Inserting $P_n^{(1)}$ of Eq. (2.47) into the second term of Eq. (2.55) gives

$$\begin{aligned} -i \sum_k A_{-k} P_k^{(1)} &= - \int_{-\infty}^{\infty} d\omega_1 \exp[(-i\omega_1 + \epsilon)t] \\ &\times \sum_k \frac{\text{sgn}(k) A_{-k} V_k^{\omega_1}}{\omega_1 - \text{sgn}(k)\omega_k + i\epsilon}. \end{aligned} \quad (2.56)$$

Comparison of Eq. (2.56) and Eq. (2.51) then identifies the linear response function as

$$\langle\langle A; V^{\omega_1} \rangle\rangle_{\omega_1+i\epsilon} = - \sum_k \frac{\text{sgn}(k) A_{-k} V_k^{\omega_1}}{\omega_1 - \text{sgn}(k)\omega_k + i\epsilon}. \quad (2.57)$$

The quadratic response function is determined from the third and fourth term in Eq. (2.55). Using Eqs. (2.47) and (2.48)

$$\begin{aligned} -i \sum_k A_{-k} P_k^{(2)} + \sum_{k,n>0} P_{-k}^{(1)} A_{k-n} P_n^{(1)} &= \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \\ &\times \exp[(-i\omega_1 - i\omega_2 + 2\epsilon)t] \left[- \sum_{k,n} \right. \\ &\times \frac{A_{-k} V_{k-n}^{\omega_1} V_n^{\omega_2}}{[\omega_1 + \omega_2 - \text{sgn}(k)\omega_k + 2i\epsilon][\omega_2 - \text{sgn}(n)\omega_n + i\epsilon]} \\ &\left. + \sum_{k,n>0} \frac{V_{-k}^{\omega_1} A_{k-n} V_n^{\omega_2}}{(\omega_1 + \omega_k + i\epsilon)(\omega_2 - \omega_n + i\epsilon)} \right]. \end{aligned} \quad (2.58)$$

The quadratic response function may be identified from a comparison of Eqs. (2.58) and (2.51). However, before we identify the quadratic response function we will make the integrand in Eq. (2.58) symmetric in the integration variables. This may be done with the operator $\frac{1}{2}P(1, 2)$ where $P(1, 2)$ creates all different permutations of the integration variables ω_1 and ω_2 . After this symmetrization has been introduced into Eq. (2.58) the quadratic response function may be identified as

$$\begin{aligned} \langle\langle A; V^{\omega_1}, V^{\omega_2} \rangle\rangle_{\omega_1+i\epsilon, \omega_2+i\epsilon} &= P(1, 2) \left[- \sum_{k,n} \frac{A_{-k} V_{k-n}^{\omega_1} V_n^{\omega_2}}{[\omega_1 + \omega_2 - \text{sgn}(k)\omega_k + 2i\epsilon][\omega_2 - \text{sgn}(n)\omega_n + i\epsilon]} \right. \\ &\left. + \sum_{k,n>0} \frac{V_{-k}^{\omega_1} A_{k-n} V_n^{\omega_2}}{(\omega_1 + \omega_k + i\epsilon)(\omega_2 - \omega_n + i\epsilon)} \right]. \end{aligned} \quad (2.59)$$

The cubic response function may be determined from the last three terms in Eq. (2.55) using a technique similar to the one used for obtaining the linear and quadratic response functions. The cubic response function becomes

$$\begin{aligned}
& \langle\langle A; V^{\omega_1}, V^{\omega_2}, V^{\omega_3} \rangle\rangle_{\omega_1+i\epsilon, \omega_2+i\epsilon, \omega_3+i\epsilon} \\
&= P(1, 2, 3) \left\{ \sum_k \frac{A_{-k} \operatorname{sgn}(k)}{\omega_1 + \omega_2 + \omega_3 - \operatorname{sgn}(k)\omega_k + 3i\epsilon} \left(\sum_n \left[-\sum_m \frac{V_{k-n}^{\omega_1} V_{n-m}^{\omega_2} V_m^{\omega_3}}{[\omega_2 + \omega_3 - \operatorname{sgn}(n)\omega_n + 2i\epsilon][\omega_3 - \operatorname{sgn}(m)\omega_m + i\epsilon]} \right. \right. \right. \\
&+ \left. \left. \frac{\theta(kn) V_n^{\omega_1} V_{-n}^{\omega_2} V_k^{\omega_3}}{[\omega_2 + \operatorname{sgn}(n)\omega_n + i\epsilon][\omega_3 - \operatorname{sgn}(k)\omega_k + i\epsilon]} \right] + \sum_{n>0} \frac{V_k^{\omega_1} V_n^{\omega_2} V_{-n}^{\omega_3}}{[\omega_2 - \operatorname{sgn}(n)\omega_n + i\epsilon][\omega_3 + \operatorname{sgn}(n)\omega_n + i\epsilon]} \right) \\
&- \sum_{m,k,n>0} \left[\frac{V_{-km}^{\omega_1} V_{-m}^{\omega_2} A_{k-n} V_n^{\omega_3}}{(\omega_1 + \omega_2 + \omega_k + 2i\epsilon)(\omega_2 + \omega_m + i\epsilon)(\omega_3 - \omega_n + i\epsilon)} \right. \\
&- \left. \frac{V_{-k}^{\omega_1} A_{k-n} V_{n-m}^{\omega_2} V_m^{\omega_3}}{(\omega_1 + \omega_k + i\epsilon)(\omega_2 + \omega_3 - \omega_n + 2i\epsilon)(\omega_3 - \omega_m + i\epsilon)} \right] \Big\}, \quad (2.60)
\end{aligned}$$

where $P(1, 2, 3)$ is the permutation operator operating on the subscripts of ω_1 , ω_2 , and ω_3 . Explicit expressions have now been determined for the linear, quadratic, and cubic response functions. In the next section we describe how a large variety of molecular properties may be described in terms of these response functions or the poles and residues of these response functions.

III. MOLECULAR PROPERTIES FROM RESPONSE FUNCTIONS

In the previous section we derived the linear, quadratic, and cubic response functions characterizing the time development of the average value of an operator A when the interaction between the molecular system and the external field is described by the interaction operator V^t of Eq. (2.1). In Sec. III A, we give explicit formulas for interaction operators representing various external fields. The interaction operators are used in Secs. III B, III C, and III D to give examples of molecular response properties that may be expressed in terms of response functions or the poles and residues of response functions. In Sec. III B we concentrate on describing molecular response properties that can be expressed in terms of linear response functions. In Secs. III C and III D, molecular response properties are described that can be expressed in terms of quadratic and cubic response functions, respectively.

A. Interaction operators

The interaction between a molecular system and a general field may be expressed in terms of the interaction operator V^t of Eq. (2.1). If the external field contains only one frequency component ω_b the interaction operator becomes

$$\begin{aligned}
V^t &= \int_{-\infty}^{\infty} d\omega [\delta(\omega - \omega_b) + \delta(\omega + \omega_b)] V^\omega \exp(-i\omega + \epsilon)t \\
&= V^{\omega_b} \exp(-i\omega_b + \epsilon)t + V^{-\omega_b} \exp(i\omega_b + \epsilon)t, \quad (3.1)
\end{aligned}$$

where $\delta(\omega)$ denotes the Dirac delta function. If the external field has several frequency components ω_b , ω_c , ω_d , etc., each of these components contribute one term of the form in Eq. (3.1).

The explicit form of the interaction operators depend on the external field.¹⁰ If the external field is a homo-

geneous periodic electric field of frequency ω_b , it can be represented as¹⁰

$$E(t) = [\exp(-i\omega_b + \epsilon)t + \exp(i\omega_b + \epsilon)t] E^0. \quad (3.2)$$

The interaction operator then becomes

$$V^t = -(E^0 \mu) [\exp(-i\omega_b + \epsilon)t + \exp(i\omega_b + \epsilon)t], \quad (3.3)$$

where $\mu = (\mu^x, \mu^y, \mu^z)$ represents the electric dipole moment operator of the molecular system.

For a homogeneous periodic magnetic field of frequency ω_b :

$$H(t) = [\exp(-i\omega_b + \epsilon)t + \exp(i\omega_b + \epsilon)t] H^0, \quad (3.4)$$

the interaction operator becomes

$$V^t = -(H^0 M) [\exp(-i\omega_b + \epsilon)t + \exp(i\omega_b + \epsilon)t], \quad (3.5)$$

where $M = (M^x, M^y, M^z)$ is the total magnetic moment of the molecular system.

If the external field is time independent, the interaction operator is also time independent and is represented by a frequency component $\omega_b = 0$. For example, a homogeneous time-independent electric field has the interaction operator

$$V^t = -E^0 \mu. \quad (3.6)$$

A comparison of Eqs. (3.1) and (3.3) shows that V^{ω_b} for a constant electric field of frequency ω_b is $-E^0 \mu$. Since $-E^0$ is a constant vector, it can be taken out of the response functions [Eq. (2.51)] and the electric dipole moment operator μ will be the operator V^{ω_b} used for a homogeneous periodic electric field. The magnetic moment M will for similar reasons be used as the operator identifying a homogeneous periodic magnetic field.

The interaction operators can also involve a field that varies in space. In this case V^t may represent terms in the multipole expansion of the field, e.g., the quadrupole moment.

When H_0 of Eq. (2.3) denotes the nonrelativistic Hamiltonian, operators of relativistic origin¹ (e.g., the spin-orbit coupling operator) act as a time-independent field on the molecular system (represents a static internal perturbation). The relativistic operators therefore may be used as interaction operators of zero frequency.

If H_0 denotes the nonrelativistic Hamiltonian at a geometry R^0 , the nonrelativistic Hamiltonian at a displaced

geometry $R^0 + \eta$ can be expanded in a power series around R^0 ^{11,31}:

$$H_0(R^0 + \eta) = H_0 + \eta H_1 + \frac{1}{2} \eta H_2 \eta + \dots, \quad (3.7)$$

and H_1 , H_2 , etc., can be used as interaction operators of zero frequency. H_1 , H_2 , etc. describe the static internal perturbations that act on the molecular electronic system at R^0 due to a infinitesimal displacement of the nuclei.

In quantum chemistry calculations a whole potential energy surface is often described in terms of a finite atomic basis which sits at the nuclei. The finite atomic basis contains a dependence of the nuclear positions which vanish in the limit where a complete atomic basis is used. If the Hamiltonian at each geometry is expanded in terms of a set of orthonormal orbitals consisting of linear combinations of the atomic orbitals then the nuclear dependence due to the use of a finite basis can be transformed into H_1 , H_2 , etc. which then contain terms involving derivatives of the atomic basis functions. In Ref. 31, explicit expressions are given for H_1 , H_2 , etc., for the case of a finite atomic basis.

If a finite atomic basis is used to describe molecular properties which contain geometry derivatives then the operators that are used to describe the molecular property contain a geometry dependence due to the use of a finite basis. For example, when a finite atomic basis is used to describe the derivative of the dipole moment with respect to a normal coordinate then the electric dipole operator appropriate for such a calculation is

$$\mu(R^0 + \eta) = \mu_0 + \eta \mu_1 + \frac{1}{2} \eta \mu_2 \eta + \dots, \quad (3.8)$$

where μ_0 is the electric dipole operator at geometry R^0 and μ_1 , μ_2 , etc., are the terms which describe the linear, quadratic, etc. dependence in the nuclear displacement. μ_1 , μ_2 , etc., contain derivatives of the atomic basis functions and vanish in the limit where a complete basis is used. In Ref. 32, explicit expressions are given for μ_1 , μ_2 , etc., for the case of a finite atomic basis.

B. Linear response

Let us first describe the case where a homogeneous periodic electric field of frequency ω_b is applied to the molecular system and where A refers to the electric dipole operator. ^{11,33} Using Eq. (2.57), the μ^a , μ^b th component of the linear response function becomes

$$\langle\langle \mu^a, \mu^b \rangle\rangle_{\omega_b + i\epsilon} = - \sum_{k>0} \left(\frac{\mu_{-k}^a \mu_k^b}{\omega_b - \omega_k + i\epsilon} - \frac{\mu_{-k}^b \mu_k^a}{\omega_b + \omega_k + i\epsilon} \right). \quad (3.9)$$

The denominators of the linear response function are of the form $\omega_b + i\epsilon \pm \omega_k$. The frequency variable may therefore be redefined to include the convergence factor $\omega_b + i\epsilon \rightarrow \omega_b$ and ω_b then becomes a complex variable. The frequency variables of the quadratic and cubic response functions may be redefined in the same way to include convergence factors.

Using Eq. (2.38), the real part of Eq. (3.9) is given by

$$\begin{aligned} & \langle\langle \mu^a, \mu^b \rangle\rangle_{\omega_b} \\ &= \sum_{k>0} \left(\frac{\langle 0 | \mu^a | k \rangle \langle k | \mu^b | 0 \rangle}{\omega_b - \omega_k} - \frac{\langle 0 | \mu^b | k \rangle \langle k | \mu^a | 0 \rangle}{\omega_b + \omega_k} \right) \end{aligned} \quad (3.10)$$

when ω_b is a real variable. Equation (3.9) is the μ^a , μ^b th component of the frequency-dependent dipole polarizability tensor at frequency ω_b . Equations (2.51) and (3.9) show that the frequency-dependent dipole polarizability describes the absorption of one photon of energy ω_b and the emission of one photon of energy ω_b .

The poles of Eq. (3.9) occur when the energy variable ω_b is equal to plus or minus the difference in energy between the reference state $|0\rangle$ and the excited state $|k\rangle$:

$$\omega_b = \pm \omega_k = \pm(E_k - E_0). \quad (3.11)$$

The corresponding residues are

$$\begin{aligned} & \lim_{\omega_b \rightarrow \omega_n} (\omega_b - \omega_n) \langle\langle \mu^a, \mu^b \rangle\rangle_{\omega_b} \\ &= -\mu_{-n}^a \mu_n^b = \langle 0 | \mu^a | n \rangle \langle n | \mu^b | 0 \rangle, \\ & \lim_{\omega_b \rightarrow -\omega_n} (\omega_b + \omega_n) \langle\langle \mu^a, \mu^b \rangle\rangle_{\omega_b} \\ &= \mu_{-n}^b \mu_n^a = -\langle 0 | \mu^b | n \rangle \langle n | \mu^a | 0 \rangle. \end{aligned} \quad (3.12)$$

The residues thus give information about the dipole transition matrix element between the reference state $|0\rangle$ and excited state $|n\rangle$.

If A is a component D^{pq} of the quadrupole moment, the linear response function $\langle\langle D^{pq}, \mu^b \rangle\rangle_{\omega_b}$ is a component of the quadrupole dipole polarizability.

If A is replaced with the orbital angular momentum operator $L = (L^x, L^y, L^z)$ the residues at $\omega_b = \omega_n$ of the linear response function become

$$\lim_{\omega_b \rightarrow \omega_n} (\omega_b - \omega_n) \langle\langle L^a, \mu^b \rangle\rangle_{\omega_b} = \langle 0 | L^a | n \rangle \langle n | \mu^b | 0 \rangle. \quad (3.13)$$

This determines the rotational strength of optically active molecules. ³⁴

If the external field is a homogeneous periodic magnetic field, and A is the magnetic moment, the linear response function describes the magnetic susceptibility. ³⁵

A large group of second-order molecular response properties that originate from static internal perturbations may be expressed in terms of linear response functions. ³³ For example the indirect nuclear spin-spin coupling constant contains several contributions that may be expressed in terms of linear response functions at zero frequency. One of these contributions describes the interaction between the Fermi contact Hamiltonian [$H_F(N)$] at nucleus N and the Fermi contact Hamiltonian at nucleus N' . The linear response function describing this interaction becomes

$$\begin{aligned} & \langle\langle H_F(N); H_F(N') \rangle\rangle_{\omega_b=0} \\ &= - \sum_{k>0} \left(\frac{\langle 0 | H_F(N) | k \rangle \langle k | H_F(N') | 0 \rangle}{\omega_k} \right. \\ & \quad \left. + \frac{\langle 0 | H_F(N') | k \rangle \langle k | H_F(N) | 0 \rangle}{\omega_k} \right), \end{aligned} \quad (3.14)$$

where the frequency parameter ω_b is set equal to zero since H_F is a static internal perturbation.

Another example is the derivative of the dipole moment with respect to a normal coordinate. This derivative determines the intensity of infrared spectra. The interaction operator for this case is H_1, H_2 , etc., of Eq. (3.7). Letting η denote a normal coordinate displacement we obtain, using Eq. (3.8):

$$\begin{aligned} \frac{d}{d\eta} \langle \tilde{0} | \mu | \tilde{0} \rangle |_{\eta=0} &= \frac{d}{d\eta} \langle \tilde{0} | \mu_0 + \eta \mu_1 + \frac{1}{2} \eta \mu_2 \eta + \dots | \tilde{0} \rangle |_{\eta=0} \\ &= \langle 0 | \mu_1 | 0 \rangle + \langle \langle \mu_0; H_1 \rangle \rangle_{\omega_b=0}. \end{aligned} \quad (3.15)$$

In a finite basis calculation the derivative of the dipole moment with respect to a normal coordinate is thus a sum of the average value of μ_1 and the linear response function $\langle \langle \mu_0; H_1 \rangle \rangle_{\omega_b=0}$.

Geometrical derivatives of potential energy surfaces may also be described using the above formalism. The operator $(d/d\eta)H(R^0 + \eta)$ then replaces A in Eq. (2.50) and H_1, H_2 , etc. of Eq. (3.7) become the interaction operators. The molecular gradient is $\langle \tilde{0} | [(d/d\eta)H(R^0 + \eta)] | \tilde{0} \rangle$ evaluated at undisplaced geometry and becomes $\langle 0 | H_1 | 0 \rangle$. The molecular Hessian is the first geometrical derivative evaluated at undisplaced geometry.

$$\begin{aligned} \frac{d}{d\eta} \langle \tilde{0} | [(d/d\eta)H(R^0 + \eta)] | \tilde{0} \rangle |_{\eta=0} &= \langle 0 | H_2 | 0 \rangle + \langle \langle H_1; H_1 \rangle \rangle_{\omega_b=0}. \end{aligned} \quad (3.16)$$

The first anharmonicity is the second geometrical derivative evaluated at undisplaced geometry etc. In the next subsection we express the first anharmonicity in terms of linear and quadratic response functions.

C. Quadratic response

Let us first describe the case where a homogeneous electric field of frequency ω_b and one of frequency ω_c are applied to the molecular system and A refers to the electric dipole operator. Using Eqs. (2.59), (2.38), and (2.41), the μ^a, μ^b, μ^c th component of the quadratic response function becomes

$$\begin{aligned} \langle \langle \mu^a; \mu^b, \mu^c \rangle \rangle_{\omega_b, \omega_c} &= \sum_{k, n > 0} \left[\frac{\langle 0 | \mu^a | k \rangle \langle k | \mu^b - \langle 0 | \mu^b | 0 \rangle | n \rangle \langle n | \mu^c | 0 \rangle}{(\omega_b + \omega_c - \omega_k)(\omega_c - \omega_n)} \right. \\ &+ \frac{\langle 0 | \mu^c | n \rangle \langle n | \mu^b - \langle 0 | \mu^b | 0 \rangle | k \rangle \langle k | \mu^a | 0 \rangle}{(\omega_b + \omega_c + \omega_k)(\omega_c + \omega_n)} \\ &- \frac{\langle 0 | \mu^b | k \rangle \langle k | \mu^a - \langle 0 | \mu^a | 0 \rangle | n \rangle \langle n | \mu^c | 0 \rangle}{(\omega_b + \omega_k)(\omega_c - \omega_n)} \\ &\left. + \frac{\langle 0 | \mu^a | k \rangle \langle k | \mu^c - \langle 0 | \mu^c | 0 \rangle | n \rangle \langle n | \mu^b | 0 \rangle}{(\omega_b + \omega_c - \omega_k)(\omega_b - \omega_n)} \right] \end{aligned}$$

$$\begin{aligned} &+ \frac{\langle 0 | \mu^b | n \rangle \langle n | \mu^c - \langle 0 | \mu^c | 0 \rangle | k \rangle \langle k | \mu^a | 0 \rangle}{(\omega_b + \omega_c + \omega_k)(\omega_b + \omega_a)} \\ &- \frac{\langle 0 | \mu^c | k \rangle \langle k | \mu^a - \langle 0 | \mu^a | 0 \rangle | n \rangle \langle n | \mu^b | 0 \rangle}{(\omega_c + \omega_k)(\omega_b - \omega_n)} \Big]. \end{aligned} \quad (3.17)$$

Equation (3.17) is identical to the μ^a, μ^b, μ^c th component of the electric frequency-dependent dipole hyperpolarizability tensor³⁵ at frequencies ω_b, ω_c . The frequency-dependent hyperpolarizability describes² the absorption of two photons, one of frequency ω_b and one of frequency ω_c , and the emission of one photon of frequency $\omega = \omega_b + \omega_c$. The case where $\omega_b = \omega_c$ is often referred to as the second harmonic generation.^{3,4,38}

The expression for the hyperpolarizability in Eq. (3.17) differs from the traditional hyperpolarizability expression³⁷ in that the reference state $|0\rangle$ is not included in the sum over intermediate states and in the use of fluctuation operators as, e.g., $\mu^a - \langle 0 | \mu^a | 0 \rangle$. However, it is straightforward to show that Eq. (3.17) is identical to the conventionally used expression for the hyperpolarizability since the fluctuation operators give exactly the contributions which in the conventional expression originate from $|0\rangle$ in the sum over intermediate states.

Molecular properties may also be expressed in terms of residues of the quadratic response function in Eq. (3.17). The residue at $\omega_c = \omega_m$ is

$$\begin{aligned} \lim_{\omega_c \rightarrow \omega_m} (\omega_c - \omega_m) \langle \langle \mu^a; \mu^b, \mu^c \rangle \rangle_{-\omega_b, \omega_c} &= \sum_{k > 0} \left[+ \frac{\langle 0 | \mu^a | k \rangle \langle k | \mu^b - \langle 0 | \mu^b | 0 \rangle | m \rangle \langle m | \mu^c | 0 \rangle}{-\omega_b + \omega_m - \omega_k} \right. \\ &- \frac{\langle 0 | \mu^b | k \rangle \langle k | \mu^a - \langle 0 | \mu^a | 0 \rangle | m \rangle \langle m | \mu^c | 0 \rangle}{-\omega_b + \omega_k} \Big] \\ &= - \sum_{k > 0} \left[\frac{\langle 0 | \mu^a | k \rangle \langle k | \mu^b - \langle 0 | \mu^b | 0 \rangle | m \rangle}{\omega_k - (\omega_m - \omega_b)} \right. \\ &\left. + \frac{\langle 0 | \mu^b | k \rangle \langle k | \mu^a - \langle 0 | \mu^a | 0 \rangle | m \rangle}{\omega_k - \omega_b} \right] \langle m | \mu^c | 0 \rangle. \end{aligned} \quad (3.18)$$

The conventional expression for the μ^a, μ^b th component of the two-photon absorption transition matrix element between state $|0\rangle$ and state $|m\rangle$ is^{3,14}

$$\sum_{k \in \{|0\rangle, |n\rangle\}} \left[\frac{\langle 0 | \mu^a | k \rangle \langle k | \mu^b | m \rangle}{\omega_k - \omega_1} + \frac{\langle 0 | \mu^b | k \rangle \langle k | \mu^a | m \rangle}{\omega_k - \omega_2} \right], \quad (3.19)$$

where

$$\omega_1 + \omega_2 = \omega_m. \quad (3.20)$$

A comparison of Eqs. (3.18) and (3.19) shows that the amplitude describing two-photon absorption may be identified from Eq. (3.18) with $\omega_2 = \omega_b$ and $\omega_1 = \omega_m - \omega_b$. We point out that the two-photon absorption cross section is an observable which is described by the cubic response function³ (see the discussion in Sec. III D). The quadratic response function may only be used to identify formal expressions for the two-photon absorption matrix element. However, this turns out to be important in approximate

response calculations, as the identification of the two-photon absorption matrix element based on the quadratic response function is much simpler than the corresponding identification based on the cubic response function.

Residues of the quadratic response function in Eq. (3.17) may also be evaluated at both the poles $\omega_c = \omega_m$ and $\omega_b = -\omega_q$. We then obtain²⁶

$$\lim_{\omega_b \rightarrow -\omega_q} [\lim_{\omega_c \rightarrow \omega_m} (\omega_c - \omega_m) \langle \langle \mu^a; \mu^b, \mu^c \rangle \rangle_{\omega_b, \omega_c} (\omega_b + \omega_q)] \\ = -\langle 0 | \mu^b | q \rangle \langle q | (\mu^a - \langle 0 | \mu^a | 0 \rangle) | m \rangle \langle m | \mu^c | 0 \rangle. \quad (3.21)$$

The quadratic response function may thus be used to identify matrix elements between excited state $|m\rangle$ and excited state $|q\rangle$, when the matrix elements between the reference state $|0\rangle$ and excited state $|m\rangle$ and $|q\rangle$ have been identified from the linear response function.

Many molecular properties may be described in terms of quadratic response functions with one or several interaction operators representing a static internal perturbation. It is impossible to describe in any detail all of these molecular properties. In the following we just give four examples of such molecular properties.

In the first example we consider the derivative of the frequency-dependent polarizability with respect to a normal coordinate. This derivative determines the intensity of Raman spectra.¹⁵ The interaction operator for this case has two components: one originates from a constant periodic electric field of frequency ω_b [see Eq. (3.2)] and one originates from the static perturbation that acts on the molecular electronic system at R^0 due to an infinitesimal displacement of the nuclei [H_1 , H_2 , etc., of Eq. (3.7)]. If η denotes a normal coordinate displacement then the derivative of the polarizability with respect to a normal coordinate becomes the terms of $d/d\eta \langle \tilde{0} | \mu | \tilde{0} \rangle_{\eta=0}$ containing two electric dipole operators. Using the expansion of the dipole moment operator in Eq. (3.8) gives that the derivative of the frequency dependent polarizability with respect to a normal coordinate can be expressed as

$$\langle \langle \mu_0; \mu_0, H_1 \rangle \rangle_{\omega_b, \omega_c=0} + \langle \langle \mu_0; \mu_1 \rangle \rangle_{\omega_b} \\ + \langle \langle \mu_1; \mu_0 \rangle \rangle_{\omega_b}, \quad (3.22)$$

and therefore evaluated as a sum of a quadratic and a linear response function. The formula for $\langle \langle \mu; \mu, H_1 \rangle \rangle_{\omega_b, \omega_c=0}$ in terms of sum over state expressions is obtained from Eq. (3.17) by replacing μ^c with H_1 and setting $\omega_c = 0$.

The second example we consider describes the experimental situation where a homogeneous static magnetic field and a homogeneous periodic electric field of frequency ω_c are simultaneously applied on the molecular system.⁴⁰ When A denotes the electric dipole operator the appropriate quadratic response function is $\langle \langle \mu; M, \mu \rangle \rangle_{\omega_b=0, \omega_c}$. The residue at $\omega_c = \omega_m$:

$$\lim_{\omega_c \rightarrow \omega_m} (\omega_c - \omega_m) \langle \langle \mu; M, \mu \rangle \rangle_{\omega_b=0, \omega_c} \quad (3.23)$$

gives the so-called B term in magnetic circular dichroism.^{40,41}

The third example we consider is the case where a dipole forbidden transition $\langle 0 | \mu | m \rangle$ becomes allowed due to a perturbation operator V . V may, e.g., be the spin-orbit coupling operator in which case phosphorescence lifetimes⁴² may be determined. The above case may be described in terms of conventional time-independent perturbation theory¹ where H_0 of Eq. (2.3) is used as the zeroth-order Hamiltonian and V is considered to be the perturbation operator. The exact states in the presence of the perturbation V are expanded in a perturbation series

$$|\tilde{m}\rangle = |m\rangle + |m^{(1)}\rangle + |m^{(2)}\rangle +, \quad (3.24)$$

where

$$|m^{(1)}\rangle = \sum_{k \neq m} |k\rangle \frac{\langle k | V | m \rangle}{\omega_k - \omega_m},$$

and the transition amplitude becomes

$$\langle \tilde{0} | \mu | \tilde{m} \rangle = \langle 0 | \mu | m \rangle + \langle 0 | \mu | m^{(1)} \rangle + \langle 0^{(1)} | \mu | m \rangle \\ + 0(2) = \sum_{k \neq m} \frac{\langle 0 | \mu | k \rangle \langle k | V | m \rangle}{\omega_k - \omega_m} \\ + \sum_{k \neq 0} \frac{\langle 0 | V | k \rangle \langle k | \mu | m \rangle}{\omega_k} + 0(2). \quad (3.25)$$

If we replace μ^b of Eq. (3.18) with V and set $\omega_b = 0$ a comparison of Eqs. (3.18) and (3.25) shows that the transition amplitudes of Eq. (3.25) can be identified from the residue of the quadratic response function

$$\lim_{\omega_c \rightarrow \omega_m} (\omega_c - \omega_m) \langle \langle \mu; V, \mu \rangle \rangle_{\omega_b=0, \omega_c}. \quad (3.26)$$

We note that the restrictions $k \neq m$ and $k \neq 0$ of Eq. (3.25) may also be imposed on the corresponding terms in the residue expression in Eq. (3.18) since we have assumed that $\langle 0 | \mu | m \rangle$ is zero.

As the last case we describe how the first anharmonicity of a potential energy surface may be evaluated. We consider the first anharmonicity in the direction η :

$$\frac{d^2}{d\eta^2} \langle \tilde{0} | \left[\frac{d}{d\eta} H(R^0 + \eta) \right] | \tilde{0} \rangle_{\eta=0} \\ = \langle 0 | H_3 | 0 \rangle + \langle \langle H_1; H_2 \rangle \rangle_{\omega_b=0} + \langle \langle H_2; H_1 \rangle \rangle_{\omega_b=0} \\ + \langle \langle H_1; H_1, H_1 \rangle \rangle_{\omega_b=0, \omega_c=0}. \quad (3.27)$$

The first anharmonicity may thus be evaluated as a sum of an average value of H_3 and linear and quadratic response functions involving H_1 and H_2 .

D. Cubic response

In this section we describe in some detail a few of the molecular properties that may be expressed in terms of cubic response functions or the residues of cubic response functions. Let us first consider the case where a periodic electric field of frequency ω_b , ω_c , and ω_d is applied to the molecular system, and where A refers to the electric dipole operator. The real part of the μ^a , μ^b , μ^c , μ^d th component of the cubic response function in Eq. (2.60):

$$\begin{aligned}
 & \langle\langle \mu^a, \mu^b, \mu^c, \mu^d \rangle\rangle_{\omega_b, \omega_c, \omega_d} \\
 &= P(b, c, d) \left\{ \left[\sum_k \frac{\mu_{-k}^a \operatorname{sgn}(k)}{\omega_b + \omega_c + \omega_d - \operatorname{sgn}(k)\omega_k} \left(\sum_n \left[-\sum_m \frac{\mu_{k-n}^b \mu_{n-m}^c \mu_m^d}{[\omega_c + \omega_d - \operatorname{sgn}(n)\omega_n][\omega_d - \operatorname{sgn}(m)\omega_m]} \right. \right. \right. \right. \\
 & \quad \left. \left. \left. + \frac{\theta(kn)\mu_n^b \mu_{-n}^c \mu_k^d}{[\omega_c + \operatorname{sgn}(n)\omega_n][\omega_d - \operatorname{sgn}(k)\omega_k]} \right] + \sum_{n>0} \frac{\mu_k^b \mu_n^c \mu_{-n}^d}{(\omega_c - \omega_n)(\omega_d + \omega_n)} \right) \right. \\
 & \quad \left. - \sum_{k,m,n>0} \left(\frac{\mu_{-km}^b \mu_{-m}^c \mu_{k-n}^a \mu_n^d}{(\omega_b + \omega_c + \omega_k)(\omega_c + \omega_m)(\omega_d - \omega_n)} - \frac{\mu_{-k}^b \mu_{k-n}^a \mu_{n-m}^c \mu_m^d}{(\omega_b + \omega_k)(\omega_c + \omega_d - \omega_n)(\omega_d - \omega_m)} \right) \right\} \quad (3.28)
 \end{aligned}$$

becomes the $\mu^a, \mu^b, \mu^c, \mu^d$ th component of the frequency-dependent second hyperpolarizability at frequencies $\omega_b, \omega_c, \omega_d$. Many spectroscopic experiments are controlled by the second hyperpolarizability as, e.g., stimulated Raman spectroscopy.⁴ The case where $\omega_b = \omega_c = \omega_d$ describes the third harmonic generation.^{2,3}

We now describe molecular properties that can be expressed in terms of residues of Eq. (3.28). Consider initially the residue

$$\begin{aligned}
 & \lim_{\omega_c + \omega_d \rightarrow \omega_f} (\omega_c + \omega_d - \omega_f) \langle\langle \mu^a, \mu^b, \mu^c, \mu^d \rangle\rangle_{-\omega_b, \omega_c, \omega_d} \\
 &= - \sum_{k,m>0} \left[\frac{\mu_{-k}^a \mu_{k-f}^b \mu_{f-m}^c \mu_m^d}{(-\omega_b - \omega_k + \omega_f)(-\omega_c + \omega_f + \omega_m)} + \frac{\mu_{-k}^a \mu_{k-f}^b \mu_{f-m}^d \mu_m^c}{(-\omega_b - \omega_k + \omega_f)(\omega_c - \omega_m)} \right] \\
 & \quad + \sum_{k,m>0} \left[\frac{\mu_{-k}^b \mu_{k-f}^a \mu_{f-m}^c \mu_m^d}{(-\omega_b + \omega_k)(-\omega_c + \omega_f - \omega_m)} + \frac{\mu_{-k}^b \mu_{k-f}^a \mu_{f-m}^d \mu_m^c}{(-\omega_b + \omega_k)(\omega_c - \omega_m)} \right] \\
 &= \sum_{k>0} \left(-\frac{\mu_{-k}^a \mu_{k-f}^b}{-\omega_b - \omega_k + \omega_f} - \frac{\mu_{-k}^b \mu_{k-f}^a}{\omega_b - \omega_k} \right) \sum_{m>0} \left(\frac{\mu_{f-m}^c \mu_m^d}{-\omega_c + \omega_f - \omega_m} + \frac{\mu_{f-m}^d \mu_m^c}{\omega_c - \omega_m} \right). \quad (3.29)
 \end{aligned}$$

This residue determines the two-photon absorption cross section. A comparison with Eq. (3.19) shows that this expression is identical to the square of the conventional expression for the two-photon absorption matrix element in Eq. (3.19).

Consider next the residue:

$$\begin{aligned}
 & \lim_{\omega_d \rightarrow \omega_f} (\omega_d - \omega_f) \langle\langle \mu^a, \mu^b, \mu^c, \mu^d \rangle\rangle_{\omega_b, \omega_c, \omega_d} \\
 &= \left\{ P(b, c) \left[\sum_{k,n>0} \left(-\frac{\mu_{-k}^a \mu_{k-n}^b \mu_{n-f}^c}{(\omega_b + \omega_c + \omega_f - \omega_k)(\omega_c + \omega_f - \omega_n)} - \frac{\mu_{-km}^b \mu_{-m}^c \mu_{k-f}^a}{(\omega_b + \omega_c + \omega_k)(\omega_c + \omega_m)} \right. \right. \right. \\
 & \quad \left. \left. + \frac{\mu_{-k}^b \mu_{k-n}^a \mu_{n-f}^c}{(\omega_b + \omega_k)(\omega_c + \omega_f - \omega_n)} \right) \right] + \sum_{k>0} \left(\frac{\mu_{-f}^a \mu_k^b \mu_{-k}^c}{(\omega_b + \omega_c)(\omega_c + \omega_k)} - \frac{\mu_k^a \mu_{-f}^b \mu_{-k}^c}{(\omega_b + \omega_c + \omega_f + \omega_k)(\omega_c + \omega_k)} \right. \\
 & \quad \left. - \frac{\mu_k^a \mu_{-k}^b \mu_{-f}^c}{(\omega_b + \omega_c + \omega_f + \omega_k)(\omega_c + \omega_f)} + \frac{\mu_{-k}^a \mu_k^b \mu_{-f}^c}{(\omega_b + \omega_c + \omega_f - \omega_k)(\omega_c + \omega_f)} \right) \left. \right\} \mu_f^d. \quad (3.30)
 \end{aligned}$$

The formula for the three-photon absorption amplitude³ is the expression inside { } of Eq. (3.30). We point out that the three-photon absorption cross section is an observable determined by the fifth hyperpolarizability. Hence, Eq. (3.30) can only be used to formally identify the amplitude.

Finally, consider the double residue which is obtained by taking the residue of Eq. (3.30) at $\omega_c = -\omega_3$:

$$\begin{aligned}
 & \lim_{\omega_c \rightarrow -\omega_e} (\omega_c + \omega_e) \left[\lim_{\omega_d \rightarrow \omega_f} (\omega_d - \omega_f) \langle\langle \mu^a, \mu^b, \mu^c, \mu^d \rangle\rangle_{\omega_b, \omega_c, \omega_d} \right] \\
 &= \mu_{-e}^c \left\{ \sum_{k>0} \left(-\frac{\mu_{-ke}^b \mu_{k-f}^a}{\omega_b - \omega_e + \omega_k} + \frac{\mu_{e-k}^a \mu_{k-f}^b}{\omega_b + \omega_f - \omega_k} \right) \right.
 \end{aligned}$$

$$\begin{aligned}
 & \left. + \frac{\mu_{-f}^a \mu_e^b}{\omega_b - \omega_e} - \frac{\mu_{-f}^b \mu_e^a}{\omega_b + \omega_f} \right. \\
 & \left. + \delta_{ef} \sum_{k>0} \left(\frac{\mu_{-k}^a \mu_k^b}{\omega_b - \omega_k} - \frac{\mu_{-k}^b \mu_k^a}{\omega_b + \omega_k} \right) \right\} \mu_f^d. \quad (3.31)
 \end{aligned}$$

In this case the expression inside { } of Eq. (3.31) gives the two-photon absorption amplitude between excited state $|f\rangle$ and excited state $|e\rangle$. When the two excited states are equal to $|f\rangle$ the expression inside { } gives the difference between the polarizability of the excited state $|f\rangle$ and the polarizability of the reference state $|0\rangle$.

A large number of experiments are controlled by the residues of the cubic response functions. We will not go

into any detail about particular experiments as this is outside the scope of the present paper. We refer to Refs. 3, 37, and 43 where a description of some of these experiments can be found.

Many experiments are controlled by cubic response functions where one or several of the perturbations refer to a static internal perturbation. One example is the derivative of the frequency-dependent hyperpolarizability with respect to the normal coordinates.⁴ This derivative is the major contributor to the intensity of hyper-Raman spectra, and contains among other terms the cubic response function

$$\langle\langle\mu; \mu, \mu, H_1\rangle\rangle_{\omega_b, \omega_c, \omega_d} = 0, \quad (3.32)$$

where H_1 is defined in Eq. (3.7). The above examples illustrate how cubic response functions may be used to describe molecular properties.

E. Discussion

We have in this section described how a large variety of molecular properties may be expressed in terms of the response functions for state $|0\rangle$. We have assumed that $|0\rangle$ was an eigenstate for the Hamiltonian of the noninteracting molecular system (H_0) and our results have been expressed in terms of the residual set of eigenstates of H_0 . The exact eigenstate $|0\rangle$ of H_0 is in general not attainable, and the results of the previous section therefore are of little practical value for evaluating molecular properties. However, the results illustrate how molecular properties may be expressed in terms of response functions, and motivate the determination of response functions for approximate states. Molecular properties may of course be evaluated from the approximate response functions in exactly the same way as they are evaluated from the exact response functions.

In Sec. V we determine the linear, quadratic, and cubic response function for a multiconfiguration self-

consistent field (MCSCF) wave function. We describe in Sec. VI computationally practical ways of evaluating the MCSCF response functions. Before we determine the MCSCF response functions we will derive the equations of motion for the exact response functions as these equations turn out to be important for understanding the conditions that we will impose on the time development of the MCSCF reference state.

IV. EQUIVALENT EXPRESSIONS FOR DIPOLE MOLECULAR PROPERTIES

In this section we describe how molecular properties that contain the electric dipole or position operator (in atomic units $\mu = r$) can be expressed in equivalent forms containing the momentum operator p .¹⁷ The equivalent expressions are straightforwardly derived from the equations of motion for the response functions.²⁶ Equivalent expressions may also be obtained from response functions for an approximate state. We will discuss the conditions that must be imposed on the time development of an approximate state to assure that equivalent property expressions can be obtained from the response functions for an approximate state.

A. Equations of motion for the response functions

In Sec. II C we used Ehrenfest's theorem to determine the time development of the reference state. In this section we determine the equations of motion for the linear, quadratic, and cubic response functions by using that Ehrenfest's theorem

$$i \frac{d}{dt} \langle \tilde{0} | A | \tilde{0} \rangle - \langle \tilde{0} | [A, H_0 + V^i] | \tilde{0} \rangle = 0 \quad (4.1)$$

is satisfied through each order in the perturbation. A is assumed not to contain an explicit time dependence. Using Eq. (2.1) and inserting the power series expansion in Eq. (2.51) for each term in Eq. (4.1) gives

$$\begin{aligned} & -\langle 0 | [A, H_0] | 0 \rangle + \int_{-\infty}^{\infty} d\omega_1 \exp[(-i\omega_1 + \epsilon)t] \{ (\omega_1 + i\epsilon) \langle\langle A; V^{\omega_1} \rangle\rangle_{\omega_1+i\epsilon} - \langle\langle [A, H_0]; V^{\omega_1} \rangle\rangle_{\omega_1+i\epsilon} - \langle 0 | [A, V^{\omega_1}] | 0 \rangle \} \\ & + \frac{1}{2} \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \exp[(-i\omega_1 - i\omega_2 + 2\epsilon)t] \{ (\omega_1 + \omega_2 + 2i\epsilon) \langle\langle A; V^{\omega_1}, V^{\omega_2} \rangle\rangle_{\omega_1+i\epsilon, \omega_2+i\epsilon} \\ & - \langle\langle [A, H_0]; V^{\omega_1}, V^{\omega_2} \rangle\rangle_{\omega_1+i\epsilon, \omega_2+i\epsilon} - D(1, 2) \langle\langle [A, V^{\omega_1}]; V^{\omega_2} \rangle\rangle_{\omega_2+i\epsilon} \} \\ & + \frac{1}{6} \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \int_{-\infty}^{\infty} d\omega_3 \exp[(-i\omega_1 - i\omega_2 - i\omega_3 + 3\epsilon)t] \{ (\omega_1 + \omega_2 + \omega_3 + 3i\epsilon) \\ & \times \langle\langle A; V^{\omega_1}, V^{\omega_2}, V^{\omega_3} \rangle\rangle_{\omega_1+i\epsilon, \omega_2+i\epsilon, \omega_3+i\epsilon} - \langle\langle [A, H_0]; V^{\omega_1}, V^{\omega_2}, V^{\omega_3} \rangle\rangle_{\omega_1+i\epsilon, \omega_2+i\epsilon, \omega_3+i\epsilon} \\ & - D(1, 2, 3) \langle\langle [A, V^{\omega_1}]; V^{\omega_2}, V^{\omega_3} \rangle\rangle_{\omega_2+i\epsilon, \omega_3+i\epsilon} \} + \dots = 0. \end{aligned} \quad (4.2)$$

The frequency decomposition of V^i in Eq. (2.1) is introduced to the contributions originating from the term $\langle \tilde{0} | [A, V^i] | \tilde{0} \rangle$ and the terms are symmetrized in the integration variables. $D(i, j, \dots)$ generates all distinct permutations when operating on the subscripts of $\omega_i, \omega_j, \dots$; for example, the last term in Eq. (4.2) only contains

three distinct contributions since the propagator is symmetric in the last two subscripts.

Equation (4.2) is valid for each order and at each frequency of the perturbation. The zeroth-order equation

$$-\langle 0 | [A, H_0] | 0 \rangle = 0 \quad (4.3)$$

is obvious since $|0\rangle$ is an eigenfunction of H_0 . The first order terms in Eq. (4.2) give the equation of motion for the linear response function

$$(\omega_1 + i\epsilon)\langle\langle A; V^{\omega_1} \rangle\rangle_{\omega_1+i\epsilon} = \langle\langle [A, H_0]; V^{\omega_1} \rangle\rangle_{\omega_1+i\epsilon} + \langle 0|[A, V^{\omega_1}]|0\rangle. \quad (4.4)$$

The second- and third-order terms give the equations of motion for the quadratic²⁶ and cubic response functions, respectively,

$$(\omega_1 + \omega_2 + 2i\epsilon)\langle\langle A; V^{\omega_1}, V^{\omega_2} \rangle\rangle_{\omega_1+i\epsilon, \omega_2+i\epsilon} = \langle\langle [A, H_0]; V^{\omega_1}, V^{\omega_2} \rangle\rangle_{\omega_1+i\epsilon, \omega_2+i\epsilon} + D(1, 2)\langle\langle [A, V^{\omega_1}]; V^{\omega_2} \rangle\rangle_{\omega_2+i\epsilon} \quad (4.5)$$

and

$$(\omega_1 + \omega_2 + \omega_3 + 3i\epsilon)\langle\langle A; V^{\omega_1}, V^{\omega_2}, V^{\omega_3} \rangle\rangle_{\omega_1+i\epsilon, \omega_2+i\epsilon, \omega_3+i\epsilon} = \langle\langle [A, H_0]; V^{\omega_1}, V^{\omega_2}, V^{\omega_3} \rangle\rangle_{\omega_1+i\epsilon, \omega_2+i\epsilon, \omega_3+i\epsilon} + D(1, 2, 3)\langle\langle [A, V^{\omega_1}]; V^{\omega_2}, V^{\omega_3} \rangle\rangle_{\omega_2+i\epsilon, \omega_3+i\epsilon}. \quad (4.6)$$

In the next section we will use the equations of motion for the linear, quadratic, and cubic response functions to derive examples of equivalent expressions to the molecular property expressions of Sec. III containing electric dipole operators.

B. Equivalent expressions for dipole molecular properties

We first discuss equivalent expressions for dipole properties described in terms of linear response functions. Dipole properties described by the quadratic response functions are then considered and a brief discussion then follows of dipole properties that can be expressed in terms of the cubic response functions.

Consider initially the equation of motion [Eq. (4.4)] for the frequency-dependent polarizability in Eq. (3.10) at the frequency ω_b . Using the operator identity

$$p = i[r, H_0], \quad (4.7)$$

we obtain

$$\omega_b \langle\langle r^a; r^b \rangle\rangle_{\omega_b} = \langle\langle [r^a, H_0]; r^b \rangle\rangle_{\omega_b} = -i \langle\langle p^a; r^b \rangle\rangle_{\omega_b}. \quad (4.8)$$

Equation (4.8) shows that the frequency-dependent dipole polarizability at frequency ω_b may be evaluated either in terms of the propagator $\langle\langle r^a; r^b \rangle\rangle_{\omega_b}$ or $-(i/\omega_b)\langle\langle p^a; r^b \rangle\rangle_{\omega_b}$.¹¹ The residue of Eq. (4.8) at the pole $\omega_b = \omega_f$ gives [see Eq. (3.11)]

$$\omega_f \langle 0|r^a|f\rangle\langle f|r^b|0\rangle = -i \langle 0|p^a|f\rangle\langle f|r^b|0\rangle. \quad (4.9)$$

Equation (4.9) shows the equivalent expressions for the transition moments in the dipole length and the dipole velocity approximation.⁴⁴

Consider now the equation of motion (Eq. 4.5) for the frequency-dependent hyperpolarizability of Eq. (3.17)

at frequency ω_b, ω_c . Using Eq. (4.7), the r^a, r^b, r^c th component of the dipole hyperpolarizability becomes

$$(\omega_b + \omega_c)\langle\langle r^a; r^b, r^c \rangle\rangle_{\omega_b, \omega_c} = -i \langle\langle p^a; r^b, r^c \rangle\rangle_{\omega_b, \omega_c}. \quad (4.10)$$

Equation (4.10) expresses two equivalent forms for the frequency-dependent dipole hyperpolarizability.

The residue of Eq. (4.10) at $\omega_c = \omega_f$ is [see Eq. (3.18)]

$$\begin{aligned} & -(\omega_b + \omega_f) \sum_{k>0} \left[\frac{\langle 0|r^a|k\rangle\langle k|r^b - \langle 0|r^b|0\rangle|f\rangle}{\omega_k - (\omega_f - \omega_b)} \right. \\ & \quad \left. + \frac{\langle 0|r^b|k\rangle\langle k|r^a - \langle 0|r^a|0\rangle|f\rangle}{\omega_k - \omega_b} \right] \langle f|r^c|0\rangle \\ & = +i \sum_{k>0} \left[\frac{\langle 0|p^a|k\rangle\langle k|r^b - \langle 0|r^b|0\rangle|f\rangle}{\omega_k - (\omega_f - \omega_b)} \right. \\ & \quad \left. + \frac{\langle 0|r^b|k\rangle\langle k|p^a - \langle 0|p^a|0\rangle|f\rangle}{\omega_k - \omega_b} \right] \langle f|r^c|0\rangle. \quad (4.11) \end{aligned}$$

Equation (4.11) expresses two equivalent forms for the two-photon absorption amplitudes between state $|0\rangle$ and state $|f\rangle$.

The residue of Eq. (4.11) at $\omega_b = -\omega_q$ becomes [see Eq. (3.21)]

$$\begin{aligned} & (\omega_q - \omega_f) \langle 0|r^b|q\rangle\langle q|r^a - \langle 0|r^a|0\rangle|f\rangle\langle f|r^c|0\rangle \\ & = i \langle 0|r^b|q\rangle\langle q|p^a|f\rangle\langle f|r^c|0\rangle. \quad (4.12) \end{aligned}$$

Equation (4.12) gives two equivalent expressions for the transition matrix elements between excited state $|f\rangle$ and excited state $|q\rangle$.

Consider finally the equation of motion [Eq. (4.6)] for the r^a, r^b, r^c, r^d th component of the second frequency-dependent dipole hyperpolarizability

$$\begin{aligned} & (\omega_b + \omega_c + \omega_d)\langle\langle r^a; r^b, r^c, r^d \rangle\rangle_{\omega_a, \omega_b, \omega_c} \\ & = -i \langle\langle p^a; r^b, r^c, r^d \rangle\rangle_{\omega_a, \omega_b, \omega_c}. \quad (4.13) \end{aligned}$$

Equation (4.13) gives two equivalent forms for the second hyperpolarizability. The residue at $\omega_d = \omega_f$ may be used to identify two equivalent expressions for the three-photon absorption amplitudes [see Eq. (3.29)]. The double residue of Eq. (4.13) at $\omega_d = \omega_f$ and $\omega_c = -\omega_e$ may be used to identify two equivalent forms for two-photon absorption amplitudes between excited state $|f\rangle$ and excited state $|e\rangle$ [see Eq. (3.31)]. We point out that many more equivalent forms may be derived for the above described molecular properties. The equivalent forms given above are only derived to illustrate a general principle about how equivalent expressions may be derived for molecular properties. We also point out that equivalent forms can be derived in a similar way for molecular properties in which one (or several) of the operators r^a, r^b, r^c, r^d in the above response functions refer to a static internal perturbation. Equivalences can also be obtained between different forms of the mixed quadrupole-dipole polarizability and between different forms of other multipole polarizabilities.

C. Discussion

The derivations in this section show that the equivalent forms for the molecular dipole properties can be derived straightforwardly from the equations of motion for the response functions. The derivations also show that equivalent dipole property expressions are obtained if the equations of motion [Eqs. (4.3)–(4.6)] are satisfied. Equivalent dipole property expressions can therefore be obtained from response functions for approximate states if the response functions for these approximate states satisfy Eqs. (4.3)–(4.6). This requires (1) the approximate state to be variationally determined [see Eq. (4.3)], (2) Ehrenfest's theorem [see Eq. (4.1)] to be used to determine the time development of the reference state, and (3) the operators that describe the time development of the approximate state span the space of all one-electron operators when operating on the time developed state $|\tilde{0}\rangle$ and $\langle\tilde{0}|$. Conditions (2) and (3) assure that Eq. (4.1) is satisfied for a general one-electron operator. When Eq. (4.1) is satisfied then Eqs. (4.3)–(4.6) are also satisfied provided condition (1) is satisfied and Eq. (4.7) can be used to obtain the equivalent dipole property expressions. We point out that equivalent molecular property results are only obtained in approximate calculations provided a complete basis is used since only then will the operator identity in Eq. (4.7) be satisfied. In the next section we derive the response functions for an MCSCF state. We also demonstrate explicitly that equivalent dipole property expressions can be derived from the MCSCF response functions.¹⁸

V. RESPONSE FUNCTIONS IN THE MCSCF APPROXIMATION

In this section we derive the response functions for an MCSCF-reference state. Our derivation of the MCSCF response functions is similar in structure to the derivation of the response functions for the exact state in Sec. II. The MCSCF response functions are determined by solving the equations for the exact response functions in a subspace spanned by the operators describing the time development of the MCSCF state. In Sec. V A we describe very shortly the MCSCF formalism. The equations defining the time evolution of the MCSCF state are derived in Sec. V B, in Sec. V C these equations are solved through third order. In Sec. V D the expectation value of an operator as a function of time is examined and a comparison with the similar equation for the exact response functions of Sec. II F is then used to identify the MCSCF response functions. The poles and residues of the MCSCF response functions are determined in Sec. V E. The Einstein convention for summation over repeated indices will be used in this section.

A. Parametrization of the time development of the MCSCF state

We assume that the unperturbed molecular system can be described by a multiconfigurational self-consistent field (MCSCF) state²⁰

$$|0\rangle = \sum_g C_{g0} |\phi_g\rangle, \quad (5.1)$$

where $\{|\phi_g\rangle\}$ is a set of configuration state functions (CSF's). Each CSF is a linear combination of Slater determinants $|\phi_f^D\rangle$:

$$|\phi_f^D\rangle = \prod_{r \in f} a_r^+ |\text{vac}\rangle, \quad (5.2)$$

where $\prod_{r \in f} a_r^+$ refers to an ordered product of spin orbitals. The configuration expansion coefficients of Eq. (5.1) and the spin-orbitals of Eq. (5.2) are fully optimized and satisfy the generalized Brillouin theorem [see Eq. (5.11)].

When a time-dependent perturbation is introduced, the spin-orbitals (a_r^+) and the configuration expansion coefficients $\{C_{g0}\}$ vary in time, and $|0\rangle$ turns into a time-dependent state $|\bar{0}\rangle$. The time evolution of $|\bar{0}\rangle$ may be conveniently described in terms of exponential unitary transformations.¹⁸

$$|\bar{0}\rangle = e^{i\kappa(t)} e^{iS(t)} |0\rangle. \quad (5.3)$$

The Hermitian operator $\kappa(t)$, generating the unitary transformation of the orbitals, contains a set of time-dependent amplitudes (κ_{rs}):

$$\begin{aligned} \kappa(t) &= \left(\sum_{r>s} \kappa_{rs} a_r^+ a_s + \kappa_{rs}^* a_s^+ a_r \right) \\ &= \sum_{\nu} (\kappa_{\nu} q_{\nu}^+ + \kappa_{\nu}^* q_{\nu}), \end{aligned} \quad (5.4)$$

and the Hermitian operator $S(t)$, which generates the unitary transformation of the configuration expansion coefficients, is parametrized in terms of a set of time-dependent amplitudes (S_0, S_n):

$$\begin{aligned} S(t) &= \sum_n (S_n |n\rangle \langle 0| + S_n^* |0\rangle \langle n|) + (S_0 + S_0^*) |0\rangle \langle 0| \\ &= \sum_n (S_n R_n^+ + S_n^* R_n) + (S_0 + S_0^*) R_0 \end{aligned} \quad (5.5)$$

where ($|0\rangle, |n\rangle$) is an orthonormal basis for $\{|\phi_g\rangle\}$, having $|0\rangle$ as its first element.

As described in Sec. II C the phase factor originating from the operator $S_0^* R_0^+$ may be factored out in the time-dependent wave function in Eq. (5.3). We then obtain

$$|\bar{0}\rangle = |\tilde{0}\rangle e^{i2S_0^*}, \quad (5.6)$$

where

$$|\tilde{0}\rangle = e^{i\kappa(t)} e^{iS(t)} |0\rangle = e^{i\kappa(t)} |\hat{0}\rangle \quad (5.7)$$

and where $e^{i2S_0^*}$ contains the phase factor. The operator $S(t)$ in Eq. (5.7) is defined as the sum over n in Eq. (5.5).

It is convenient to collect the operators in a row vector, and the amplitudes in a column vector

$$\begin{aligned} (T) &= (t^+, t) = (q^+, R^+, q, R), \\ (\beta) &= \begin{pmatrix} \eta \\ \eta^* \end{pmatrix} = \begin{pmatrix} \kappa \\ S \\ \kappa^* \\ S^* \end{pmatrix}. \end{aligned} \quad (5.8)$$

In order to get a unique correspondence between a set of parameters $\{\kappa, S\}$ and a given point $|\bar{0}\rangle$, care must be exercised to assure that only nonredundant operators are included in (T) . According to the discussion of Ref. 20 one must therefore exclude from (T) all operators ($a_r^+ a_s$, $a_s^+ a_r$) which are generators for a subgroup of $U(N)$ and which satisfies the equations

$$\begin{aligned} a_r^+ a_s |\bar{0}\rangle &= \sum_n C_n^{rs} |\bar{n}\rangle, \\ a_s^+ a_r |\bar{0}\rangle &= \sum_n C_n^{sr} |\bar{n}\rangle, \end{aligned} \quad (5.9)$$

where

$$|\bar{n}\rangle = e^{iS(n)} |n\rangle.$$

For example, operators q_{ij}^+ where both indices i and j refer to either completely occupied or to completely unoccupied orbitals must be excluded.

The condition that the MCSCF reference state is fully optimized (satisfies the generalized Brillouin theorem) can be written as

$$-i\langle 0 | [\delta\kappa + \delta S, H_0] | 0 \rangle = 0 \quad (5.10)$$

or

$$\begin{pmatrix} \langle 0 | [q^+, H_0] | 0 \rangle \\ \langle 0 | [R^+, H_0] | 0 \rangle \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}. \quad (5.11)$$

The set of elementary operators (T) in Eq. (5.8) is convenient to use as a basis for the MCSCF optimization and for describing the change of the MCSCF state when a time-independent perturbation is applied.⁴⁵ When a time-dependent perturbation is applied, the time development of the MCSCF state must be described in a more general basis for the operators

$$(O) = (Q^+, Q) = (t^+, t)X. \quad (5.12)$$

X is a nonsingular matrix which conserves the adjoint nature of the operator basis and therefore must be of the structure

$$X = \begin{pmatrix} 1X^2X^* \\ 2X^1X^* \end{pmatrix}. \quad (5.13)$$

The operator $\kappa(t) + S(t)$ can now be written as

$$\begin{aligned} \kappa(t) + S(t) &= (T)(\beta) = (T)XX^{-1}(\beta) \\ &= (O)X^{-1}(\beta) = (O)(\alpha), \end{aligned} \quad (5.14)$$

where (α) are the amplitudes for $\kappa(t) + S(t)$ in the operator basis (O) . It is easy to demonstrate that the adjoint nature of $(\beta) = \begin{pmatrix} \gamma \\ \gamma^* \end{pmatrix}$ is conserved in (α) so we have

$$(\alpha) = \begin{pmatrix} \gamma \\ \gamma^* \end{pmatrix}. \quad (5.15)$$

As for the exact case we introduce a notation which explicitly contains the adjoint nature of (O) and (α) [see Eqs. (2.13)–(2.16)],

$$\begin{pmatrix} O_j \\ O_{-j} \end{pmatrix} = \begin{pmatrix} Q_j^+ \\ Q_j \end{pmatrix} \quad (j > 0) \quad (5.16)$$

and write

$$\begin{aligned} \kappa(t) + S(t) &= \sum_{j=1}^d (\gamma_j Q_j^+ + \gamma_j^* Q_j) \\ &= \sum_{j=1}^d (\gamma_j O_j + \gamma_{-j} O_{-j}) \\ &= \sum_{j=-d}^d \alpha_j O_j, \end{aligned} \quad (5.17)$$

where we have defined $\gamma_{-j} = \gamma_j^*$.

The operator O_j can be split into a sum of two parts: O_{c_j} involving only the configuration operators $\{R^+, R\}$ and O_{o_j} involving only the orbital operators $\{q^+, q\}$:

$$O_j = O_{c_j} + O_{o_j}. \quad (5.18)$$

With this partitioning of O_j we can identify the operators $\kappa(t)$ and $S(t)$ in Eq. (5.17) as

$$\begin{aligned} \kappa(t) &= \sum_{j=-d}^d \alpha_j O_{o_j}, \\ S(t) &= \sum_{j=-d}^d \alpha_j O_{c_j}. \end{aligned} \quad (5.19)$$

In the following when otherwise not stated we will assume that the summation over repeated indices runs from $-d$ to d , omitting $|0\rangle$.

B. Equations for the time development of an MCSCF state

In the previous subsection we described the parameter space in which the MCSCF state was allowed to develop. We now proceed by defining the equations that determine the evolution of $|\bar{0}\rangle$ in Eq. (5.7). We first discuss how the equations that determine the time development of the MCSCF state may be chosen such that equivalent molecular property expressions are obtained for properties involving the electric dipole operator. We then derive matrix equations that may be used to determine the response of the MCSCF state in each order of the perturbation.

1. The time development of the MCSCF state

As in Sec. II C we determine the time evolution of $|\bar{0}\rangle$ by requiring Ehrenfest's theorem to be fulfilled for the set of operators describing the time evolution of $|\bar{0}\rangle$. This set is restricted to be of the form in Eq. (5.8). For reasons that will become clear shortly we will describe the time evolution in the time transformed basis

$$(\tilde{T}^+) = \begin{pmatrix} \tilde{q} \\ \tilde{R} \\ \tilde{q}^+ \\ \tilde{R}^+ \end{pmatrix}, \quad (5.20)$$

where

$$\begin{aligned} \tilde{q}_i^+ &= e^{i\kappa(t)} q_i^+ e^{-i\kappa(t)}, & \tilde{q}_i &= e^{i\kappa(t)} q_i e^{-i\kappa(t)}, \\ \tilde{R}_n^+ &= e^{i\kappa(t)} e^{iS(t)} R_n^+ e^{-iS(t)} e^{-i\kappa(t)}, \\ \tilde{R}_n &= e^{i\kappa(t)} e^{iS(t)} R_n e^{-iS(t)} e^{-i\kappa(t)}. \end{aligned} \quad (5.21)$$

The time transformed operators in Eq. (5.21) correspond to using orbitals at time t :

$$\tilde{a}_k^\dagger(t) = e^{i\kappa(t)} a_k^\dagger e^{-i\kappa(t)} \quad (5.22)$$

to define the orbital excitation operators. The time evolution of the MCSCF state is thus determined from Ehrenfest's theorem for the time-dependent operators (\tilde{T}^+) of Eq. (5.20):

$$\frac{d}{dt} \langle \tilde{0} | \tilde{T}^+ | \tilde{0} \rangle = \langle \tilde{0} | \dot{\tilde{T}}^+ | \tilde{0} \rangle - i \langle \tilde{0} | [\tilde{T}^+, H_0 + V^q] | \tilde{0} \rangle \quad (5.23)$$

or, in expanded form,

$$\frac{d}{dt} \begin{pmatrix} \langle \tilde{0} | \tilde{q} | \tilde{0} \rangle \\ \langle \tilde{0} | \tilde{R} | \tilde{0} \rangle \\ \langle \tilde{0} | \tilde{q}^+ | \tilde{0} \rangle \\ \langle \tilde{0} | \tilde{R}^+ | \tilde{0} \rangle \end{pmatrix} = \begin{pmatrix} \langle \tilde{0} | \dot{\tilde{q}} | \tilde{0} \rangle \\ \langle \tilde{0} | \dot{\tilde{R}} | \tilde{0} \rangle \\ \langle \tilde{0} | \dot{\tilde{q}}^+ | \tilde{0} \rangle \\ \langle \tilde{0} | \dot{\tilde{R}}^+ | \tilde{0} \rangle \end{pmatrix} - i \begin{pmatrix} \langle \tilde{0} | [\tilde{q}, H_0 + V^q] | \tilde{0} \rangle \\ \langle \tilde{0} | [\tilde{R}, H_0 + V^q] | \tilde{0} \rangle \\ \langle \tilde{0} | [\tilde{q}^+, H_0 + V^q] | \tilde{0} \rangle \\ \langle \tilde{0} | [\tilde{R}^+, H_0 + V^q] | \tilde{0} \rangle \end{pmatrix}. \quad (5.24)$$

It is convenient to transform Eq. (5.23) to a more general basis similar to the one of Eq. (5.12) for the operator set (T). Multiplying Eq. (5.23) from the left with X^+ of Eq. (5.13) gives

$$\frac{d}{dt} \langle \tilde{0} | \tilde{O}^+ | \tilde{0} \rangle = \langle \tilde{0} | \dot{\tilde{O}}^+ | \tilde{0} \rangle - i \langle \tilde{0} | [\tilde{O}^+, H_0 + V^q] | \tilde{0} \rangle, \quad (5.25)$$

where

$$\begin{aligned} \tilde{O}_{c_j} &= e^{i\kappa(t)} e^{iS(t)} O_{c_j} e^{-iS(t)} e^{-i\kappa(t)}, \\ \tilde{O}_{o_j} &= e^{i\kappa(t)} O_{o_j} e^{-i\kappa(t)}, \\ \tilde{O}_j &= \tilde{O}_{c_j} + \tilde{O}_{o_j}, \end{aligned} \quad (5.26)$$

and where O_{c_j} and O_{o_j} are defined in Eq. (5.18). As in Sec. II C the phase factor can be eliminated from Eq. (5.25) and Eq. (5.25) then becomes

$$\frac{d}{dt} \langle \tilde{0} | \tilde{O}^+ | \tilde{0} \rangle = \langle \tilde{0} | \dot{\tilde{O}}^+ | \tilde{0} \rangle - i \langle \tilde{0} | [\tilde{O}^+, H_0 + V^q] | \tilde{0} \rangle. \quad (5.27)$$

The phase of Eq. (5.6) may be determined from Eq. (2.20).

Equation (5.27) supplemented with the boundary condition $|\tilde{0}\rangle \rightarrow |0\rangle$ for $t \rightarrow -\infty$, i.e.,

$$\begin{aligned} \lim_{t \rightarrow -\infty} \kappa(t) &= 0, \\ \lim_{t \rightarrow -\infty} S(t) &= 0, \end{aligned} \quad (5.28)$$

determine the time development of the MCSCF state. Before we derive explicit formulas for the time development of the MCSCF state we will in Secs. V B 2 and V B 3 examine some of the consequences of using Eq. (5.27) to determine the time development of the MCSCF state.

2. Equivalence relations for dipole molecular properties

The time development of the MCSCF state is described by Eq. (5.27) and determines the MCSCF response functions (see Sec. V D). We now show that molecular dipole property expressions derived from the MCSCF response functions satisfies the same equivalence relations as the exact response functions (see Sec. IV B). To prove this we show that conditions (1)–(3) of Sec. IV C are satisfied. These conditions are (1) the MCSCF state has to be variationally determined, (2) Ehrenfest's theorem must be used to determine the time development of the MCSCF state, and (3) the operators which describe the time development of the MCSCF state must span the space of all one electron operators when operating on $|\tilde{0}\rangle$ and $\langle \tilde{0}|$. Conditions (1) and (2) are obviously fulfilled. In the following we prove that condition (3) is satisfied. We begin by expanding an arbitrary one-body operator A in terms of the time transformed orbitals of Eq. (5.22):

$$A = A_{rs} \tilde{a}_r^\dagger \tilde{a}_s. \quad (5.29)$$

The summation in Eq. (5.29) extends both over the nonredundant orbital operators of Eq. (5.8) and the orbital operators which are redundant in the sense of Eq. (5.9). To examine the effect of A operating on $|\tilde{0}\rangle$ we split A up in two parts,

$$A = \sum_{j>0} (A_j \tilde{q}_j^\dagger + A'_j \tilde{q}_j) + \sum_{r,s:\text{red}} A_{rs} \tilde{a}_r^\dagger \tilde{a}_s, \quad (5.30)$$

where the first summation contains the nonredundant set of one-body operators and the second summation is over the redundant operators. We now show that the redundant set of operators in Eq. (5.30) when operating on $|\tilde{0}\rangle$ and $\langle \tilde{0}|$ can be expanded in terms of the state transfer operators in Eq. (5.20). Using Eqs. (5.6), (5.9), (5.21), and (5.22) we obtain

$$\begin{aligned} A|\tilde{0}\rangle &= \sum_{j>0} (A_j \tilde{q}_j^\dagger + A'_j \tilde{q}_j) |\tilde{0}\rangle + \sum_{r,s:\text{red}} A_{rs} \tilde{a}_r^\dagger \tilde{a}_s |\tilde{0}\rangle \\ &= \sum_{j>0} (A_j \tilde{q}_j^\dagger + A'_j \tilde{q}_j) |\tilde{0}\rangle \\ &\quad + \sum_{r,s:\text{red}} A_{rs} e^{i\kappa(t)} a_r^\dagger a_s e^{iS(t)} |0\rangle e^{2iS} \\ &= \sum_{j>0} (A_j \tilde{q}_j^\dagger + A'_j \tilde{q}_j) |\tilde{0}\rangle \\ &\quad + \sum_{r,s:\text{red}} \sum_n A_{rs} C_n^{rs} e^{i\kappa(t)} e^{iS(t)} |n\rangle e^{2iS} \\ &= \sum_{j>0} (A_j \tilde{q}_j^\dagger + A'_j \tilde{q}_j) |\tilde{0}\rangle \\ &\quad + \sum_{r,s:\text{red}} \sum_n A_{rs} C_n^{rs} \tilde{R}_n^+ |\tilde{0}\rangle. \end{aligned} \quad (5.31)$$

Similarly,

$$\begin{aligned} \langle \tilde{0} | A &= \langle \tilde{0} | \left[\sum_{j>0} (A_j \tilde{q}_j^\dagger + A'_j \tilde{q}_j) \right. \\ &\quad \left. + \sum_{r,s:\text{red}} \left(A_{rs} \sum_n C_n^{sr} \tilde{R}_n \right) \right]. \end{aligned} \quad (5.32)$$

The operator A when operating on either $|\bar{0}\rangle$ or $\langle\bar{0}|$ can thus be replaced with an operator A^P , that consists of a sum of operators from (\tilde{T}^+) ,

$$\begin{aligned} A^P &= \sum_{j>0} (A_j \tilde{q}_j^+ + A_j' \tilde{q}_j) \\ &+ \sum_{r,s:\text{red}} \left[A_{rs} \sum_n (C_n^{rs} \tilde{R}_n^+ + C_n^{sr} \tilde{R}_n) \right] \\ &= a_j \tilde{T}_j^+ \end{aligned} \quad (5.33)$$

and condition (3) is fulfilled. This concludes the proof that equivalent molecular dipole property expressions are obtained from the MCSCF response functions.

If the set (T^+) of Eq. (5.8) was used instead of the set (\tilde{T}^+) in Eq. (5.20), a relation similar to Eq. (5.33) cannot in general be obtained. The reason is that when A is expanded in the basis (T^+) , terms occur in $A|\bar{0}\rangle$ of the type $a_r^+ a_s |\bar{0}\rangle$, where $a_r^+ a_s$ corresponds to a redundant operator in the sense of Eq. (5.9). These terms cannot be expanded in state transfer operators as was done in Eq. (5.31) due to the occurrence of $e^{i\kappa(t)}$ in $|\bar{0}\rangle$. Equivalent molecular dipole property expressions therefore cannot be obtained from MCSCF response functions if the basis (T^+) is used to describe the time development of the MCSCF state.

3. Connection to McLachlan–Ball's variational principle

Another motivation for defining the time development of the MCSCF state as in Eq. (5.24) is that these equations are identical to the ones obtained by using the time-dependent variational principle of McLachlan and Ball.⁴⁶ To see this we write the McLachlan–Ball time-dependent variational principle for $|\bar{0}\rangle$ of Eq. (5.7) as

$$\text{Re} \left\langle \delta\tilde{0} \left| i \frac{d}{dt} - H_0 - V \right| \bar{0} \right\rangle = 0. \quad (5.34)$$

Considering η and η^* of Eq. (5.8) as variational parameters an arbitrary first-order variation of $|\bar{0}\rangle$ is

$$|\delta\tilde{0}\rangle = i(\delta\eta_j^* \tilde{q}_j^+ + \delta\eta_j \tilde{q}_j + \delta\eta_n \tilde{R}_n^+ + \delta\eta_n^* \tilde{R}_n) |\bar{0}\rangle. \quad (5.35)$$

Inserting the variation of Eq. (5.35) in Eq. (5.34) we obtain Eq. (5.24). In the limit where the external perturbation is absent (i.e., $t \rightarrow -\infty$), Eq. (5.24) becomes the generalized Brillouin theorem [see Eq. (5.11)].

4. Matrix equation for the time development of the MCSCF

In this subsection we derive a matrix representation of Eq. (5.27). Consider initially the terms in Eq. (5.27) which contain a time differentiation. Straightforward differentiation of these terms gives a plethora of terms which are very tedious to contract. The expressions in Appendix A for the time derivative of a BCH expansion can be used to simplify the derivation. Using Eqs. (5.7) and (5.26) the terms of Eq. (5.27) containing time derivatives becomes

$$\begin{aligned} &\frac{d}{dt} \langle \bar{0} | \tilde{O}_j^+ | \bar{0} \rangle - \langle \bar{0} | \dot{\tilde{O}}_j^+ | \bar{0} \rangle \\ &= \frac{d}{dt} \langle 0 | e^{-iS} O_{oj}^+ e^{iS} | 0 \rangle + \frac{d}{dt} \langle 0 | O_{cj}^+ | 0 \rangle \\ &- \langle 0 | e^{-iS} e^{-i\kappa} \frac{\partial}{\partial t} (e^{i\kappa} O_{oj}^+ e^{-i\kappa}) e^{i\kappa} e^{iS} | 0 \rangle \\ &- \langle 0 | e^{-iS} e^{-i\kappa} \frac{\partial}{\partial t} (e^{i\kappa} e^{iS} O_{cj}^+ e^{-iS} e^{-i\kappa}) e^{i\kappa} e^{iS} | 0 \rangle. \end{aligned} \quad (5.36)$$

In Eq. (5.36) and in the rest of this section we will not write out explicitly the time dependence in $\kappa(t)$ and $S(t)$. Using Eq. (A8) the first term on the right-hand side of Eq. (5.36) becomes

$$\begin{aligned} &\frac{d}{dt} \langle 0 | e^{-iS} O_{oj}^+ e^{iS} | 0 \rangle \\ &= \sum_{n=0}^{\infty} \sum_{k=0}^n \frac{(-1)^k (i)^{n+1}}{k!(n-k+1)!} \\ &\times \langle 0 | (\hat{S}^k [O_{oj}^+, (\hat{S}^{n-k} \dot{S}')] | 0 \rangle. \end{aligned} \quad (5.37)$$

The second term on the right-hand side of Eq. (5.36) is zero. Using the first equality sign in Eq. (A9) the third term becomes

$$\begin{aligned} &\langle 0 | e^{-iS} e^{-i\kappa} \frac{d}{dt} (e^{i\kappa} O_{oj}^+ e^{-i\kappa}) e^{i\kappa} e^{iS} | 0 \rangle \\ &= \sum_{n=0}^{\infty} \frac{(-1)^n (i)^{n+1}}{(n+1)!} \langle 0 | e^{-iS} e^{-i\kappa} (e^{i\kappa} [(\hat{\kappa}^n \dot{\kappa}), O_{oj}^+] e^{-i\kappa}) e^{i\kappa} e^{iS} | 0 \rangle \\ &= \sum_{n=0}^{\infty} \frac{(-1)^n (i)^{n+1}}{(n+1)!} \langle 0 | e^{-iS} [(\hat{\kappa}^n \dot{\kappa}), O_{oj}^+] e^{iS} | 0 \rangle \\ &= \sum_{n=0}^{\infty} \sum_{k=0}^n \left(\frac{(-1)^n (i)^{n+1}}{k!(n-k+1)!} \langle 0 | (\hat{S}^k [(\hat{\kappa}^{n-k} \dot{\kappa}), O_{oj}^+] | 0 \rangle \right). \end{aligned} \quad (5.38)$$

Similarly, the fourth term on the right-hand side of Eq. (5.36) becomes

$$\begin{aligned} &\langle 0 | e^{-iS} e^{-i\kappa} \frac{d}{dt} (e^{i\kappa} e^{iS} O_{cj}^+ e^{-iS} e^{-i\kappa}) e^{i\kappa} e^{iS} | 0 \rangle \\ &= \langle 0 | e^{-iS} \frac{d}{dt} (e^{iS} O_{cj}^+ e^{-iS}) e^{iS} | 0 \rangle \\ &+ \sum_{n=0}^{\infty} \frac{(-1)^n (i)^{n+1}}{(n+1)!} \langle 0 | [(e^{-iS} (\hat{\kappa}^n \dot{\kappa}) e^{iS}), O_{cj}^+] | 0 \rangle \\ &= \sum_{n=0}^{\infty} \frac{(-1)^n (i)^{n+1}}{(n+1)!} \langle 0 | [(\hat{S}^n \dot{S}'), O_{cj}^+] | 0 \rangle \\ &+ \sum_{n=0}^{\infty} \sum_{k=0}^n \frac{(-1)^n (i)^{n+1}}{k!(n-k+1)!} \langle 0 | [(\hat{S}^k (\hat{\kappa}^{n-k} \dot{\kappa}), O_{cj}^+) | 0 \rangle. \end{aligned} \quad (5.39)$$

We thus have

$$\begin{aligned} &\frac{d}{dt} \langle \bar{0} | \tilde{O}_j^+ | \bar{0} \rangle - \langle \bar{0} | \dot{\tilde{O}}_j^+ | \bar{0} \rangle \\ &= \sum_{n=0}^{\infty} (i)^{n+1} \left(\sum_{k=0}^n \frac{1}{k!(n-k+1)!} \{ (-1)^k \langle 0 | (\hat{S}^k [O_{oj}^+, \right. \end{aligned}$$

$$\begin{aligned} & \times (\hat{S}^{n-k} \hat{S})|0\rangle + (-1)^n \langle 0 | (\hat{S}^k [O_{oj}^+, (\hat{\kappa}^{n-k} \hat{\kappa})] |0\rangle \\ & + (-1)^n \langle 0 | [O_{cj}^+, (\hat{S}^k (\hat{\kappa}^{n-k} \hat{\kappa}))] |0\rangle \rangle \\ & + \sum_{n=0}^{\infty} \frac{(i)^{n+1} (-1)^n}{(n+1)!} \langle 0 | [O_{cj}^+, (\hat{S}^n \hat{S})] |0\rangle. \end{aligned} \quad (5.40)$$

We now introduce the expansion of S and κ given in Eq. (5.19) into Eq. (5.40). Using the notation for the k th power of the superoperator

$$\hat{S}^k = (\alpha_j \hat{O}_{cj})^k = \left(\prod_{\mu=1}^k \hat{O}_{c_{j\mu}} \right) \left(\prod_{\mu=1}^k \alpha_{j\mu} \right) \quad (5.41)$$

we write Eq. (5.40) as

$$\begin{aligned} & \frac{d}{dt} \langle \tilde{0} | \tilde{O}_j^+ | \tilde{0} \rangle - \langle \tilde{0} | \dot{\tilde{O}}_j^+ | \tilde{0} \rangle \\ & = \sum_{n=0}^{\infty} (i)^{n+1} \left\{ \sum_{k=0}^n \frac{1}{k!(n-k+1)!} \left\{ (-1)^k \langle 0 | \left(\left(\prod_{\mu=1}^k \hat{O}_{cl_\mu} \right) \left[O_{oj}^+, \left(\left(\prod_{\mu=k+1}^n \hat{O}_{cl_\mu} \right) O_{cm} \right) \right] \right) |0\rangle \right. \right. \\ & \quad + (-1)^n \langle 0 | \left(\left(\prod_{\mu=1}^k O_{cl_\mu} \right) \left[O_{oj}^+, \left(\left(\prod_{\mu=k+1}^n \hat{O}_{ol_\mu} \right) O_{om} \right) \right] \right) |0\rangle + (-1)^n \langle 0 | \left[O_{cj}^+, \left(\left(\prod_{\mu=1}^k \hat{O}_{cl_\mu} \right) \left(\left(\prod_{l=k+1}^n \hat{O}_{ol_\mu} \right) O_{om} \right) \right) \right] |0\rangle \right\} \\ & \quad + \frac{(-1)^n}{(n+1)!} \langle 0 | \left[O_{cj}^+, \left(\left(\prod_{\mu=1}^n O_{cl_\mu} \right) O_{cm} \right) \right] |0\rangle \right\} \alpha_m \prod_{\mu=1}^n \alpha_{l_\mu} = \sum_{n=1}^{\infty} i^n S_{j l_1 \dots l_n}^{[n+1]} \alpha_{l_1} \prod_{\mu=2}^n \alpha_{l_\mu}, \end{aligned} \quad (5.42)$$

where $S_{j l_1 \dots l_n}^{[n+1]}$ is defined as

$$\begin{aligned} S_{j l_1 \dots l_n}^{[n+1]} & = \sum_{k=0}^n \frac{1}{k!(n-k)!} \left\{ (-1)^k \langle 0 | \left(\left(\prod_{\mu=2}^{k+1} \hat{O}_{cl_\mu} \right) \left[O_{oj}^+, \left(\left(\prod_{\mu=k+2}^n \hat{O}_{cl_\mu} \right) O_{cl_1} \right) \right] \right) |0\rangle \right. \\ & \quad + (-1)^{n-1} \langle 0 | \left(\left(\prod_{\mu=2}^{k+1} \hat{O}_{cl_\mu} \right) \left[O_{oj}^+, \left(\left(\prod_{\mu=k+2}^n \hat{O}_{ol_\mu} \right) O_{ol_1} \right) \right] \right) |0\rangle + (-1)^{n-1} \langle 0 | \left[O_{cj}^+, \left(\left(\prod_{\mu=2}^{k+1} \hat{O}_{cl_\mu} \right) \right. \right. \\ & \quad \left. \left. \times \left(\left(\prod_{\mu=k+2}^n \hat{O}_{ol_\mu} \right) O_{ol_1} \right) \right] \right) |0\rangle \right\} + \frac{(-1)^{n-1}}{n!} \langle 0 | \left[O_{cj}^+, \left(\left(\prod_{\mu=2}^n \hat{O}_{cl_\mu} \right) O_{cl_1} \right) \right] |0\rangle \right\}. \end{aligned} \quad (5.43)$$

The term on the right-hand side of Eq. (5.27) involving H_0 becomes

$$\begin{aligned} & -i \langle 0 | e^{-iS} e^{-i\kappa} [\tilde{O}_{cj}^+ + \tilde{O}_{oj}^+, H_0] e^{iS} e^{i\kappa} |0\rangle \\ & = -i \langle 0 | [O_{cj}^+, e^{-iS} e^{-i\kappa} H_0 e^{i\kappa} e^{iS}] |0\rangle \\ & - i \langle 0 | e^{-iS} [O_{oj}^+, e^{-i\kappa} H_0 e^{i\kappa}] e^{iS} |0\rangle. \end{aligned} \quad (5.44)$$

The expansion of exponentials of Eq. (A1) then gives

$$\begin{aligned} & \langle \tilde{0} | [\tilde{O}_j^+, H_0] | \tilde{0} \rangle \\ & = -i \sum_{n=0}^{\infty} \sum_{k=0}^n \frac{(-1)^n (i)^n}{k!(n-k)!} \left\{ \langle 0 | [O_{cj}^+, (\hat{S}^k (\hat{\kappa}^{n-k} H_0))] |0\rangle \right. \\ & \quad \left. + \langle 0 | (\hat{S}^k [O_{oj}^+, (\hat{\kappa}^{n-k} H_0)]) |0\rangle \right\}. \end{aligned} \quad (5.45)$$

Using Eq. (5.19) we thus obtain

$$\begin{aligned} \langle \tilde{0} | [\tilde{O}_j^+, H_0] | \tilde{0} \rangle & = -i \sum_{n=0}^{\infty} \left\{ \sum_{k=0}^n \frac{(-1)^n (i)^n}{k!(n-k)!} \left\{ \langle 0 | \left[O_{cj}^+, \left(\left(\prod_{\mu=1}^k \hat{O}_{cl_\mu} \right) \left(\left(\prod_{\mu=k+1}^n \hat{O}_{ol_\mu} \right) H_0 \right) \right) \right] |0\rangle \right. \right. \\ & \quad \left. \left. + \langle 0 | \left(\left(\prod_{\mu=1}^k \hat{O}_{cl_\mu} \right) \left[O_{oj}^+, \left(\left(\prod_{\mu=k+1}^n \hat{O}_{ol_\mu} \right) H_0 \right) \right] \right) |0\rangle \right\} \right\} \prod_{\mu=1}^n \alpha_{l_\mu} = - \sum_{n=0}^{\infty} (i)^{n+1} E_{j l_1 \dots l_n}^{[n+1]} \prod_{\mu=1}^n \alpha_{l_\mu}, \end{aligned} \quad (5.46)$$

where the last equality sign defines $E^{[n+1]}$. In a similar way it can be straightforwardly shown that

$$\begin{aligned} -i \langle \tilde{0} | [\tilde{O}_j^+, V^t] | \tilde{0} \rangle & = -i \sum_{n=0}^{\infty} \left\{ \sum_{k=0}^n \frac{(-1)^n (i)^n}{k!(n-k)!} \left\{ \langle 0 | \left[O_{cj}^+, \left(\left(\prod_{\mu=1}^k \hat{O}_{cl_\mu} \right) \left(\left(\prod_{\mu=k+1}^n \hat{O}_{ol_\mu} \right) V^t \right) \right) \right] |0\rangle \right. \right. \\ & \quad \left. \left. + \langle 0 | \left(\left(\prod_{\mu=1}^k \hat{O}_{cl_\mu} \right) \left[O_{oj}^+, \left(\left(\prod_{\mu=k+1}^n \hat{O}_{ol_\mu} \right) V^t \right) \right] \right) |0\rangle \right\} \right\} \prod_{\mu=1}^n \alpha_{l_\mu} = - \sum_{n=0}^{\infty} (i)^{n+1} V_{j l_1 \dots l_n}^{[n+1]} \prod_{\mu=1}^n \alpha_{l_\mu}. \end{aligned} \quad (5.47)$$

Introducing the explicit form of V^t from Eq. (2.1) we obtain

$$-i \langle \tilde{0} | [\tilde{O}_j^+, V^t] | \tilde{0} \rangle = -i \sum_{n=0}^{\infty} \left\{ \sum_{k=0}^n \frac{(-1)^n (i)^n}{k!(n-k)!} \int d\omega_1 e^{-i(\omega_1 + \epsilon)t} \left\{ \langle 0 | \left[O_{cj}^+, \left(\left(\prod_{\mu=1}^k \hat{O}_{cl_\mu} \right) \left(\left(\prod_{\mu=k+1}^n \hat{O}_{ol_\mu} \right) V^{\omega_1} \right) \right) \right] |0\rangle \right. \right.$$

$$\begin{aligned}
 & + \langle 0 | \left(\left(\prod_{\mu=1}^k \hat{O}_{c_{l_\mu}} \right) \left[O_{d_j}^+, \left(\left(\prod_{\mu=k+1}^n \hat{O}_{o_{l_\mu}} \right) V^{\omega_1} \right) \right] | 0 \rangle \right) \prod_{\mu=1}^n \alpha_{l_\mu} \\
 & = - \sum_{n=0}^{\infty} (i)^{n+1} \int d\omega_1 (e^{-i(\omega_1+i\epsilon)t} V_{j l_1 \dots l_n}^{\omega_1 [n+1]}) \prod_{\mu=1}^n \alpha_{l_\mu}. \tag{5.48}
 \end{aligned}$$

All terms have now been expanded and we can write Eq. (5.27) in the compact notation

$$\begin{aligned}
 \sum_{n=1}^{\infty} (i)^n S_{j l_1 \dots l_n}^{[n+1]} \dot{\alpha}_{l_1} \prod_{\mu=2}^n \alpha_{l_\mu} & = - \sum_{n=0}^{\infty} (i)^{n+1} E_{j l_1 \dots l_n}^{[n+1]} \prod_{\mu=1}^n \alpha_{l_\mu} \\
 - \sum_{n=0}^{\infty} (i)^{n+1} V_{j l_1 \dots l_n}^{[n+1]} \prod_{\mu=1}^n \alpha_{l_\mu} & \tag{5.49}
 \end{aligned}$$

or

$$\begin{aligned}
 \sum_{n=1}^{\infty} (i)^n S_{j l_1 \dots l_n}^{[n+1]} \dot{\alpha}_{l_1} \prod_{\mu=2}^n \alpha_{l_\mu} & \\
 = - \sum_{n=0}^{\infty} (i)^{n+1} E_{j l_1 \dots l_n}^{[n+1]} \prod_{\mu=1}^n \alpha_{l_\mu} - \sum_{n=0}^{\infty} (i)^{n+1} & \\
 \times \int d\omega_1 (e^{-i(\omega_1+i\epsilon)t} V_{j l_1 \dots l_n}^{\omega_1 [n+1]}) \prod_{\mu=1}^n \alpha_{l_\mu}, & \tag{5.50}
 \end{aligned}$$

where the matrices $S^{[n+1]}$, $E^{[n+1]}$, and $V^{\omega_1 [n+1]}$ are defined in Eqs. (5.43), (5.46), and (5.48). Aspects of the actual calculation of terms involving S , E , and V matrices are described in Sec. VI.

C. Solution of the time-dependent MCSCF equations through third order

The equations which determine the response of the MCSCF reference state through third order in the perturbation V^t will now be derived. We first derive from Eq. (5.50) a set of coupled linear differential equations for the linear, quadratic, and cubic response of the MCSCF reference state. We then show how the transformation matrix X of Eq. (5.13) can be chosen such that the differential equations separate. The solutions to the separated differential equations are then obtained.

1. Coupled differential equations for the time development of the MCSCF state

The parameters α of Eq. (5.15) which determine the response of the MCSCF state to the perturbation V^t in Eq. (2.1) can be expanded in orders of the perturbation

$$\alpha_l = \alpha_l^{(1)} + \alpha_l^{(2)} + \alpha_l^{(3)} + \dots, \tag{5.51}$$

where the zeroth-order coefficient vanishes since $E^{[1]}$ in Eq. (5.50) is zero (the generalized Brillouin theorem). The parameters $\alpha^{(i)}$, $i = 1, 2, \dots$ may be determined by requiring Eq. (5.50) to be valid in each order of the perturbation. We will derive explicit expressions for $\alpha^{(1)}$, $\alpha^{(2)}$, and $\alpha^{(3)}$. In Eq. (5.52) we have written all terms of Eq. (5.50) which contribute to the evaluation of $\alpha^{(1)}$, $\alpha^{(2)}$, and $\alpha^{(3)}$.

$$\begin{aligned}
 & iS_{jl}^{[2]} \dot{\alpha}_l - S_{jlm}^{[3]} \dot{\alpha}_l \alpha_m - iS_{jlmn}^{[4]} \dot{\alpha}_l \alpha_m \alpha_n \\
 & = E_{jl}^{[2]} \alpha_l + iE_{jlm}^{[3]} \alpha_l \alpha_m - E_{jlmn}^{[4]} \alpha_l \alpha_m \alpha_n \\
 & \quad - iV_j^{[1]} + V_{jl}^{[2]} \alpha_l + iV_{jlm}^{[3]} \alpha_l \alpha_m. \tag{5.52}
 \end{aligned}$$

In Eq. (5.52) we have again used that $E_j^{[1]}$ equals zero [see Eq. (5.11)]. Inserting the expansion of α from Eq. (5.51) and collecting terms of first order gives the first-order equations

$$iS_{jl}^{[2]} \dot{\alpha}_l^{(1)} - E_{jl}^{[2]} \alpha_l^{(1)} = -iV_j^{[1]}. \tag{5.53}$$

The second-order equations are

$$\begin{aligned}
 & iS_{jl}^{[2]} \dot{\alpha}_l^{(2)} - E_{jl}^{[2]} \alpha_l^{(2)} \\
 & = S_{jlm}^{[3]} \dot{\alpha}_l^{(1)} \alpha_m^{(1)} + iE_{jlm}^{[3]} \alpha_l^{(1)} \alpha_m^{(1)} + V_{jl}^{[2]} \alpha_l^{(1)} \tag{5.54}
 \end{aligned}$$

and the third-order equations become

$$\begin{aligned}
 & iS_{jl}^{[2]} \dot{\alpha}_l^{(3)} - E_{jl}^{[2]} \alpha_l^{(3)} \\
 & = S_{jlm}^{[3]} (\dot{\alpha}_l^{(1)} \alpha_m^{(2)} + \dot{\alpha}_l^{(2)} \alpha_m^{(1)}) + iS_{jlmn}^{[4]} \dot{\alpha}_l^{(1)} \alpha_m^{(1)} \alpha_n^{(1)} \\
 & \quad + iE_{jlm}^{[3]} (\alpha_l^{(2)} \alpha_m^{(1)} + \alpha_l^{(1)} \alpha_m^{(2)}) - E_{jlmn}^{[4]} \alpha_l^{(1)} \alpha_m^{(1)} \alpha_n^{(1)} \\
 & \quad + V_{jl}^{[2]} \alpha_l^{(2)} + iV_{jlm}^{[3]} \alpha_l^{(1)} \alpha_m^{(1)}. \tag{5.55}
 \end{aligned}$$

Equations (5.53) to (5.55) all have the structure

$$iS_{jl}^{[2]} \dot{\alpha}_l^{(k)} - E_{jl}^{[2]} \alpha_l^{(k)} = f_j^{(k)}(t), \tag{5.56}$$

where $\{\alpha_l^{(k)}\}$ are the unknown variables and $f_j^{(k)}(t)$ is determined from the lower-order equations. If we can find a representation where $S^{[2]}$ and $E^{[2]}$ are simultaneously diagonal:

$$\begin{aligned}
 S_{jl}^{[2]} & = \delta_{jl} \sigma_j, \\
 E_{jl}^{[2]} & = \delta_{jl} \omega_j, \tag{5.57}
 \end{aligned}$$

then Eq. (5.56) becomes a set of separated linear differential equations:

$$i\sigma_j \dot{\alpha}_j^{(k)} - \omega_j \alpha_j^{(k)} = f_j^{(k)}(t). \tag{5.58}$$

2. Simultaneous diagonalization of $S^{[2]}$ and $E^{[2]}$

We describe now how to simultaneously diagonalize $S^{[2]}$ and $E^{[2]}$. Using the notation that ${}^eE^{[2]}$ and ${}^eS^{[2]}$ are the $E^{[2]}$ and $S^{[2]}$ matrices in the elementary basis [see Eq. (5.8)] we see by inserting (O) of Eq. (5.12) into the definition of $E^{[2]}$ and $S^{[2]}$ [see Eqs. (5.46) and (5.43)] that Eq. (5.57) corresponds to

$$\begin{aligned}
 (X^+ {}^eE^{[2]} X)_{jl} & = \omega_j \delta_{jl}, \\
 (X^+ {}^eS^{[2]} X)_{jl} & = \sigma_j \delta_{jl}. \tag{5.59}
 \end{aligned}$$

This is equivalent to solving the generalized eigenvalue problem⁴⁷

$${}^e\mathbf{E}^{[2]}\mathbf{X}_j = \lambda_j {}^e\mathbf{S}^{[2]}\mathbf{X}_j; \quad (\lambda_j = \omega_j \sigma_j^{-1}). \quad (5.60)$$

In Sec. V E we show that ω_j becomes the excitation energy between state $|0\rangle$ and state $|j\rangle$. A complete set of eigenvectors \mathbf{X}_j can be found *de jure* if ${}^e\mathbf{E}^{[2]}$ is positive definite.⁴⁸ The matrix $\mathbf{E}^{[2]}$ is the second derivative of the unperturbed energy at $|0\rangle$. For an MCSCF stationary point $|0\rangle$ representing a ground state $\mathbf{E}^{[2]}$ is positive definite and a matrix \mathbf{X} which simultaneously diagonalizes ${}^e\mathbf{S}^{[2]}$ and ${}^e\mathbf{E}^{[2]}$ exists. For a stationary point representing an excited state, $\mathbf{E}^{[2]}$ is not positive definite and it is not clear whether $\mathbf{S}^{[2]}$ and $\mathbf{E}^{[2]}$ can be simultaneously diagonalized. In the cases we have considered where the Hessian had the required characteristics of an excited state⁴⁸ a simultaneous diagonalization of ${}^e\mathbf{S}^{[2]}$ and ${}^e\mathbf{E}^{[2]}$ could be performed. It can furthermore be shown⁴⁷ that if ${}^e\mathbf{E}^{[2]}$ is positive definite the eigenvalues ω_j are real and positive, and the eigenvalues σ_j are real. In the following we assume that ω_j and σ_j are real also for excited states. With these assumptions we now prove that the matrix \mathbf{X} has the structure of Eq. (5.13). The adjoint nature of the operator set (T) implies that ${}^e\mathbf{E}^{[2]}$ has the structure

$${}^e\mathbf{E}^{[2]} = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix}, \quad (5.61)$$

where

$$\mathbf{A} = \begin{pmatrix} \langle 0|[q_i, [H_0, q_j^\dagger]]|0\rangle & \langle 0|[[q_i, H_0], R_j^\dagger]|0\rangle \\ \langle 0|[R_i, [H_0, q_j^\dagger]]|0\rangle & \langle 0|[R_i, [H_0, R_j^\dagger]]|0\rangle \end{pmatrix} \quad (5.62)$$

and

$$\mathbf{B} = \begin{pmatrix} \langle 0|[q_i, [H_0, q_j]]|0\rangle & \langle 0|[[q_i, H_0], R_j]|0\rangle \\ \langle 0|[R_i, [H_0, q_j]]|0\rangle & \langle 0|[R_i, [H_0, R_j]]|0\rangle \end{pmatrix}. \quad (5.63)$$

The matrix ${}^e\mathbf{S}^{[2]}$ is

$${}^e\mathbf{S}^{[2]} = \begin{pmatrix} \Sigma & \Delta \\ -\Delta^* & -\Sigma^* \end{pmatrix}, \quad (5.64)$$

where

$$\Sigma = \begin{pmatrix} \langle 0|[q_i, q_j^\dagger]|0\rangle & \langle 0|[q_i, R_j^\dagger]|0\rangle \\ \langle 0|[R_i, q_j^\dagger]|0\rangle & \langle 0|[R_i, R_j^\dagger]|0\rangle \end{pmatrix} \quad (5.65)$$

and

$$\Delta = \begin{pmatrix} \langle 0|[q_i, q_j]|0\rangle & \langle 0|[q_i, R_j]|0\rangle \\ \langle 0|[R_i, q_j]|0\rangle & \langle 0|[R_i, R_j]|0\rangle \end{pmatrix}. \quad (5.66)$$

Let $\mathbf{X}_j = \begin{pmatrix} {}^1\mathbf{X}_j \\ {}^2\mathbf{X}_j \end{pmatrix}$ be an eigenvector to the generalized eigenvalue problem in Eq. (5.60),

$${}^e\mathbf{E}^{[2]} \begin{pmatrix} {}^1\mathbf{X}_j \\ {}^2\mathbf{X}_j \end{pmatrix} = \lambda_j {}^e\mathbf{S}^{[2]} \begin{pmatrix} {}^1\mathbf{X}_j \\ {}^2\mathbf{X}_j \end{pmatrix}; \quad (\lambda_j = \omega_j \sigma_j^{-1}). \quad (5.67)$$

Using Eqs. (5.61) and (5.64) we obtain

$${}^e\mathbf{E}^{[2]} \begin{pmatrix} {}^2\mathbf{X}_j^* \\ {}^1\mathbf{X}_j^* \end{pmatrix} = -\lambda_j {}^e\mathbf{S}^{[2]} \begin{pmatrix} {}^2\mathbf{X}_j^* \\ {}^1\mathbf{X}_j^* \end{pmatrix}. \quad (5.68)$$

The vector $\begin{pmatrix} {}^2\mathbf{X}_j^* \\ {}^1\mathbf{X}_j^* \end{pmatrix}$ is thus an eigenvector for the generalized eigenvalue problem in Eq. (5.60). The elements of the diagonal forms of Eq. (5.59) corresponding to $\begin{pmatrix} {}^2\mathbf{X}_j^* \\ {}^1\mathbf{X}_j^* \end{pmatrix}$ becomes

$$\begin{aligned} ({}^2\mathbf{X}_j^* {}^1\mathbf{X}_j^*) {}^e\mathbf{S}^{[2]} \begin{pmatrix} {}^2\mathbf{X}_j^* \\ {}^1\mathbf{X}_j^* \end{pmatrix} &= -\sigma_j, \\ ({}^2\mathbf{X}_j^* {}^1\mathbf{X}_j^*) {}^e\mathbf{E}^{[2]} \begin{pmatrix} {}^2\mathbf{X}_j^* \\ {}^1\mathbf{X}_j^* \end{pmatrix} &= \omega_j. \end{aligned} \quad (5.69)$$

If σ_j differs from zero it is seen from Eq. (5.69) that the two eigenvectors $\begin{pmatrix} {}^1\mathbf{X}_j \\ {}^2\mathbf{X}_j \end{pmatrix}$ and $\begin{pmatrix} {}^2\mathbf{X}_j^* \\ {}^1\mathbf{X}_j^* \end{pmatrix}$ corresponds to different eigensolutions of Eq. (5.60).

The case σ_j equals zero is allowed and may give reasonable excitation-energies. However, this case occurs only for particular choices of the configuration state functions and the singularities generally disappear when the set of operators (T) is enlarged. We therefore assume that the σ_j all are nonzero. The \mathbf{X} vectors therefore can be scaled such that the normalization of $\sigma_j = \pm 1$ is fulfilled. If we collect all eigenvectors with $\sigma_j = 1$ in the columns of \mathbf{X} with positive index, and the eigenvectors with $\sigma_j = -1$ in the columns with negative index, i.e.,

$$\begin{aligned} (\mathbf{X}^+ {}^e\mathbf{E}^{[2]}\mathbf{X})_{ij} &= E_{ij}^{[2]} = \omega_j \delta_{ij}, \quad \omega_{-j} = \omega_j, \\ (\mathbf{X}^+ {}^e\mathbf{S}^{[2]}\mathbf{X})_{ij} &= S_{ij}^{[2]} = \text{sgn}(j) \delta_{ij}, \end{aligned} \quad (5.70)$$

then \mathbf{X} has the structure

$$\begin{pmatrix} {}^1\mathbf{X} & {}^2\mathbf{X}^* \\ {}^2\mathbf{X} & {}^1\mathbf{X}^* \end{pmatrix}, \quad (5.71)$$

which is the one we required in Eq. (5.13). Under typical circumstances a matrix of the form in Eq. (5.13) which simultaneously diagonalized ${}^e\mathbf{S}^{[2]}$ and ${}^e\mathbf{E}^{[2]}$ can be found. In Sec. VI we discuss the computational aspects of determining the eigenvalues and eigenvectors of Eq. (5.60).

3. First-, second-, and third-order time dependence of the MCSCF state

Using the basis of Eq. (5.59) the set of coupled inhomogeneous differential equations in Eqs. (5.53), (5.54), and (5.55) will separate. The Einstein summation convention will be used in this subsection with the exception that j is a fixed index. The first-order equation becomes

$$i \text{sgn}(j) \dot{\alpha}_j^{(1)} - \omega_j \alpha_j^{(1)} = -i V_j^{[1]}. \quad (5.72)$$

The second- and third-order equations read

$$\begin{aligned} i \text{sgn}(j) \dot{\alpha}_j^{(2)} - \omega_j \alpha_j^{(2)} &= S_{jlm}^{[3]} \dot{\alpha}_l^{(1)} \alpha_m^{(1)} + i E_{jlm}^{[3]} \alpha_l^{(1)} \alpha_m^{(1)} + V_{jl}^{[2]} \alpha_l^{(1)}, \end{aligned} \quad (5.73)$$

$$\begin{aligned} i \text{sgn}(j) \dot{\alpha}_j^{(3)} - \omega_j \alpha_j^{(3)} &= S_{jlm}^{[3]} (\dot{\alpha}_l^{(1)} \alpha_m^{(2)} + \dot{\alpha}_l^{(2)} \alpha_m^{(1)}) + i S_{jlmn}^{[4]} \dot{\alpha}_l^{(1)} \alpha_m^{(1)} \alpha_n^{(1)} \\ &+ i E_{jlm}^{[3]} (\alpha_l^{(2)} \alpha_m^{(1)} + \alpha_l^{(1)} \alpha_m^{(2)}) - E_{jlmn}^{[4]} \alpha_l^{(1)} \alpha_m^{(1)} \alpha_n^{(1)} \\ &+ V_{jl}^{[2]} \alpha_l^{(2)} + i V_{jlm}^{[3]} \alpha_l^{(1)} \alpha_m^{(1)}. \end{aligned} \quad (5.74)$$

Equations (5.72), (5.73), and (5.74) with the initial conditions of Eq. (5.28) have the same general form as the Eqs. (2.37), (2.40), and (2.42) of Sec. II E for the exact responses. The equations can therefore be solved in an analogous manner using the solution of Eq. (2.43) given in Eq. (2.45). The first-order amplitudes become

$$\alpha_j^{(1)} = -i \int_{-\infty}^{\infty} d\omega_1 \exp[-i(\omega_1 + i\epsilon)t] \times \frac{\text{sgn}(j)V_j^{\omega_1[1]}}{\omega_1 - \text{sgn}(j)\omega_j + i\epsilon}. \quad (5.75)$$

Introducing the notation

$$f_j^{(1)}(\omega_1) = \frac{V_j^{\omega_1[1]}}{\omega_1 - \text{sgn}(j)\omega_j + i\epsilon}, \quad (5.76)$$

we can write Eq. (5.75) as

$$\alpha_j^{(1)} = -i \text{sgn}(j) \int_{-\infty}^{\infty} d\omega_1 \times \exp[-i(\omega_1 + i\epsilon)t] f_j^{(1)}(\omega_1). \quad (5.77)$$

Substituting the first-order amplitudes of Eq. (5.77) in the second-order equation [Eq. (5.73)] gives

$$i \text{sgn}(j)\dot{\alpha}_j^{(2)} - \omega_j\alpha_j^{(2)} = i \text{sgn}(l) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\omega_1 d\omega_2 \exp[-i(\omega_1 + \omega_2 + 2i\epsilon)t] \times \{ \text{sgn}(m)[S_{jlm}^{[3]}(\omega_1 + i\epsilon) - E_{jlm}^{[3]}] \times f_l^{(1)}(\omega_1)f_m^{(1)}(\omega_2) - V_{jl}^{\omega_1[2]}f_l^{(1)}(\omega_2) \}. \quad (5.78)$$

Using Eq. (2.45) the second-order amplitudes become

$$\alpha_j^{(2)} = -i \text{sgn}(j) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\omega_1 d\omega_2 f_j^{(2)}(\omega_1, \omega_2) \times \exp[-i(\omega_1 + \omega_2 + 2i\epsilon)t], \quad (5.79)$$

where $f_j^{(2)}(\omega_1, \omega_2)$ is chosen as the symmetrical form

$$f_j^{(2)}(\omega_1, \omega_2) = \left\{ \frac{1}{2} \text{sgn}(lm)(E_{jml}^{[3]} + E_{jlm}^{[3]} - S_{jlm}^{[3]}(\omega_1 + i\epsilon) - S_{jml}^{[3]}(\omega_2 + i\epsilon))f_l^{(1)}(\omega_1)f_m^{(1)}(\omega_2) + \frac{1}{2} \text{sgn}(l)(V_{jl}^{\omega_1[2]}f_l^{(1)}(\omega_2) + V_{jl}^{\omega_2[2]}f_l^{(1)}(\omega_1)) \right\} \times \frac{1}{\omega_1 + \omega_2 - \text{sgn}(j)\omega_j + 2i\epsilon}. \quad (5.80)$$

Inserting the first- and second-order amplitudes [Eqs. (5.77) and (5.79)] into the third-order equation in Eq. (5.74) gives

$$i \text{sgn}(j)\dot{\alpha}_j^{(3)} - \omega_j\alpha_j^{(3)} = i \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\omega_1 d\omega_2 d\omega_3 \exp[-i(\omega_1 + \omega_2 + \omega_3 + 3i\epsilon)t] \{ \text{sgn}(lm)S_{jlm}^{[3]}[f_l^{(1)}(\omega_1)(\omega_1 + i\epsilon)f_m^{(2)}(\omega_2, \omega_3) + f_l^{(2)}(\omega_2, \omega_3)(\omega_2 + \omega_3 + 2i\epsilon)f_m^{(1)}(\omega_1)]$$

$$- \text{sgn}(lm)(E_{jml}^{[3]} + E_{jlm}^{[3]})f_l^{(2)}(\omega_1, \omega_2)f_m^{(1)}(\omega_3) + \text{sgn}(lmn)(S_{jlmn}^{[4]}(\omega_1 + i\epsilon) - E_{jlmn}^{[4]})f_l^{(1)}(\omega_1)f_m^{(1)}(\omega_2) \times f_n^{(1)}(\omega_3) - \text{sgn}(lm)V_{jlm}^{\omega_1[3]}f_l^{(1)}(\omega_2)f_m^{(1)}(\omega_3) - \text{sgn}(l)V_{jl}^{\omega_1[2]}f_l^{(2)}(\omega_2, \omega_3) \} = -i \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\omega_1 d\omega_2 d\omega_3 \exp[-i(\omega_1 + \omega_2 + \omega_3 + 3i\epsilon)t] h_j(\omega_1, \omega_2, \omega_3), \quad (5.81)$$

where the last equality sign implicitly defines $h_j(\omega_1, \omega_2, \omega_3)$. The third-order amplitudes become

$$\alpha_j^{(3)} = -i \text{sgn}(j) \iiint d\omega_1 d\omega_2 d\omega_3 f_j^{(3)}(\omega_1, \omega_2, \omega_3) \times \exp[-i(\omega_1 + \omega_2 + \omega_3 + 3i\epsilon)t], \quad (5.82)$$

where we have introduced the shorthand notation

$$f_j^{(3)}(\omega_1, \omega_2, \omega_3) = \frac{P(1, 2, 3)h_j(\omega_1, \omega_2, \omega_3)}{6[\omega_1 + \omega_2 + \omega_3 - \text{sgn}(j)\omega_j + 3i\epsilon]}. \quad (5.83)$$

$P(1, 2, 3)$ is the symmetric permutation operator operating on the subscripts of ω_1, ω_2 , and ω_3 . Expressions for the first three amplitudes have now been derived.

D. Derivation of MCSCF response functions

In this section we use the amplitudes $\alpha^{(1)}$, $\alpha^{(2)}$, and $\alpha^{(3)}$ to describe the time development of the expectation value of an operator A . By comparing this expectation value with the exact time development in Eq. (2.51) we determine MCSCF approximations to the linear, quadratic, and cubic response functions. We stress that the derivation in this section parallels the one of Sec. II F where the response functions are determined for an exact state.

The expectation value of A ,

$$\langle \bar{0} | A | \bar{0} \rangle = \langle 0 | \exp(-iS) \exp(i\kappa) A \exp(i\kappa) \exp(iS) | 0 \rangle \quad (5.84)$$

can be expanded with the BCH formulas of Eq. (A1) of the Appendix:

$$\langle \bar{0} | A | \bar{0} \rangle = \sum_{n=0}^{\infty} (-i)^n \sum_{k=0}^n \frac{1}{k!(n-k)!} \times \langle 0 | (\hat{S}^k (\hat{\kappa}^{n-k} A)) | 0 \rangle. \quad (5.85)$$

When $\hat{\kappa}$ and \hat{S} are expanded in the O basis [see Eq. (5.19)], Eq. (5.85) becomes

$$\langle \bar{0} | A | \bar{0} \rangle = \sum_{n=0}^{\infty} (i)^n \left\{ (-1)^n \sum_{k=0}^n \frac{1}{k!(n-k)!} \times \langle 0 | \left(\left(\prod_{\mu=1}^k \hat{O}_{c_{\mu}} \right) \left(\prod_{\mu=k+1}^n \hat{O}_{o_{\mu}} A \right) \right) | 0 \rangle \right\} \times \prod_{\mu=1}^n \alpha_{\mu} = \sum_{n=0}^{\infty} (i)^n A_{1, \dots, n}^{[n]} \prod_{\mu=1}^n \alpha_{\mu}. \quad (5.86)$$

In Eq. (5.86) we have implicitly defined $A^{[n]}$. Note that the definition of $A^{[n]}$ differs slightly from the definition

of, e.g., $E^{[3]}$ in Eq. (5.46). By inserting the expansion of α through third order in Eq. (5.86) and writing only the terms explicitly through third order we obtain

$$\begin{aligned} \langle \bar{0}|A|\bar{0}\rangle - \langle 0|A|0\rangle &= iA_j^{[1]}\alpha_j^{(1)} + iA_j^{[1]}\alpha_j^{(2)} - A_{jk}^{[2]}\alpha_j^{(1)}\alpha_k^{(1)} + iA_j^{[1]}\alpha_j^{(3)} \end{aligned}$$

$$\begin{aligned} &- A_{jk}^{[2]}(\alpha_j^{(1)}\alpha_k^{(2)} + \alpha_j^{(2)}\alpha_k^{(1)}) \\ &- iA_{jkl}^{[3]}\alpha_j^{(1)}\alpha_k^{(1)}\alpha_l^{(1)} + \dots \end{aligned} \quad (5.87)$$

Introducing the expressions for $\alpha_j^{(1)}$, $\alpha_j^{(2)}$, and $\alpha_j^{(3)}$ of Eqs. (5.77), (5.79), and (5.82) gives

$$\begin{aligned} \langle \bar{0}|A|\bar{0}\rangle - \langle 0|A|0\rangle &= \int_{-\infty}^{\infty} d\omega_1 \exp[-i(\omega_1 + i\epsilon)t] \text{sgn}(j) A_j^{[1]} f_j^{(1)}(\omega_1) + \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\omega_1 d\omega_2 \exp[-i(\omega_1 + \omega_2 + 2i\epsilon)t] \\ &\times \{ \text{sgn}(jk) f_j^{(1)}(\omega_1) f_k^{(1)}(\omega_2) A_{jk}^{[2]} + \text{sgn}(j) A_j^{[1]} f_j^{(2)}(\omega_1, \omega_2) \} + \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\omega_1 d\omega_2 d\omega_3 \\ &\times \exp[-i(\omega_1 + \omega_2 + \omega_3 + 3i\epsilon)t] \{ \text{sgn}(jkl) A_{jkl}^{[3]} f_j^{(1)}(\omega_1) f_k^{(1)}(\omega_2) f_l^{(1)}(\omega_3) \\ &+ \text{sgn}(jk) A_{jk}^{[2]} [f_j^{(1)}(\omega_1) f_k^{(2)}(\omega_2, \omega_3) + f_j^{(2)}(\omega_1, \omega_2) f_k^{(1)}(\omega_3)] \\ &+ \text{sgn}(j) A_j^{[1]} f_j^{(3)}(\omega_1, \omega_2, \omega_3) \} + \dots \end{aligned} \quad (5.88)$$

Comparison with Eq. (2.51) gives the linear response function.

$$\langle \langle A; V^{\omega_1} \rangle \rangle_{\omega_1+i\epsilon} = \text{sgn}(j) f_j^{(1)}(\omega_1) A_j^{[1]}. \quad (5.89)$$

The quadratic and cubic response functions were defined to be symmetric in the integration variables. Symmetrizing Eq. (5.88) and comparing with Eq. (2.51) shows that the MCSCF quadratic response function is

$$\begin{aligned} \langle \langle A; V^{\omega_1}, V^{\omega_2} \rangle \rangle_{\omega_1+i\epsilon, \omega_2+i\epsilon} &= P(1, 2) \{ \text{sgn}(jk) A_{jk}^{[2]} f_j^{(1)}(\omega_1) f_k^{(1)}(\omega_2) \\ &+ \text{sgn}(j) A_j^{[1]} f_j^{(2)}(\omega_1, \omega_2) \} \end{aligned} \quad (5.90)$$

and the cubic MCSCF response function reads

$$\begin{aligned} \langle \langle A; V^{\omega_1}, V^{\omega_2}, V^{\omega_3} \rangle \rangle_{\omega_1+i\epsilon, \omega_2+i\epsilon, \omega_3+i\epsilon} &= P(1, 2, 3) \{ \text{sgn}(jkl) A_{jkl}^{[3]} f_j^{(1)}(\omega_1) f_k^{(1)}(\omega_2) f_l^{(1)}(\omega_3) \\ &+ \text{sgn}(jk) A_{jk}^{[2]} [f_j^{(1)}(\omega_1) f_k^{(2)}(\omega_2, \omega_3) \\ &+ f_j^{(2)}(\omega_1, \omega_2) f_k^{(1)}(\omega_3)] + \text{sgn}(j) A_j^{[1]} f_j^{(3)}(\omega_1, \omega_2, \omega_3) \}. \end{aligned} \quad (5.91)$$

Explicit expressions have now been determined for the linear, quadratic, and cubic response functions. In the next section explicit expressions will be derived for residues of these response functions which may then be used to determine the molecular properties of Sec. III.

E. Molecular properties from MCSCF response functions

We will now examine the MCSCF linear and quadratic response functions of Sec. V D in order to derive MCSCF expressions for the molecular properties of Sec. III. The MCSCF expressions for the molecular properties in Sec. III is of course obtained by replacing the exact response functions of Sec. III with the corresponding MCSCF response functions. We first consider the MCSCF linear response function and the poles and residues of this response function, then we carry out a similar analysis

for the quadratic MCSCF response function. For brevity we choose not to discuss the derivation of MCSCF expressions for molecular properties that are determined by the residues of the cubic response function. The Einstein summation convention will be used in this subsection with the exception that f and g are used as fixed state indices.

The MCSCF linear response function may be determined by inserting the expression (5.76) into Eq. (5.89):

$$\langle \langle A; B \rangle \rangle_{\omega_1+i\epsilon} = \frac{\langle 0|[O_j, A]|0\rangle \text{sgn}(j) \langle 0|[B, O_j^+]|0\rangle}{\omega_1 - \text{sgn}(j)\omega_j + i\epsilon} \quad (5.92)$$

$$= \frac{A_j^{[1]} \text{sgn}(j) B_j^{[1]}}{\omega_1 - \text{sgn}(j)\omega_j + i\epsilon}, \quad (5.93)$$

where $A^{[1]}$ is defined in Eq. (5.86) and where $B_j^{[1]}$ is defined in accordance with the definition of $V_j^{\omega_j[1]}$ in Eq. (5.50). Equation (5.93) has poles at $\omega = \pm\omega_j$ and the ω_j 's are therefore MCSCF approximations to the excitation energies. The corresponding residues become

$$\lim_{\omega_1 \rightarrow \omega_j} (\omega_1 - \omega_j) \langle \langle A; B \rangle \rangle_{\omega_1+i\epsilon} = A_j^{[1]} B_j^{[1]}, \quad (5.94)$$

$$\lim_{\omega_1 \rightarrow -\omega_j} (\omega_1 + \omega_j) \langle \langle A; B \rangle \rangle_{\omega_1+i\epsilon} = -A_{-j}^{[1]} B_{-j}^{[1]}. \quad (5.95)$$

By comparing Eqs. (5.94) and (5.95) and Eqs. (3.12) and (3.13) we identify the square of the transition matrix element as

$$\langle 0|A|f\rangle \langle f|B|0\rangle = A_f^{[1]} B_f^{[1]}. \quad (5.96)$$

Equation (5.96) does not by itself allow us to identify $\langle 0|A|f\rangle$ but only $|\langle 0|A|f\rangle|$. The sign of the transition matrix element is however not important for the description of molecular properties as transition matrix elements are always squared in molecular property expressions. We choose the identification

$$\langle 0|A|f\rangle = \langle 0|[A, O_j^+]|0\rangle = \langle 0|[A, Q_f^+]|0\rangle, \quad (5.97)$$

in agreement with the exact limit where $|f\rangle = Q_f^\dagger|0\rangle$ and $Q_f|0\rangle = 0$. When A and B refer to the various interaction operators of Sec. III A we can obtain MCSCF expressions for second-order molecular properties, transition matrix elements, and excitation energies. These MCSCF quantities

have been calculated with promising results for small MCSCF configuration lists.²⁵

We will now examine the MCSCF quadratic response function. By inserting the expressions of Eqs. (5.80) and (5.76) for $f^{(2)}$ and $f^{(1)}$, respectively, in Eq. (5.90) the MCSCF quadratic response function becomes

$$\begin{aligned} \langle\langle A; B, C \rangle\rangle_{\omega_1+i\epsilon, \omega_2+i\epsilon} &= + \frac{\text{sgn}(jl)A_j^{[1]}B_{jl}^{[2]}C_l^{[1]}}{[\omega_1 + \omega_2 - \text{sgn}(j)\omega_j + 2i\epsilon][\omega_2 - \text{sgn}(l)\omega_l + i\epsilon]} \\ &+ \frac{\text{sgn}(jl)A_j^{[1]}C_{jl}^{[2]}B_l^{[1]}}{[\omega_1 + \omega_2 - \text{sgn}(j)\omega_j + 2i\epsilon][\omega_1 - \text{sgn}(l)\omega_l + i\epsilon]} + \frac{\text{sgn}(jk)B_j^{[1]}(A_{jk}^{[2]} + A_{kj}^{[2]})C_k^{[1]}}{[\omega_1 - \text{sgn}(j)\omega_j + i\epsilon][\omega_2 - \text{sgn}(k)\omega_k + i\epsilon]} \\ &+ \frac{\text{sgn}(jlm)A_j^{[1]}(E_{jml}^{[3]} + E_{jlm}^{[3]} - S_{jlm}^{[3]}(\omega_1 + i\epsilon) - S_{jlm}^{[3]}(\omega_2 + i\epsilon))B_l^{[1]}C_m^{[1]}}{[\omega_1 + \omega_2 - \text{sgn}(j)\omega_j + 2i\epsilon][\omega_2 - \text{sgn}(m)\omega_m + i\epsilon][\omega_1 - \text{sgn}(l)\omega_l + i\epsilon]}. \end{aligned} \quad (5.98)$$

The residue of Eq. (5.98) corresponding to the one of Eq. (3.18) for the exact response function becomes

$$\begin{aligned} \lim_{\omega_2 \rightarrow \omega_f} (\omega_2 - \omega_f) \langle\langle A; B, C \rangle\rangle_{-\omega_1+i\epsilon, \omega_2+i\epsilon} &= \frac{\text{sgn}(j)A_j^{[1]}B_{jf}^{[2]}C_f^{[1]}}{\omega_f - \omega_1 - \text{sgn}(j)\omega_j + 2i\epsilon} + \frac{\text{sgn}(j)B_j^{[1]}(A_{jf}^{[2]} + A_{fj}^{[2]})C_f^{[1]}}{-\omega_1 - \text{sgn}(j)\omega_j + i\epsilon} \\ &+ \frac{\text{sgn}(jl)A_j^{[1]}[E_{jfl}^{[3]} + E_{jfl}^{[3]} - S_{jfl}^{[3]}(-\omega_1 + i\epsilon) - S_{jfl}^{[3]}(\omega_f + i\epsilon)]B_l^{[1]}C_f^{[1]}}{[\omega_f - \omega_1 - \text{sgn}(j)\omega_j + 2i\epsilon][-\omega_1 - \text{sgn}(l)\omega_l + i\epsilon]}. \end{aligned} \quad (5.99)$$

By comparing Eqs. (5.99) and (3.18) we identify

$$\begin{aligned} &\left\{ \frac{\langle 0|A|j\rangle\langle j|(B - \langle 0|B|0\rangle)|f\rangle}{\omega_j - \omega_f + \omega_1} + \frac{\langle 0|B|j\rangle\langle j|(A - \langle 0|A|0\rangle)|f\rangle}{\omega_j - \omega_1} \right\} \\ &= \left\{ \frac{\text{sgn}(j)A_j^{[1]}B_{jf}^{[2]}}{\omega_f - \omega_1 - \text{sgn}(j)\omega_j} + \frac{\text{sgn}(j)B_j^{[1]}(A_{jf}^{[2]} + A_{fj}^{[2]})}{-\omega_1 - \text{sgn}(j)\omega_j} + \frac{\text{sgn}(jl)A_j^{[1]}(E_{jfl}^{[3]} + E_{jfl}^{[3]} + S_{jfl}^{[3]}\omega_1 - S_{jfl}^{[3]}\omega_f)B_l^{[1]}}{[\omega_f - \omega_1 - \text{sgn}(j)\omega_j][-\omega_1 - \text{sgn}(l)\omega_l]} \right\}. \end{aligned} \quad (5.100)$$

Equation (5.100) shows for example how to calculate the two-photon transition matrix element in the MCSCF approximation.

The double residue corresponding to Eq. (3.21) becomes

$$\begin{aligned} &\lim_{(\omega_1 \rightarrow -\omega_g)} (\omega_1 + \omega_g) [\lim_{\omega_2 \rightarrow \omega_f} (\omega_2 - \omega_f) \langle\langle A; B, C \rangle\rangle_{\omega_1, \omega_2}] \\ &= -B_{-g}^{[1]}(A_{-gf}^{[2]} + A_{f-g}^{[2]})C_f^{[1]} - \frac{\text{sgn}(j)A_j^{[1]}(E_{jfg}^{[3]} + E_{j-gf}^{[3]} + S_{j-gf}^{[3]}\omega_g - S_{jfg}^{[3]}\omega_f)B_{-g}^{[1]}C_f^{[1]}}{\omega_f - \omega_g - \text{sgn}(j)\omega_j}. \end{aligned} \quad (5.101)$$

By comparing Eqs. (5.101) and (3.21) and by using Eq. (5.97) we identify

$$\begin{aligned} &\langle g|(A - \langle 0|A|0\rangle)|f\rangle \\ &= A_{-g}^{[2]} + A_{f-g}^{[2]} \\ &\quad - \frac{\text{sgn}(j)A_j^{[1]}(E_{jfg}^{[3]} + E_{j-gf}^{[3]} + S_{j-gf}^{[3]}\omega_g - S_{jfg}^{[3]}\omega_f)}{\omega_f - \omega_g - \text{sgn}(j)\omega_j}. \end{aligned} \quad (5.102)$$

Equation (5.102) enables us to calculate the MCSCF approximations to transition moments between two states different from the reference state. From the MCSCF quadratic response function and the poles and residues of the MCSCF quadratic response function we can therefore evaluate MCSCF expressions for the molecular properties that have been discussed in Sec. III C. MCSCF expressions for molecular properties that can be expressed in terms of residues of the cubic response function may

be derived from the MCSCF cubic response function in Eq. (5.91) in a similar manner as described above for the MCSCF quadratic response function.

We point out that in the limit where the perturbation is frequency independent the MCSCF response functions become identically to the ones that are determined in a time-independent variational calculation.⁴⁵ The MCSCF response functions therefore determine the analytical analogs to finite field MCSCF calculations for both frequency-dependent and frequency-independent molecular properties. For example, the analytical expression for the derivative with respect to a normal coordinate of the frequency-dependent polarizability is obtained from Eq. (3.22) when MCSCF response functions replace the exact response functions, and the analytical expression for the anharmonicity of a MCSCF potential energy surface is obtained from Eq. (3.27) when the exact expressions are

replaced by the corresponding MCSCF expressions. We will discuss in more detail in a future publication how the results of a time-independent variational calculation are obtained in the limit where the perturbation is frequency independent.⁵¹

In the exact limit the configuration space of an MCSCF calculation becomes a full CI calculation and the MCSCF orbital excitation operators are redundant operators. The MCSCF response functions then becomes identical to the exact response functions.

The MCSCF linear response function is given in Eq. (5.93). In the exact limit all the orbital operators are redundant and it is then straightforward to see that there is a one to one correspondence between the terms of the MCSCF linear response function and those of the exact linear response function in Eq. (2.57).

The MCSCF quadratic response function is given in Eq. (5.98). The terms in the quadratic response function involving $E^{[3]}$ and $S^{[3]}$ are zero in the exact limit as the orbital excitation operator part vanishes, and the state transfer part always is zero for these matrices. The orbital excitation part also vanishes in the rest of the terms in Eq. (5.98). Using the definition of $A^{[2]}$ and $B^{[2]}$ in Eqs. (5.86) and (5.48), respectively, it can be shown that Eq. (5.98) reproduces the exact quadratic response function in Eq. (2.59). Note that the terms involving $S^{[3]}$ and $E^{[3]}$ are introduced in the MCSCF quadratic response function because the orbital excitation operators are many-body operators and therefore do not satisfy a closure relation, that is when two orbital excitation operators operate on each other an excitation operator is formed which is not a member of the set of MCSCF orbital excitation operators.

VI. COMPUTATIONAL ASPECTS OF THE CALCULATION OF MCSCF-RESPONSE FUNCTIONS AND THEIR RESIDUES

In this section we outline how the MCSCF response functions and their residues may be efficiently evaluated. The techniques²⁰ we use to bring the response functions to a computationally tractable form are similar to the ones that have been successfully used in large scale direct second-order MCSCF calculations.²² We again confine our discussion to the calculation of properties related to the linear and quadratic response function.

The MCSCF linear and quadratic response functions contain summation indices referring to the whole set of eigensolutions to Eq. (5.60). Before the MCSCF response functions can be evaluated for large configuration state function (CSF) lists the specific reference to the eigensolutions has to be eliminated. The MCSCF response functions also contain explicit reference to the vectors $E^{[1]}$, $V^{[1]}$, the matrices $E^{[2]}$, $V^{[2]}$, $A^{[2]}$, and the supermatrices $S^{[3]}$ and $E^{[3]}$. While $E^{[1]}$ and $V^{[1]}$ can be evaluated for large CSF lists the matrices $E^{[2]}$, $V^{[2]}$, $A^{[2]}$ and supermatrices $S^{[3]}$ and $E^{[3]}$ can only be explicitly evaluated for relatively small CSF lists. In this section we describe how the calculation of the MCSCF response functions may be expressed in terms of $E^{[1]}$ -type vectors containing no explicit reference to the set of eigenstates of Eq. (5.60).

In Sec. VI A the terms containing summations over the eigenvectors of Eq. (5.60) are recasted, so the evaluation of these terms instead require the solution of linear sets of equations. In Sec. VI B we show how the expressions where $E^{[2]}$ is involved, i.e., the solution of linear equations and the calculation of selected eigensolutions, can be formulated such that $E^{[2]}$ always appears as $E^{[2]}$ times a vector. We then demonstrate how $E^{[2]}$ times a vector can be calculated as a sum of two vectors of $E^{[1]}$ -type containing modified Hamilton operators and modified density matrices. In Sec. VI C we use that $E^{[3]}$ always occurs as $E^{[3]}$ times two vectors to show that the terms from $E^{[3]}$ can be calculated as a sum of four vectors of $E^{[1]}$ type with modified Hamilton operators and modified density matrices. We also note that the terms involving $A^{[2]}$, $V^{[2]}$, $S^{[2]}$, $S^{[3]}$, etc. can be evaluated in a similar way. In Sec. VI D we discuss how the orthogonal space $\{|n\rangle\}$ can be chosen so $E^{[1]}$ can be efficiently calculated in the CSF basis.

A. Elimination of explicit summations over "intermediate" states

In the linear and quadratic response function and in residues of the quadratic response function [see, e.g., Eq. (5.99)] there appear summations of the type

$$\frac{f_j \operatorname{sgn}(j)g_j}{C - \operatorname{sgn}(j)\omega_j} = \frac{-f_j g_j}{\omega_j - \operatorname{sgn}(j)C}, \quad (6.1)$$

where C is a constant consisting, e.g., of an energy parameter and f_j and g_j depend linearly upon O_j . We assume f_j to contain explicit reference to (O) and g_j to (O^+) . Straightforward application of Eq. (6.1) requires knowledge of the complete set of eigenvectors and eigenvalues for the generalized eigenvalue problem of Eq. (5.60). This complete diagonalization is feasible⁴⁷ if the dimension of $E^{[2]}$ and $S^{[2]}$, i.e., the number of variables in (T) is of the order $\sim 10^2$. A much larger number of variables 10^3 – 10^5 seems, however, to be necessary to obtain reliable properties even for small molecules. A complete diagonalization is unrealistic for this number of variables. It is thus mandatory to avoid the explicit reference to the set of eigenvectors X_j and eigenvalues ω_j , σ_j in the intermediate sums. We first observe from Eq. (5.59) that

$$\omega - C\sigma = X^+(E^{[2]} - C^e S^{[2]})X, \quad (6.2)$$

so

$$(\omega - C\sigma)^{-1} = (X)^{-1}(E^{[2]} - C^e S^{[2]})^{-1}(X^+)^{-1}. \quad (6.3)$$

Using Eq. (5.12) we obtain

$$f_j = e^f X_{ij}, \quad (6.4)$$

$$g_j = X_{ji}^+ e^g. \quad (6.5)$$

By inserting Eqs. (6.2), (6.4), and (6.5) in Eq. (6.1) and using $\sigma_j = \operatorname{sgn}(j)$, we obtain

$$\frac{-f_j g_j}{\omega_j - \operatorname{sgn}(j)C} = -e^f (E^{[2]} - C^e S^{[2]})^{-1} e^g. \quad (6.6)$$

The terms involving summation over intermediate states can thus be evaluated by solving one set of linear equations.

We consider now the evaluation of the linear response function. By introducing Eq. (6.6) in Eq. (5.93) we obtain

$$\langle\langle A; B \rangle\rangle_{\omega_1} = -e\mathbf{A}^{[1]}(e\mathbf{E}^{[2]} - \omega_1 e\mathbf{S}^{[2]})^{-1}e\mathbf{B}^{[1]}. \quad (6.7)$$

If we solve the linear set of equations

$$N^b(\omega_1) = (e\mathbf{E}^{[2]} - \omega_1 e\mathbf{S}^{[2]})^{-1}e\mathbf{B}^{[1]}, \quad (6.8)$$

the linear response function at frequency ω_1 is obtained as

$$\langle\langle A; B \rangle\rangle_{\omega_1} = -eA_j^{[1]}N_j^b(\omega_1). \quad (6.9)$$

This expression represents a compact way for evaluating linear response functions at a frequency ω_1 .

By comparing Eq. (6.6) with Eq. (5.98) we see that the evaluation of the quadratic response function at frequencies ω_1, ω_2 requires the solution of three sets of linear equations

$$\begin{aligned} N^a(\omega_1 + \omega_2) &= [(e\mathbf{E}^{[2]} - (\omega_1 + \omega_2)e\mathbf{S}^{[2]})^{-1}e\mathbf{A}^{[1]}]^{++}, \\ N^b(\omega_1) &= (e\mathbf{E}^{[2]} - \omega_1 e\mathbf{S}^{[2]})^{-1}e\mathbf{B}^{[1]}, \\ N^c(\omega_2) &= (e\mathbf{E}^{[2]} - \omega_2 e\mathbf{S}^{[2]})^{-1}e\mathbf{C}^{[1]}. \end{aligned} \quad (6.10)$$

Inserting the vectors of Eq. (6.10) in Eq. (5.98) gives

$$\begin{aligned} \langle\langle A; B, C \rangle\rangle_{\omega_1, \omega_2} &= N_j^a(\omega_1 + \omega_2)eB_{ji}^{[2]}N_i^c(\omega_2) + N_j^a(\omega_1 + \omega_2)eC_{ji}^{[2]}N_i^b(\omega_1) \\ &+ N_j^b(\omega_1)(eA_{jk}^{[2]} + eA_{kj}^{[2]})N_k^c(\omega_2) \\ &+ N_j^a(\omega_1 + \omega_2)(eE_{jml}^{[3]} + eE_{jlm}^{[3]} - eS_{jlm}^{[3]}\omega_1 \\ &+ eS_{jml}^{[3]}\omega_2)N_l^b(\omega_1)N_m^c(\omega_2). \end{aligned} \quad (6.11)$$

By solving three sets of linear equations we can thus generate any quadratic response function for example the first hyperpolarizability at frequencies ω_1, ω_2 . One or several of the vectors in Eq. (6.10) may already be known from a preceding linear response calculation.

We consider now the evaluation of the residue of the quadratic response function in Eq. (5.100). Introducing Eq. (6.6) and the expansion of O_f in Eq. (5.12) into Eq. (5.100) gives

$$\begin{aligned} &\left\{ \frac{\langle 0|A|j\rangle\langle j|(B - \langle 0|B|0\rangle)|f\rangle}{\omega_j - \omega_f + \omega_1} \right. \\ &\quad \left. + \frac{\langle 0|B|j\rangle\langle j|(A - \langle 0|A|0\rangle)|f\rangle}{\omega_j - \omega_1} \right\} \\ &= N_j^a(\omega_f - \omega_1)eB_{jk}^{[2]}X_{kf} + N_j^b(-\omega_1)(eA_{jk}^{[2]} + eA_{kj}^{[2]})X_{kf} \\ &\quad + N_j^a(\omega_f - \omega_1)(eE_{jkl}^{[3]} + eE_{jlk}^{[3]} + eS_{jlk}^{[3]}\omega_1 \\ &\quad - eS_{jkl}^{[3]}\omega_f)N_l^b(-\omega_1)X_{lf}. \end{aligned} \quad (6.12)$$

If the eigenvector X_f and the eigenvalue ω_f are known we can thus calculate, e.g., the two-photon transition matrix element for a given frequency ω_1 by solving two sets of linear equations.

The transition matrix element between two excited states $|f\rangle$ and $|g\rangle$ becomes from Eq. (5.102):

$$\begin{aligned} &\langle g|A|f\rangle - \delta_{gf}\langle 0|A|0\rangle \\ &= (eA_{kl}^{[2]} + eA_{lk}^{[2]})X_{k-g}X_{lf} + N_f^a(\omega_f - \omega_g)(eE_{jkl}^{[3]} \\ &\quad + eE_{jlk}^{[3]} - eS_{jlk}^{[3]}\omega_g + eS_{jkl}^{[3]}\omega_f)X_{kf}X_{l-g}. \end{aligned} \quad (6.13)$$

If the eigenvectors X_f, X_{-g} and the eigenvalues ω_f and ω_g are known, the transition moment $\langle g|A|f\rangle$ can be obtained by solving a single set of linear equations. We have now eliminated all explicit reference to sum over intermediate states that appear in the formulas in Sec. V E.

Both the evaluation of the linear and the quadratic response function requires only that linear sets of equations of the form in Eq. (6.8) are solved. These linear sets of equations determine the first-order perturbation correction to the MCSCF wave function due to the external field. The first order perturbation correction to the wave function determines in general the energy through third order in agreement with the fact that the linear and the quadratic response functions describe the second- and third-order perturbation corrections, respectively, to the total energy. The fourth-order perturbation correction to the total energy requires the second-order correction to the wave function to be explicitly evaluated. The cubic response function which determines the fourth-order energy correction therefore requires explicit evaluation of the second-order correction to the MCSCF wave function. The linear sets of equation which have to be solved to determine the second-order correction to the wave function are of a more complicated structure than the ones which determine the first-order correction to the wave function. This is one of the reasons why the evaluation of the cubic response function is more complicated than the evaluation of the quadratic response function.

B. The solution of linear equations and the calculation of individual eigenvectors

In order to calculate properties involving an initial or final state which differ from the reference state the eigenvectors and eigenvalues for the corresponding states must be determined from the generalized eigenvalue problem of Eq. (5.60). Due to the large dimensions of $e\mathbf{E}^{[2]}$ and $e\mathbf{S}^{[2]}$ one must use direct iterative techniques to determine the eigenvalues and eigenvectors. It is profitable to rewrite Eq. (5.60) to obtain inverse excitation energies

$$e\mathbf{S}^{[2]}X_j = \omega_j^f e\mathbf{E}^{[2]}X_j, \quad \omega_j^f = 1/\omega_j. \quad (6.14)$$

We are usually interested in determining the lowest excitation energies and therefore can concentrate on determining the largest eigenvalues of Eq. (6.14). The largest eigenvalues and corresponding eigenvectors are the eigensolutions which can be most reliably determined with direct iterative methods. In ground state calculations the matrix $e\mathbf{E}^{[2]}$ is positive definite and may then be considered as the metric. The eigenvalues and eigenvectors may, e.g., be determined using the generalized Lanczos algorithm or the generalized Rayleigh quotient method (see Ref. 47 and references therein). A common characteristic of these algorithms is that they either require several solutions of sets of linear equations of the type

$$(\alpha_k {}^e\mathbf{S}^{[2]} + \beta_k {}^e\mathbf{E}^{[2]})X_{k+1} = \mathbf{f}_k \quad (6.15)$$

or they require many calculations of the type

$$(\alpha_k {}^e\mathbf{S}^{[2]} + \beta_k {}^e\mathbf{E}^{[2]})\mathbf{f}_k. \quad (6.16)$$

In Eqs. (6.15) and (6.16), α_k and β_k are scalars and \mathbf{f}_k is a vector, all of which depend on the method used. Selected eigensolutions (X_j , ω_j , σ_j) can thus be obtained by either solving sets of linear equations [Eq. (6.15)] or by iterative linear transformations [Eq. (6.16)]. Both methods require linear transformations

$$(\alpha_k {}^e\mathbf{E}^{[2]} + \beta_k {}^e\mathbf{S}^{[2]})\mathbf{N} \quad (6.17)$$

to be carried out. In order to carry out such linear transformations the matrices ${}^e\mathbf{E}^{[2]}$ and ${}^e\mathbf{S}^{[2]}$ are not needed explicitly, only procedures for calculating ${}^e\mathbf{E}^{[2]}$ and ${}^e\mathbf{S}^{[2]}$ times a vector must be known. For the case where \mathbf{N} has the structure

$$\begin{pmatrix} \kappa \\ S \\ -\kappa \\ -S \end{pmatrix}, \quad (6.18)$$

the linear transformation has routinely been carried out in large scale direct second-order MCSCF calculations.¹⁹⁻²¹ The elements κ and $-\kappa$ forms an antisymmetric matrix

$$(\kappa)_{rs} = \begin{cases} \kappa_{rs} & \text{for } r > s \\ 0 & \text{for } r = s \\ -\kappa_{rs} & \text{for } r < s. \end{cases} \quad (6.19)$$

κ may thus both be considered as a matrix with two indices and as a vector with a single index. The vector \mathbf{N} in Eq. (6.17) required to determine the eigenvectors of Eq. (6.14) has the more general structure

$$\mathbf{N} = \begin{pmatrix} \kappa \\ S \\ \kappa' \\ S' \end{pmatrix}, \quad (6.20)$$

corresponding to the matrix definition for κ and κ' :

$$(\kappa)_{rs} = \begin{cases} \kappa_{rs} & \text{for } r > s \\ 0 & \text{for } r = s \\ \kappa'_{rs} & \text{for } r < s. \end{cases} \quad (6.21)$$

We now generalize our previous algorithm to accommodate vectors of the type of Eq. (6.20). The analysis is done separately for each of the four operator types (q^+ , R^+ , q , R) [see Eq. (5.8)]. For j corresponding to an orbital excitation q_j^+ ,

$${}^eE_{jk}^{[2]}N_k = -\langle 0 | [(S_n R_n^+ + S'_n R_n), [q_j, H_0]] | 0 \rangle - \langle 0 | [q_j [\kappa_k q_k^+ + \kappa'_k q_k], H_0] | 0 \rangle. \quad (6.22)$$

Note that the index j refers to the set (T^+) of Eq. (5.8) according to the definition of ${}^e\mathbf{E}$ in Eq. (5.46). If H_0 is composed of a one-body and a two-body term

$$H_0 = h_{rs} a_r^+ a_s + \frac{1}{2} (rs|tu) a_r^+ a_t^+ a_u a_s, \quad (6.23)$$

one obtains

$$\begin{aligned} & [\kappa_i q_i^+ + \kappa'_i q_i, H_0] \\ &= [\kappa_{mn} a_m^+ a_n, H_0] \\ &= \tilde{h}_{rs} a_r^+ a_s + \frac{1}{2} (rs|tu) a_r^+ a_t^+ a_u a_s. \end{aligned} \quad (6.24)$$

In Eq. (6.24) we have introduced the one-index transformed integrals

$$\begin{aligned} \tilde{h}_{rs} &= \kappa_{rp} h_{ps} - \kappa_{ps} h_{rp}, \\ (rs|tu) &= \kappa_{rp} (ps|tu) - \kappa_{ps} (rp|tu) + \kappa_{tp} (rs|pu) - \kappa_{pu} (rs|tp). \end{aligned} \quad (6.25)$$

The commutator on the left-hand side of Eq. (6.24) can thus be considered as a Hamiltonian with modified integrals, so we write

$$H_0(\kappa) = [\kappa_i q_i^+ + \kappa'_i q_i, H_0]. \quad (6.26)$$

It is also convenient to introduce modified states

$$\begin{aligned} |0^R\rangle &= -S_n R_n^+ |0\rangle = -S_n |n\rangle, \\ \langle 0^L| &= \langle 0 | (S'_n R_n) = S'_n \langle n|. \end{aligned} \quad (6.27)$$

The calculation of these modified states is discussed in Sec. VI D. By introducing Eqs. (6.24) and (6.27) in Eq. (6.22), one obtains

$$\begin{aligned} {}^eE_{jk}^{[2]}N_k &= -\{\langle 0^L | [q_j, H_0] | 0 \rangle + \langle 0 | [q_j, H_0] | 0^R \rangle \\ &+ \langle 0 | [q_j, H_0(\kappa)] | 0 \rangle\}. \end{aligned} \quad (6.28)$$

In the same way one obtains for j corresponding to an orbital deexcitation operator q_j ,

$$\begin{aligned} {}^eE_{jk}^{[2]}N_k &= -\{\langle 0^L | [q_j^+, H_0] | 0 \rangle + \langle 0 | [q_j^+, H_0] | 0^R \rangle \\ &+ \langle 0 | [q_j^+, H_0(\kappa)] | 0 \rangle\}. \end{aligned} \quad (6.29)$$

For j corresponding to a state excitation R_j^+ we obtain using the definition of ${}^e\mathbf{E}^{[2]}$ from Eq. (5.46),

$$\begin{aligned} {}^eE_{jk}^{[2]}N_k &= -\{\langle 0 | [R_j, [(S_k R_k^+ + S'_k R_k), H_0]] | 0 \rangle \\ &+ \langle 0 | [R_j, [(\kappa_k q_k^+ + \kappa'_k q_k), H_0]] | 0 \rangle\}. \end{aligned} \quad (6.30)$$

The introduction of Eqs. (6.24) and (6.27) in Eq. (6.30) gives

$$\begin{aligned} {}^eE_{jk}^{[2]}N_k &= -\{\langle j | H_0 | 0^R \rangle \\ &+ S_j \langle 0 | H_0 | 0 \rangle + \langle j | H_0(\kappa) | 0 \rangle\}. \end{aligned} \quad (6.31)$$

For j corresponding to a state deexcitation operator R_n one similarly obtains

$${}^eE_{jk}^{[2]}N_k = -\{-\langle 0^L | H_0 | j \rangle + S'_j \langle 0 | H_0 | 0 \rangle - \langle 0 | H_0(\kappa) | j \rangle\}. \quad (6.32)$$

By collecting Eqs. (6.28), (6.29), (6.31), and (6.32), the vector ${}^eE_{jk}^{[2]}N_k$ can be written as

$$\begin{aligned} & \begin{pmatrix} \langle 0^L | [q_j, H_0] | 0 \rangle + \langle 0 | [q_j, H_0] | 0^R \rangle \\ \langle j | H_0 | 0^R \rangle \\ \langle 0^L | [q_j^+, H_0] | 0 \rangle + \langle 0 | [q_j^+, H_0] | 0^R \rangle \\ -\langle 0^L | H_0 | j \rangle \end{pmatrix} \\ & - \begin{pmatrix} \langle 0 | [q_j, H_0(\kappa)] | 0 \rangle \\ \langle j | H_0(\kappa) | 0 \rangle \\ \langle 0 | [q_j^+, H_0(\kappa)] | 0 \rangle \\ -\langle 0 | H_0(\kappa) | j \rangle \end{pmatrix} - \langle 0 | H_0 | 0 \rangle \begin{pmatrix} 0 \\ S_j \\ 0 \\ S'_j \end{pmatrix}. \end{aligned} \quad (6.33)$$

From a comparison of Eq. (6.33) and ${}^eE^{[1]}$ of Eq. (5.46) given by

$${}^eE^{[1]} = \begin{pmatrix} \langle 0|[q_j, H]|0\rangle \\ \langle j|H|0\rangle \\ \langle 0|[q_j^+, H]|0\rangle \\ -\langle 0|H|j\rangle \end{pmatrix}, \quad (6.34)$$

we notice that the first vector of Eq. (6.33) corresponds to an ${}^eE^{[1]}$ -type vector with a modified density matrix and the second vector corresponds to an ${}^eE^{[1]}$ -type vector with a modified Hamiltonian. A comparison of the vector ${}^eE^{[1]}$ and the gradient of a normal MCSCF calculation;

$$\begin{pmatrix} \langle 0|[q_j, H]|0\rangle \\ \langle j|H|0\rangle \end{pmatrix} \quad (6.35)$$

shows that ${}^eE^{[1]}$ roughly corresponds to the evaluation of two MCSCF gradients.

Formulas for the calculation of ${}^eS^{[2]}$ times a vector can easily be obtained from the definition [Eq. (5.43)]. It is easily recognized that this calculation only involves the calculation of one electron density and transition density matrix elements.

C. Calculations of contributions from ${}^eE^{[3]}$ and ${}^eS^{[3]}$

The determination of the quadratic response function and residues of the quadratic response function requires the calculation of terms of the type

$$\begin{aligned} &({}^eE_{jkl}^{[3]} + {}^eE_{jlk}^{[3]})^1 N_k^2 N_l, \\ &{}^eS_{jkl}^{[3]} {}^1 N_k^2 N_l, \end{aligned} \quad (6.36)$$

and

$$({}^eA_{jk}^{[2]} + {}^eA_{kj}^{[2]}) {}^1 N_k. \quad (6.36)$$

The calculation of ${}^eA_{jk}^{[2]} {}^1 N_k$ can be done using the scheme developed in Sec. VI B. A technique for the calculation of ${}^eE_{jkl}^{[3]} {}^1 N_k^2 N_l$ has been developed for the case where ${}^1 N$ and ${}^2 N$ have the structure of Eq. (6.18).^{19,20} The vectors of Eq. (6.36) are in general of the same form as in Eq. (6.20):

$${}^1 N = \begin{pmatrix} {}^1 \kappa \\ {}^1 S \\ {}^1 \kappa' \\ {}^1 S' \end{pmatrix}, \quad {}^2 N = \begin{pmatrix} {}^2 \kappa \\ {}^2 S \\ {}^2 \kappa' \\ {}^2 S' \end{pmatrix}. \quad (6.37)$$

We now demonstrate how the techniques of Sec. VI B can be generalized so that ${}^eE^{[3]}$ times two vectors can be calculated directly. Again we study the four types of operators separately. For j corresponding to an orbital excitation operator q_j^+ one obtains from the definition of ${}^eE^{[3]}$ in Eq. (5.46) with (O) replaced by (T)

$$\begin{aligned} &({}^eE_{jkl}^{[3]} + {}^eE_{jlk}^{[3]})^1 N_k^2 N_l \\ &= \frac{1}{2} \langle 0|[q_j, [({}^1 \kappa_k q_k^+ + {}^1 \kappa'_k q_k), [{}^2 \kappa_l q_l^+ + {}^2 \kappa'_l q_l, H_0]]|0\rangle \\ &+ \frac{1}{2} \langle 0|[q_j, [({}^2 \kappa_k q_k^+ + {}^2 \kappa'_k q_k), [{}^1 \kappa_l q_l^+ + {}^1 \kappa_l, H_0]]|0\rangle \end{aligned}$$

$$\begin{aligned} &+ \langle 0|[({}^1 S_k R_k^+ + {}^1 S'_k R_k), [q_j, [{}^2 \kappa_l q_l^+ + {}^2 \kappa'_l q_l, H_0]]|0\rangle \\ &+ \langle 0|[({}^2 S_k R_k^+ + {}^2 S'_k R_k), [q_j, [{}^1 \kappa_l q_l^+ + {}^1 \kappa'_l q_l, H_0]]|0\rangle \\ &+ \frac{1}{2} \langle 0|[({}^1 S_k R_k^+ + {}^1 S'_k R_k), [({}^2 S_l R_l^+ + {}^2 S'_l R_l), [q_j, H_0]]|0\rangle \\ &+ \frac{1}{2} \langle 0|[({}^2 S_k R_k^+ + {}^2 S'_k R_k), [({}^1 S_l R_l^+ + {}^1 S'_l R_l), [q_j, H_0]]|0\rangle. \end{aligned} \quad (6.38)$$

Using the notation of Eq. (6.26),

$$H_0({}^1 \kappa) = [({}^1 \kappa_l q_l^+ + {}^1 \kappa'_l q_l), H_0], \quad (6.39)$$

$$H_0({}^2 \kappa) = [({}^2 \kappa_l q_l^+ + {}^2 \kappa'_l q_l), H_0] \quad (6.40)$$

and introducing the modified states

$$\begin{aligned} |0^{1R}\rangle &= -{}^1 S_n R_n^+ |0\rangle = -{}^1 S_n |n\rangle, \\ |0^{2R}\rangle &= -{}^2 S_n R_n^+ |0\rangle = -{}^2 S_n |n\rangle, \\ \langle 0^{1L}| &= \langle 0|({}^1 S'_n R_n) = {}^1 S'_n \langle n|, \\ \langle 0^{2L}| &= \langle 0|({}^2 S'_n R_n) = {}^2 S'_n \langle n|, \end{aligned} \quad (6.41)$$

we obtain

$$\begin{aligned} &({}^eE_{jkl}^{[3]} + {}^eE_{jlk}^{[3]})^1 N_k^2 N_l \\ &= \langle 0|[q_j, [({}^2 \kappa_k q_k^+ + {}^2 \kappa'_k q_k), H_0({}^1 \kappa)]]|0\rangle \\ &+ \frac{1}{2} \langle 0|[q_j, [[({}^1 \kappa_k q_k^+ + {}^1 \kappa'_k q_k), ({}^2 \kappa_l q_l^+ + {}^2 \kappa'_l q_l), H_0]|0\rangle \\ &+ \langle 0^{1L}|[q_j, H_0({}^2 \kappa)]|0\rangle + \langle 0|[q_j, H_0({}^2 \kappa)]|0^{1R}\rangle \\ &+ \langle 0^{2L}|[q_j, H_0({}^1 \kappa)]|0\rangle + \langle 0|[q_j, H_0({}^1 \kappa)]|0^{2R}\rangle \\ &+ \frac{1}{2} \langle 0^{1L}|[q_j, H_0]|0^{2R}\rangle \\ &+ \frac{1}{2} \langle 0^{2L}|[q_j, H_0]|0^{1R}\rangle. \end{aligned} \quad (6.42)$$

Inserting the definition

$$H_0({}^1 \kappa, {}^2 \kappa) = [({}^2 \kappa_k q_k^+ + {}^2 \kappa'_k q_k), H_0({}^1 \kappa)] \quad (6.43)$$

and

$${}^3 \kappa = {}^1 \kappa^2 \kappa - {}^2 \kappa^1 \kappa \quad (6.44)$$

into Eq. (6.42) gives

$$\begin{aligned} &({}^eE_{jkl}^{[3]} + {}^eE_{jlk}^{[3]})^1 N_k^2 N_l \\ &= \langle 0|[q_j, (H_0({}^1 \kappa, {}^2 \kappa) + \frac{1}{2} H_0({}^3 \kappa))]|0\rangle \\ &+ \langle 0^{1L}|[q_j, H_0({}^2 \kappa)]|0\rangle + \langle 0|[q_j, H_0({}^2 \kappa)]|0^{1R}\rangle \\ &+ \langle 0^{2L}|[q_j, H_0({}^1 \kappa)]|0\rangle + \langle 0|[q_j, H_0({}^1 \kappa)]|0^{2R}\rangle \\ &+ \frac{1}{2} \langle 0^{1L}|[q_j, H_0]|0^{2R}\rangle \\ &+ \frac{1}{2} \langle 0^{2L}|[q_j, H_0]|0^{1R}\rangle. \end{aligned} \quad (6.45)$$

We thus see that for j representing an orbital excitation the term $({}^eE_{jkl}^{[3]} + {}^eE_{jlk}^{[3]})^1 N_k^2 N_l$ can be written as a sum of terms whose structure is like ${}^eE^{[1]}$, where modified states and modified Hamiltonians are introduced.

In a similar way we obtain for j corresponding to an orbital deexcitation operator q_j ,

$$\begin{aligned} &({}^eE_{jkl}^{[3]} + {}^eE_{jlk}^{[3]})^1 N_k^1 N_l \\ &= \langle 0|[q_j^+, (H_0({}^1 \kappa, {}^2 \kappa) + \frac{1}{2} H_0({}^3 \kappa))]|0\rangle \\ &+ \langle 0^{1L}|[q_j^+, H_0({}^2 \kappa)]|0\rangle + \langle 0|[q_j^+, H_0({}^2 \kappa)]|0^{1R}\rangle \\ &+ \langle 0^{2L}|[q_j^+, H_0({}^1 \kappa)]|0\rangle + \langle 0|[q_j^+, H_0({}^1 \kappa)]|0^{2R}\rangle \\ &+ \frac{1}{2} \langle 0^{1L}|[q_j^+, H_0]|0^{2R}\rangle + \frac{1}{2} \langle 0^{2L}|[q_j^+, H_0]|0^{1R}\rangle. \end{aligned} \quad (6.46)$$

For j corresponding to a state-excitation operator R_n^+ we obtain

$$\begin{aligned} & ({}^e E_{jkl}^{[3]} + {}^e E_{jlk}^{[3]})^1 N_k^2 N_l \\ &= \frac{1}{2} \langle 0 | [R_j, [({}^1 \kappa_k q_k^+ + {}^1 \kappa'_k q_k), [({}^2 \kappa_i q_i^+ + {}^2 \kappa'_i q_i), H_0]]] | 0 \rangle \\ &+ \frac{1}{2} \langle 0 | [R_j, [({}^2 \kappa_k q_k^+ + {}^2 \kappa'_k q_k), [{}^1 \kappa_i q_i^+ + {}^1 \kappa'_i q_i, H_0]]] | 0 \rangle \\ &+ \langle 0 | [R_j, [({}^1 S_k R_k^+ + {}^1 S'_k R_k), [{}^2 \kappa_i q_i^+ + {}^2 \kappa'_i q_i, H_0]]] | 0 \rangle \\ &+ \langle 0 | [R_j, [({}^2 S_k R_k^+ + {}^2 S'_k R_k), [{}^1 \kappa_i q_i^+ + {}^1 \kappa'_i q_i, H_0]]] | 0 \rangle \\ &+ \frac{1}{2} \langle 0 | [R_j, [({}^1 S_k R_k^+ + {}^1 S'_k R_k), [{}^2 S_i R_i^+ + {}^2 S'_i R_i, H_0]]] | 0 \rangle \\ &+ \frac{1}{2} \langle 0 | [R_j, [({}^2 S_k R_k^+ + {}^2 S'_k R_k), [{}^1 S_i R_i^+ + {}^1 S'_i R_i, H_0]]] | 0 \rangle. \end{aligned} \quad (6.47)$$

Using Eqs. (6.39), (6.40), (6.41), and (6.43) gives

$$\begin{aligned} & ({}^e E_{jkl}^{[3]} + {}^e E_{jlk}^{[3]})^1 N_k^2 N_l = \langle j | H_0({}^1 \kappa, {}^2 \kappa) + \frac{1}{2} H_0({}^3 \kappa) | 0 \rangle \\ &+ \langle j | H_0({}^2 \kappa) | 0^{1R} \rangle + \langle j | H_0({}^1 \kappa) | 0^{2R} \rangle. \end{aligned} \quad (6.48)$$

The terms on the right-hand side of Eq. (6.48) are again a sum over ${}^e E^{[1]}$ -type terms.

In a similar way one obtains for j corresponding to a state deexcitation operator

$$\begin{aligned} & ({}^e E_{jkl}^{[3]} + {}^e E_{jlk}^{[3]})^1 N_k^2 N_l \\ &= -\langle 0 | H_0({}^1 \kappa, {}^2 \kappa) + \frac{1}{2} H_0({}^3 \kappa) | n \rangle - \langle 0^{1L} | H_0({}^2 \kappa) | j \rangle \\ &- \langle 0^{2L} | H_0({}^1 \kappa) | j \rangle. \end{aligned} \quad (6.49)$$

By combining Eqs. (6.45), (6.46), (6.48), and (6.49) we have for $({}^e E_{jkl}^{[3]} + {}^e E_{jlk}^{[3]})^1 N_k^2 N_l$ where j runs over the four types of operators

$$\begin{aligned} & ({}^e E_{jkl}^{[3]} + {}^e E_{jlk}^{[3]})^1 N_k^2 N_l \\ &= \left(\begin{aligned} & \langle 0 | [q_j, (H_0({}^1 \kappa, {}^2 \kappa) + \frac{1}{2} H_0({}^3 \kappa))] | 0 \rangle \\ & \langle j | (H_0({}^1 \kappa, {}^2 \kappa) + \frac{1}{2} H_0({}^3 \kappa)) | 0 \rangle \\ & \langle 0 | [q_j^+, (H_0({}^1 \kappa, {}^2 \kappa) + \frac{1}{2} H_0({}^3 \kappa))] | 0 \rangle \\ & - \langle 0 | (H_0({}^1 \kappa, {}^2 \kappa) + \frac{1}{2} H_0({}^3 \kappa)) | j \rangle \end{aligned} \right) \\ &+ \left(\begin{aligned} & \langle 0^{1L} | [q_j, H_0({}^2 \kappa)] | 0 \rangle + \langle 0 | [q_j, H_0({}^2 \kappa)] | 0^{1R} \rangle \\ & \langle j | H_0({}^2 \kappa) | 0^{1R} \rangle \\ & \langle 0^{1L} | [q_j^+, H_0({}^2 \kappa)] | 0 \rangle + \langle 0 | [q_j^+, H_0({}^2 \kappa)] | 0^{1R} \rangle \\ & - \langle 0^{1L} | H_0({}^2 \kappa) | j \rangle \end{aligned} \right) \\ &+ \left(\begin{aligned} & \langle 0^{2L} | [q_j, H_0({}^1 \kappa)] | 0 \rangle + \langle 0 | [q_j, H_0({}^1 \kappa)] | 0^{2R} \rangle \\ & \langle j | H_0({}^1 \kappa) | 0^{2R} \rangle \\ & \langle 0^{2L} | [q_j^+, H_0({}^1 \kappa)] | 0 \rangle + \langle 0 | [q_j^+, H_0({}^1 \kappa)] | 0^{2R} \rangle \\ & - \langle 0^{2L} | H_0({}^1 \kappa) | j \rangle \end{aligned} \right) \\ &+ \frac{1}{2} \left(\begin{aligned} & \langle 0^{1L} | [q_j, H_0] | 0^{2R} \rangle + \langle 0^{2L} | [q_j, H_0] | 0^{1R} \rangle \\ & 0 \\ & \langle 0^{1L} | [q_j^+, H_0] | 0^{2R} \rangle + \langle 0^{2L} | [q_j^+, H_0] | 0^{1R} \rangle \\ & 0 \end{aligned} \right). \end{aligned} \quad (6.50)$$

Equation (6.50) shows that $({}^e E_{jkl}^{[3]} + {}^e E_{jlk}^{[3]})^1 N_k^2 N_l$ can be evaluated as a sum of four ${}^e E^{[1]}$ -type terms with one-index transformed Hamiltonians and with transition density matrices.

An algorithm for the direct construction of ${}^e \tilde{S}^{[3]}$ times two vectors can be derived. Only terms involving one-electron density and transition density matrices are involved.

D. The treatment of large CI expansions

The evaluation of the linear and quadratic response functions has been expressed in Secs. VI B and VI C in terms of only $E^{[1]}$ -type matrix elements, where $E^{[1]}$ was expressed in the basis $\{|n\rangle\}$ spanning the orthogonal complement to $|0\rangle$ [see, e.g., Eq. (6.31)]. We now show how the basis $\{|n\rangle\}$ can be chosen such that $E^{[1]}$ can be evaluated directly in the CSF basis $\{|\phi_m\rangle\}$.

Our technique starts by defining a set of parameters S'_g and a "basic CSF" $|\phi_0\rangle$:

$$|0\rangle = \exp \left\{ - \sum_{g \neq 0} S'_g (|\phi_g\rangle \langle \phi_0| - |\phi_0\rangle \langle \phi_g|) \right\} |\phi_0\rangle. \quad (6.51)$$

By expanding the exponential of Eq. (6.51) one obtains

$$|0\rangle = \cos d |\phi_0\rangle - \frac{\sin d}{d} \sum_{g \neq 0} S'_g |\phi_g\rangle,$$

where

$$d = \left(\sum_{g \neq 0} S_g'^2 \right)^{1/2}. \quad (6.52)$$

Equation (6.51) is fulfilled if we choose S'_g as

$$S'_g = \frac{-C_{g0} d}{\sin d}, \quad d = \cos^{-1} C_{00}. \quad (6.53)$$

Since the exponential operator of Eq. (6.51) is unitary the basis $\{|n\rangle\}$ for the orthogonal complement space can be chosen as $(|\phi_n\rangle \neq |\phi_0\rangle)$:

$$\begin{aligned} |n\rangle &= \exp \left(- \sum_{g \neq 0} S'_g (|\phi_g\rangle \langle \phi_0| - |\phi_0\rangle \langle \phi_g|) \right) |\phi_n\rangle \\ &= |\phi_n\rangle + \frac{\sin d}{d} S'_n |\phi_0\rangle + S'_n \left(\frac{\cos d - 1}{d^2} \right) \sum_{k \neq 0} S'_k |\phi_k\rangle \\ &= |\phi_n\rangle - C_{n0} |\phi_0\rangle + C_{n0} \frac{C_{00} - 1}{(1 - C_{00}^2)} \sum_{k \neq 0} C_{k0} |\phi_k\rangle \\ &= |\phi_n\rangle - \frac{C_{n0}}{(1 + C_{00})} [|\phi_0\rangle + |0\rangle]. \end{aligned} \quad (6.54)$$

It should be noticed that any reference to S'_g vanishes in Eq. (6.54).

Modified states of the type of Eq. (6.27) can be written as

$$\begin{aligned} - \sum_{n \neq 0} S_n |n\rangle &= - \sum_{n \neq 0} S_n \left[|\phi_n\rangle - \frac{C_{n0}}{1 + C_{00}} (|0\rangle + |\phi_0\rangle) \right] \\ &= \sum_{k \neq 0} - (S_k + \alpha C_{k0}) |\phi_k\rangle - \alpha (1 + C_{00}) |\phi_0\rangle, \end{aligned} \quad (6.55)$$

where

$$\alpha = \frac{- \sum_{n \neq 0} S_n C_{n0}}{1 + C_{00}}. \quad (6.56)$$

We can now write

$$- \sum_{n \neq 0} S_n |n\rangle = - \sum_k {}^{\text{CSF}} S_k |\phi_k\rangle, \quad (6.57)$$

where

$$\begin{aligned} \text{CSF}S_0 &= \alpha(1 + C_{00}), \\ \text{CSF}S_k &= S_k + \alpha C_{k0}. \end{aligned} \quad (6.58)$$

The sum over states in the orthogonal basis is thus easily transformed to a sum over configuration state functions.

Explicit reference to the basis $\{|n\rangle\}$ is also made in terms of the type $\langle n|\tilde{H}|0\rangle$. Using Eq. (6.54) we obtain

$$\begin{aligned} \langle n|\tilde{H}|0\rangle &= \langle \phi_n|\tilde{H}|0\rangle - \frac{C_{n0}}{1 + C_{00}} (\langle \phi_0|\tilde{H}|0\rangle \\ &+ \langle 0|\tilde{H}|0\rangle). \end{aligned} \quad (6.59)$$

The terms $\langle n|\tilde{H}|0\rangle$ can thus be readily obtained from the calculation of $\langle \phi_n|\tilde{H}|0\rangle$.

We have thus shown that the terms involving the orthogonal states can be recasted so that the evaluation of these terms occurs in the configuration state function basis.

VII. DISCUSSION

We have derived the linear, quadratic, and cubic response functions for an MCSCF state and discussed how a large variety of molecular properties may be expressed in terms of these response functions. The examples include frequency-dependent hyperpolarizabilities, the derivatives with respect to the normal coordinates of the dipole moment, phosphorescence lifetimes, and two-photon absorption cross sections. We have also shown how the MCSCF molecular property expressions containing the electric dipole operator can be expressed in equivalent forms containing the momentum operator.

The MCSCF response functions have been written in a form that allows direct techniques to be used. This is done by eliminating explicit reference to summation indices over intermediate states and by expressing the evaluation of the response function in a configuration state function basis. Direct CI techniques [as, e.g., the graphical unitary group approach (GUGA)]⁵⁰ and one-index transformations of the Hamiltonian can then be straightforwardly used and MCSCF response functions can with this technique be evaluated for very large configuration lists, as demonstrated in recent direct second-order MCSCF calculations with 10^3 – 10^5 configuration state functions.

A very crucial step in deriving the MCSCF response functions is that the time development of the MCSCF reference state is parametrized in terms of explicit unitary exponential time dependent transformations of the orbital space and of the configuration state function space. This parametrization makes the normalization conditions redundant and allows the phase factor to be eliminated from the response function analysis. It also allows the response of the MCSCF wave function to a perturbation to be determined by requiring Ehrenfest's theorem to be satisfied in each order of the perturbation. The MCSCF response functions are therefore determined by solving the equations for the exact response functions in a subspace spanned by the operators describing the time development of the MCSCF state. We note that the

MCSCF results in the limit where the perturbation is frequency independent becomes the ones of a time independent variational calculation.⁵¹

When explicit unitary exponential transformations are used to derive time-dependent and time-independent perturbation theory, considerations related to the normalization condition and to the phase factor are avoided. In our opinion the standard textbook treatment of perturbation theory is simplified significantly and becomes more lucid if carried out using explicit unitary exponential transformations.

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APPENDIX: THE TIME DERIVATIVE OF A BAKER-CAMPBELL-HAUSDORF EXPANSION

The Baker–Campbell–Hausdorff (BCH) expansion formula is

$$e^{-iA} B e^{iA} = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} (\hat{A}^n B), \quad (A1)$$

where \hat{A} is the superoperator which is defined as

$$\hat{A}B = [A, B]. \quad (A2)$$

We will in this Appendix derive a compact expression for the time derivative of the BCH formula in Eq. (A1).

To do this it is convenient first to derive a formula for the time derivative of an exponential operator²⁰

$$\begin{aligned} \frac{\partial}{\partial \tau} e^{iA(\tau)} \Big|_{\tau=t} &= \lim_{\delta \rightarrow 0} \frac{1}{\delta} (e^{iA(t+\delta)} - e^{iA(t)}) \\ &= \lim_{\delta \rightarrow 0} \frac{1}{\delta} (e^{i[A(t)+\hat{A}(t)\delta]} - e^{iA(t)}). \end{aligned} \quad (A3)$$

Through first order in δ ,

$$\begin{aligned} e^{i[A(t)+\hat{A}(t)\delta]} - e^{iA(t)} &= \int_0^1 dz \frac{d}{dz} (e^{i\{[A(t)+\hat{A}(t)\delta]z\}} e^{-i[A(t)z]} e^{iA(t)}) \\ &= i\delta \int_0^1 dz (e^{iA(t)z} \hat{A}(t) e^{-iA(t)z}) e^{iA(t)} \\ &= i\delta \int_0^1 dz \left(\sum_{n=0}^{\infty} \frac{(iz)^n}{n!} [\hat{A}^n(t) \hat{A}(t)] \right) e^{iA(t)} \\ &= \delta \sum_{n=0}^{\infty} \frac{i^{(n+1)}}{(n+1)!} [\hat{A}^n(t) \hat{A}(t)] e^{iA(t)}. \end{aligned} \quad (A4)$$

We thus have from Eq. (A3),

$$\frac{\partial}{\partial t} e^{iA(t)} = \sum_{n=0}^{\infty} \frac{i^{n+1}}{(n+1)!} [\hat{A}^n(t) \hat{A}(t)] e^{iA(t)}. \quad (A5)$$

In the following, all time-dependent operators have the same time argument t , and for notational convenience we drop the explicit time references.

In the same way as in Eqs. (A3)–(A5) we obtain

$$\frac{\partial}{\partial t} e^{-iA} = -e^{-iA} \sum_{n=0}^{\infty} \frac{(i)^{n+1}}{(n+1)!} (\hat{A}^n \dot{A}). \quad (\text{A6})$$

The time derivative of the operator of Eq. (A1) can now be evaluated

$$\begin{aligned} \frac{\partial}{\partial t} (e^{-iA} B e^{iA}) &= e^{-iA} \dot{B} e^{iA} + \left(\frac{\partial}{\partial t} e^{-iA} \right) B e^{iA} + e^{-iA} B \left(\frac{\partial}{\partial t} e^{iA} \right) \\ &= e^{-iA} \dot{B} e^{iA} + e^{-iA} \left[B, \sum_{n=0}^{\infty} \frac{(i)^{n+1}}{(n+1)!} (\hat{A}^n \dot{A}) \right] e^{iA}. \end{aligned} \quad (\text{A7})$$

Introducing the BCH expansion of Eq. (A1) into Eq. (A7) and collecting terms of equal order in A , we obtain

$$\begin{aligned} \frac{\partial}{\partial t} (e^{-iA} B e^{iA}) &= \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} (\hat{A}^n \dot{B}) + \sum_{n=0}^{\infty} \sum_{k=0}^n \\ &\quad \times \frac{(-1)^k (i)^{n+1}}{k!(n-k+1)!} (\hat{A}^k [B, (\hat{A}^{n-k} \dot{A})]). \end{aligned} \quad (\text{A8})$$

Substituting A with $-A$ gives

$$\begin{aligned} \frac{\partial}{\partial t} (e^{iA} B e^{-iA}) &= \sum_{n=0}^{\infty} \frac{(i)^n}{n!} (\hat{A}^n \dot{B}) + e^{iA} \left[\sum_{n=0}^{\infty} \frac{(-1)^n (i)^{n+1}}{(n+1)!} (\hat{A}^n \dot{A}), B \right] e^{-iA} \\ &= \sum_{n=0}^{\infty} \frac{(i)^n}{n!} (\hat{A}^n \dot{B}) + \sum_{n=0}^{\infty} \sum_{k=0}^n \frac{(i)^{n+1} (-1)^{n-k}}{k!(n-k+1)!} \\ &\quad \times (\hat{A}^k [(\hat{A}^{n-k} \dot{A}), B]). \end{aligned} \quad (\text{A9})$$

Equations (A7)–(A9) give the desired formulas for the time derivative of the BCH expansion.

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