Response Functions from Fourier Component Variational Perturbation Theory Applied to a Time-Averaged Quasienergy

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ABSTRACT: It is demonstrated that frequency-dependent response functions can conveniently be derived from the time-averaged quasienergy. The variational criteria for the quasienergy determines the time-evolution of the wave-function parameters and the time-averaged time-dependent Hellmann–Feynman theorem allows an identification of response functions as derivatives of the quasienergy. The quasienergy therefore plays the same role as the usual energy in time-independent theory, and the same techniques can be used to obtain computationally tractable expressions for response properties, as for energy derivatives in time-independent theory. This includes the use of the variational Lagrangian technique for obtaining expressions for molecular properties in accord with the $2n + 1$ and $2n + 2$ rules. The derivation of frequency-dependent response properties becomes a simple extension of variational perturbation theory to a Fourier component variational perturbation theory. The generality and simplicity of this approach are illustrated by derivation of linear and higher-order response functions for both exact and approximate wave functions and for both variational and nonvariational wave functions. Examples of approximate models discussed in this article are coupled-cluster, self-consistent field, and second-order Møller–Plesset perturbation theory. A discussion of symmetry properties of the response functions and their relation to molecular properties is also given, with special attention to the calculation of transition- and excited-state properties. © 1998 John Wiley & Sons, Inc. Int J Quant Chem 68: 1–52, 1998

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1. Introduction

Response theory [1–7] has become a valuable theoretical tool for accurate calculations of atomic and molecular properties. For exact theory, it is straightforward to obtain abstract expressions for molecular properties, while it is more complicated to identify computational tractable expressions in an approximate theory. Molecular properties for an approximate model can be identified based on an analogy with response theory for an exact state. From the linear response function, expressions are obtained for frequency-dependent second-order molecular properties and a pole and residue analysis gives expressions for the determination of excitation energies and transition matrix elements. The quadratic response function determines third-order molecular properties, second-order transition matrix elements and transition matrix elements between excited states, and so on. The response functions according for the response of the electronic degrees of freedom to external perturbations enter as fundamental constants in the interpretation of molecular spectroscopy experiments. An important example is the field of linear and nonlinear optics [8–16] where the fundamental molecular properties are the molecular polarizability and the first and second hyperpolarizabilities, which are determined from the linear, quadratic, and cubic response functions, respectively. It is therefore important to establish a formalism where response functions can be obtained for any approximate theory in a simple and straightforward manner.

In the time-independent limit, response functions give properties that can be obtained by differentiation of the total energy. The wide range of frequency-independent properties that are not directly related to transition processes is thus a subset of the properties that can be obtained from response theory. The determination of energy-derivative properties is, however, often discussed within a framework that is not related to response theory in spite of the similarities. For variational wave functions, the energy derivative technique gives straightforwardly expressions for molecular properties that are in accordance with Wigners $2n + 1$ rule, that is, the wave-function response to order n determines the molecular properties to order $2n + 1$. For nonvariational theories, similar simplifications can be obtained by formulating the differentiation in terms of a variational Lagrangian [17, 18]. The variational Lagrangian energy functional incorporates the equations for the wave-function parameters as constraints multiplied by Lagrangian multipliers. Similar to variational theory, a $2n + 1$ rule is obtained for wave-function parameters and the Lagrangian multipliers satisfy the stronger $2n + 2$ rule. The Lagrangian approach automatically comprises the Dalgarno–Stewart interchange theorem [19]. In quantum chemistry, the interchange technique is often employed for simplifying expressions for calculating molecular gradients for nonvariational wave functions under the name of the Handy–Schaefer Z-vector technique [20].

In this article, we developed a unified approach for the determination of response functions, covering both exact theory and approximate theory and applicable for variational as well as nonvariational models. For the latter, it becomes a straightforward generalization of the Lagrangian technique of time-independent theory. The time-dependent and time-independent cases are thus treated in similar ways and the time-dependent case gives the time-independent results in the limit of a static perturbation.

In time-dependent theory, there is no well-defined energy. However, assuming that the perturbation can be decomposed into Fourier components, the quasienergy can be introduced as the time-averaged expectation value of $H_0 - i[\partial/(\partial t)]$ over the phase-isolated time-dependent wave function. The quasienergy reduces to the usual energy in the limit of a time-independent perturbation. The variational condition for the quasienergy functional determines the time evolution of the wave function [21] and the time-averaged time-dependent Hellmann–Feynman theorem can be used to show that frequency-dependent response functions can be obtained as derivatives of the quasienergy [21–23]. The fundamental achievement in this formulation is that the variational conditions and the response functions are determined from differentiation of the same functional: the quasienergy. For perturbations periodic in time, the Fourier component variational perturbation theory is a natural extension of ordinary variational perturbation theory for time-independent properties. The well-known techniques and formulations of energy derivative theory, for

example, the $2n + 1$ and $2n + 2$ rules, carry over to the response functions using Fourier component variational perturbation theory.

The lack of a well-defined energy and variational condition in time-dependent theory has led to some confusion on how to determine the time-evolution in approximate theories and different approaches have been proposed [21, 24–30]. We follow a route leading to the time-dependent variational principle in the formulation of Langhoff et al. [21]. For perturbations periodic in time, Langhoff et al. advocated the use of a time-averaged formulation.

Some confusion has also existed about how to obtain response functions as derivatives of some generalized ''energy'' functional. It was first in the work of Sasagane et al. [7] that the correct frequency combination for the Fourier components of the field strength parameters was identified for general polychromatic perturbations. Sasagane et al. did not use time-averaging in their work but still relied on periodicity in the perturbations. The wave-function parameters were determined using the time-dependent variational principle without time-averaging. This means that the time-evolution of the approximate states was not obtained from the functional that was used for determining the response functions by differentiation. Results in agreement with the $2n + 1$ rule could therefore first be obtained after manipulations.

In this article the time-averaging is central both for the determination of the time evolution of the state and in the identification of the response functions. We find that the time-average theory is the natural extension of the time-independent theory for periodic perturbations and adequate to describe the time evolution of all observables in the presence of periodic perturbations. We may treat variational and nonvariational wave functions in the same manner. In fact, a wave function need not be defined in any rigorous sense. A definition of the quasienergy and the time-dependent parameter equations is sufficient. No complications arise from the non-Hermitian nature of the $i[\partial/(\partial t)]$ operator. This may in some sense be seen as a consequence of the close connection with the Floquet theorem [31, 32] and the extended Hilbert space approach by Sambe [33], recently also advocated by Kutzelnigg [31]. Our choice of approach was directed by (1) simplicity in the derivation of the response function, (2) clear exposition of what is **necessary** to describe the relevant physical content of the time-dependent Schrödinger equation, (3) the highest possible equivalence between the treatment of exact and approximate wave functions, (4) similarity between the treatment of variational and nonvariational wave functions, and (5) close connection to ordinary energy derivative techniques for time-independent properties. To achieve these objectives, we combined Fourier component variational perturbation theory with a quasienergy Lagrangian. The Fourier components of the wave-function parameters and the Lagrangian multipliers become, then, the variational variables and intermediates in response equations and response functions are most naturally defined in terms of partial derivatives of the quasienergy Lagrangian with respect to these variables and the perturbation strengths. This leads to a very general, compact, and mathematical transparent notation that allows one to derive expressions for response equations, response functions, transition moments, excited state properties, etc., in a formulation which is independent of the method used to obtain the wave function.

Using this approach, the derivation of response functions for exact theory as well as for approximate theories such as self-consistent field (SCF), multiconfigurational self-consistent field (MCSCF), coupled-cluster (CC), and second-order Møller-Plesset (MP2) theories become a matter of straightforward differentiation after the quasienergy Lagrangian has been defined. We derive response functions for SCF, CC, and MP2 with emphasis on the fundamental structures, symmetries, etc., of the obtained response functions. Expressions for variational methods are related to the more general expressions for nonvariational methods by straightforward simplifications.

We discuss the use of response theory techniques for the calculation of transition- and excited-state properties. Common for both variational and nonvariational methods is that the excited states are not represented by a variational wave function. However, it is demonstrated how variational Lagrangian techniques can be used to derive expressions for excited-state properties, and computationally tractable expressions are identified for the calculation of excited-state properties and transition probabilities. Particularly interesting special cases are the excited-state molecular gradients and Hessians that are important for an

efficient calculation of excited-state gradients and vibrational frequencies. Excited-state gradients for coupled-cluster theory have previously been derived in other contexts [34–36]. The Lagrangian for an excited state is another example of the strength of the variational Lagrangian technique. Here, a new carrier functional is defined by incorporating the appropriate constraints multiplied by Lagrangian multipliers and the usual Lagrangian machinery then assures that the $2n + 1$ and $2n + 2$ rules are obeyed. The definition of intermediates in terms of partial derivatives of a quasienergy Lagrangian combined with the $2n + 1$ and $2n + 2$ rules also provides the means for a flexible and computational efficient implementation.

In Section 2 we discuss general aspects of the response theory and describe the basic theory, allowing the determination of response functions using Fourier component variational perturbation theory. In Section 3, we discuss the derivation of response function in an explicit but yet not specified parametrization, and in Section 4, we apply the results to the derivation of response functions for exact and SCF response functions. In Section 5, we discuss the derivation of CC response functions as well as give a brief discussion on the evaluation of MP2 dynamic properties. In Section 6, the evaluation of molecular properties from response theory is discussed. Finally, section 7 contains some concluding remarks.

2. Response Theory for Exact and Approximate Wave Functions

2.A. RESPONSE FUNCTIONS

Consider a molecular system described by a time-independent Hamiltonian H_0 and apply a general time-dependent perturbation V^t. The time development of the wave function is determined by the time-dependent Schrödinger equation

$$H|\bar{0}\rangle = i\frac{\partial}{\partial t}|\bar{0}\rangle, \tag{2.1}$$

where

$$H = H_0 + V^t. \tag{2.2}$$

It is understood that $|\bar{0}\rangle$ is a function of time. For ease of notation, we suppress the explicit time dependency. We consider perturbations that can be described as a sum of periodic perturbations:

$$\begin{aligned} V^t &= \sum_{k=-N}^{N} \exp(-i\omega_k t) V^{\omega_k} \\ &= \sum_{k=-N}^{N} \exp(-i\omega_k t) \sum_x \varepsilon_x(\omega_k) X. \end{aligned} \tag{2.3}$$

Thus, the perturbation may contain several monochromatic oscillating perturbations V^{ω_k}, consisting of a sum of perturbation operators X and strength parameters $\varepsilon_x(\omega_k)$. The perturbation operator is Hermitian:

$$V^t = V^{t\dagger}, \tag{2.4}$$

This is fulfilled if

$$X^\dagger = X, \tag{2.5}$$

$$\omega_{-k} = -\omega_k, \tag{2.6}$$

and

$$\varepsilon_x^*(\omega_k) = \varepsilon_x(\omega_{-k}). \tag{2.7}$$

The summation index k in Eq. (2.3) runs over $2N + 1$ frequencies. When nothing else is indicated, we will assume that such summations always are from $-N$ to N as in Eq. (2.3). The strength parameters are at our disposal and we may thus treat $\varepsilon_x(\omega_k)$ and $\varepsilon_x(-\omega_k)$ as independent variables. If we express the strength parameters in terms of real and imaginary components,

$$\varepsilon_x(\omega_k) = \varepsilon_x^R(\omega_k) + i\varepsilon_x^I(\omega_k). \tag{2.8}$$

The pairing of frequencies in Eq. (2.7) gives that the periodic perturbation in Eq. (2.3) can be written as

$$\begin{aligned} V^t &= \sum_x \varepsilon_x(0) X \\ &\quad + \sum_{k=1}^{N} (\exp(-i\omega_k t) + \exp(+i\omega_k t)) \\ &\quad \times \sum_x \varepsilon_x^R(\omega_k) X \\ &\quad + i \sum_{k=1}^{N} (\exp(-i\omega_k t) - \exp(+i\omega_k t)) \\ &\quad \times \sum_x \varepsilon_x^I(\omega_k) X \\ &= \sum_x \varepsilon_x(0) X + 2 \sum_{k=1}^{N} \cos(\omega_k t) \sum_x \varepsilon_x^R(\omega_k) X \\ &\quad + 2 \sum_{k=1}^{N} \sin(\omega_k t) \sum_x \varepsilon_x^I(\omega_k) X, \end{aligned} \tag{2.9}$$

where the sum over frequencies is now restricted to positive frequencies. The form of the perturbation (2.9) is adequate for describing the perturbations most commonly encountered in molecular physics. The first term represents the static perturbations, for example, the Fermi contact operator or static magnetic field. The next two terms describe periodic perturbations. The second term can, for example, be used to represent the perturbation from a homogeneous periodic real electric field. Equation (2.9) is also appropriate for describing optical activity [11, 37]. We have not included in the perturbation operator any switching functions, since we have assumed that these converged to unity. Furthermore, no terms depending quadratically or in higher order on the strength parameters have been included. This simplifies the equations that we derive later and the relevant perturbations of this form are usually more appropriately described by a compound strength parameter and related frequency.

Differentiating the perturbation operator in the form in Eq. (2.3) with respect to one particular strength parameter $\varepsilon_x(\omega_k)$ gives a simple periodic perturbation

$$\frac{\partial V^t}{\partial \varepsilon_x(\omega_k)} = X \exp(-i\omega_k t). \tag{2.10}$$

The sum over frequencies contains all the considered physical fields. However, we may also choose to include in the sum fields that are not among the applied physical perturbations, but are introduced with the sole purpose to simplify the identification of the response functions. It is legitimate to include these fields because the application of these fields is controlled by the strength parameters. The importance of introducing such fields will be clear later.

We may write the wave function in the phase isolated form as

$$|\bar{0}\rangle = e^{-iF(t)}|\tilde{0}\rangle, \tag{2.11}$$

where F is a function of time. The $|\tilde{0}\rangle$ wave function will, of course, in general, still be a function of time. We require that $|\tilde{0}\rangle$ reduces to the time-independent $|0\rangle$ wave function in the unperturbed limit, and Eq. (2.11) is in this limit the usual separation into a time-dependent phase and a time-independent wave function. We will later see that the phase can be related to the calculation of molecular properties as the stationary energy in time-independent theory. By introducing the ansatz in Eq. (2.11) into the time-dependent Schrödinger equation, we obtain

$$e^{-iF(t)}\left(H - i\frac{\partial}{\partial t} - \dot{F}(t)\right)|\tilde{0}\rangle = 0, \tag{2.12}$$

or, in phase isolated form,

$$\left(H - i\frac{\partial}{\partial t} - \dot{F}(t)\right)|\tilde{0}\rangle = 0. \tag{2.13}$$

Projection onto $\langle\tilde{0}|$ determines $\dot{F}(t)$ as

$$\dot{F}(t) = \left\langle \tilde{0}\middle|\left(H - i\frac{\partial}{\partial t}\right)\middle|\tilde{0}\right\rangle. \tag{2.14}$$

Before we switch on the perturbation, we assume that $|0\rangle$ is the solution to the time-independent Schrödinger equation:

$$H_0|0\rangle = E_0|0\rangle, \tag{2.15}$$

$$\langle 0|0\rangle = 1. \tag{2.16}$$

Let X be a Hermitian operator describing an observable. The time evolution of $|\tilde{0}\rangle$ can be obtained from the time-dependent Schrödinger equation and response functions may be determined by expanding the average value of X in orders of the perturbation

$$\begin{aligned}\langle X\rangle(t) &= \langle\bar{0}|X|\bar{0}\rangle = \langle\tilde{0}|X|\tilde{0}\rangle \\ &= \langle X\rangle_0 + \sum_{k_1}\exp(-i\omega_{k_1}t) \\ &\quad\times\sum_y \langle\langle X;Y\rangle\rangle_{\omega_{k_1}}\varepsilon_y(\omega_{k_1}) \\ &\quad+\frac{1}{2}\sum_{k_1,k_2}\exp\bigl(-i(\omega_{k_1}+\omega_{k_2})t\bigr) \\ &\quad\times\sum_{y,z}\langle\langle X;Y,Z\rangle\rangle_{\omega_{k_1},\omega_{k_2}}\varepsilon_y(\omega_{k_1})\varepsilon_z(\omega_{k_2}) \\ &\quad+\cdots\end{aligned} \tag{2.17}$$

We assume that X does not contain differentiation with respect to time and the reference to F therefore cancels in the expectation value. The linear response function, $\langle\langle X;Y\rangle\rangle_{\omega_{k_1}}$, the quadratic response function, $\langle\langle X;Y,Z\rangle\rangle_{\omega_{k_1},\omega_{k_2}}$, and so on are the expansion coefficients of the Fourier components. For time-independent perturbations where the frequency parameters of the perturbations are zero, Eq. (2.17) reduces to an ordinary

Taylor expansion of the static expectation value of X where the response functions $\langle\langle X;Y\rangle\rangle_0$, $\langle\langle X;Y,Z\rangle\rangle_{0,0}$ $\cdots$ are the expansion coefficients.

The complex conjugated of the expectation value in Eq. (2.17) becomes using Eqs. (2.6) and (2.7)

$$\begin{aligned}
\langle X\rangle^*(t) &= \langle X\rangle_0^* + \sum_{k_1}\exp(+i\omega_{k_1}t)\\
&\quad\times\sum_y\langle\langle X;Y\rangle\rangle^*_{\omega_{k_1}}\varepsilon_y^*(\omega_{k_1})\\
&\quad+\frac{1}{2}\sum_{k_1,k_2}\exp\bigl(+i(\omega_{k_1}+\omega_{k_2})t\bigr)\\
&\quad\times\sum_{y,z}\langle\langle X;Y,Z\rangle\rangle^*_{\omega_{k_1},\omega_{k_2}}\varepsilon_y^*(\omega_{k_1})\varepsilon_z^*(\omega_{k_2})\\
&\quad+\cdots\\
&= \langle X\rangle_0^* + \sum_{k_1}\exp(-i\omega_{k_1}t)\\
&\quad\times\sum_y\langle\langle X;Y\rangle\rangle^*_{-\omega_{k_1}}\varepsilon_y(\omega_{k_1})\\
&\quad+\frac{1}{2}\sum_{k_1,k_2}\exp\bigl(-i(\omega_{k_1}+\omega_{k_2})t\bigr)\\
&\quad\times\sum_{y,z}\langle\langle X;Y,Z\rangle\rangle^*_{-\omega_{k_1},-\omega_{k_2}}\varepsilon_y(\omega_{k_1})\varepsilon_z(\omega_{k_2})\\
&\quad+\cdots
\end{aligned}\tag{2.18}$$

The expectation value of a Hermitian operator is real. Comparing Eqs. (2.17) and (2.18) show that the response functions satisfy the following symmetry properties:

$$\langle X\rangle_0 = \langle X\rangle_0^* \tag{2.19}$$

$$\langle\langle X;Y\rangle\rangle_{\omega_{k_1}} = \langle\langle X;Y\rangle\rangle^*_{-\omega_{k_1}} \tag{2.20}$$

$$\langle\langle X;Y,Z\rangle\rangle_{\omega_{k_1},\omega_{k_2}} = \langle\langle X;Y,Z\rangle\rangle^*_{-\omega_{k_1},-\omega_{k_2}} \tag{2.21}$$

$$\langle\langle X;Y,Z,\cdots\rangle\rangle_{\omega_{k_1},\omega_{k_2},\cdots} = \langle\langle X;Y,Z,\cdots\rangle\rangle^*_{-\omega_{k_1},-\omega_{k_2},\cdots}. \tag{2.22}$$

These are fundamental symmetry properties of the response functions that are crucial for a successful determination of molecular properties from the response functions. Although well known for the response function in the special case of the frequency-dependent polarizability, the symmetry relations have been discussed in the literature only superficially for higher-order response functions. We shall return to the importance of these symmetry relations in Section 6. We may also straightforwardly impose symmetries between combined operator and frequency sets (Y,ω_{k_1}), (Z,ω_{k_2}), and (U,ω_{k_3}). We discuss the symmetry relations between combined operator-frequency sets in Section 2.C where the background is given for a more complete discussion of these symmetries.

Various routes have been followed to obtain solutions to the time-dependent Schrödinger equation and to subsequently identify the response functions. In this article, put emphasis on a route that straightforwardly can be used also when $|0\rangle$ is not an exact state [Eq. (2.15)], but one of the commonly used approximate wave-function models.

2.B. VARIATIONAL TIME-DEPENDENT THEORY

We now return to the solution of the time-dependent Schrödinger equation. In the absence of the perturbation, we find

$$\dot{F}(t) = E_0, \tag{2.23}$$

in agreement with the fact that we can take the solution of the time-dependent Schrödinger equation as

$$|\tilde{0}\rangle = e^{-iE_0t}|0\rangle. \tag{2.24}$$

In general, $\dot{F}$ is a real function of time:

$$\begin{aligned}
\dot{F}(t)^* &= \langle H\tilde{0}|\tilde{0}\rangle + \left\langle -i\frac{\partial\tilde{0}}{\partial t}\middle|\tilde{0}\right\rangle\\
&= \langle\tilde{0}|H|\tilde{0}\rangle + i\left[\frac{d\langle\tilde{0}|\tilde{0}\rangle}{dt} - \left\langle\tilde{0}\middle|\frac{\partial\tilde{0}}{\partial t}\right\rangle\right]\\
&= \left\langle\tilde{0}\middle|\left(H - i\frac{\partial}{\partial t}\right)\middle|\tilde{0}\right\rangle = \dot{F}(t),
\end{aligned}\tag{2.25}$$

since the time-dependent Schrödinger equation ensures that the norm is conserved and, therefore,

$$\frac{d}{dt}\langle\tilde{0}|\tilde{0}\rangle = \frac{d}{dt}\langle\tilde{0}|\tilde{0}\rangle = \left\langle\frac{\partial\tilde{0}}{\partial t}\middle|\tilde{0}\right\rangle + \left\langle\tilde{0}\middle|\frac{\partial\tilde{0}}{\partial t}\right\rangle = 0. \tag{2.26}$$

If the phase is known before we turn on the perturbation, for example, as given by Eq. (2.24), and if we have determined the time evolution of $|\tilde{0}\rangle$, then we can integrate $\dot{F}(t)$ and determine the absolute phase $F(t)$. The wave function that satisfies the time-dependent Schrödinger equation can,

in turn, be obtained from Eq. (2.11). Therefore, the determination of $|\tilde{0}\rangle$ and $\dot{F}(t)$ is equivalent to solving the time-dependent Schrödinger equation.

Since $\dot{F}(t)$ reduces to E_0 in the time-independent limit [Eq. (2.23)], we denote this quantity,

$$Q(t) = \dot{F}(t) = \left\langle \tilde{0} \middle| \left(H - i\frac{\partial}{\partial t} \right) \middle| \tilde{0} \right\rangle, \quad (2.27)$$

the time-dependent quasienergy. The time-dependent quasienergy is what Langhoff et al. denoted level-shift [21] and other names have been proposed [31]. $Q(t)$ was denoted quasienergy by Sasagane et al. [7], however, we reserve the term quasienergy for the time-average of $Q(t)$ in agreement with earlier work [33]. We shall see later that it is the time-averaged quasi-energy that in the deviation of response functions takes the role closest to the one of the energy in usual time-independent theory. The time-dependent quasienergy can be obtained from Eq. (2.27) once we have determined $|\tilde{0}\rangle$. We shall therefore concentrate on the determination of the $|\tilde{0}\rangle$ wave function in the remainder of this subsection. The time-dependent Schrödinger equation in the phase-isolated form becomes according to Eq. (2.13)

$$\left(H - i\frac{\partial}{\partial t} - Q \right) |\tilde{0}\rangle = 0. \quad (2.28)$$

Projecting this ansatz onto a first-order variation $|\delta\bar{0}\rangle$ of the complete wave function $|\bar{0}\rangle$ gives

$$\left\langle \delta\bar{0} \middle| \left(H - i\frac{\partial}{\partial t} - Q \right) \middle| \tilde{0} \right\rangle = 0. \quad (2.29)$$

In accordance with Eq. (2.11), we may separate the variation $|\delta\bar{0}\rangle$ into

$$|\delta\bar{0}\rangle = e^{-iF}|\delta\tilde{0}\rangle - i\delta F\, e^{iF}|\tilde{0}\rangle. \quad (2.30)$$

Since $|\delta\tilde{0}\rangle$ and δF are independent variations, we obtain by inserting Eq. (2.30) into Eq. (2.29) Frenkel's time-dependent variational principle [24]:

$$\left\langle \delta\tilde{0} \middle| \left(H - i\frac{\partial}{\partial t} - Q \right) \middle| \tilde{0} \right\rangle = 0. \quad (2.31)$$

together with the equation for Q in Eq. (2.27). From the normalization condition on $\langle\bar{0}|$,

$$\langle\bar{0}|\bar{0}\rangle = \langle\tilde{0}|\tilde{0}\rangle = 1, \quad (2.32)$$

an allowed variation of $\langle \delta\tilde{0}|$ must fulfill that

$$\langle \delta\tilde{0}|\tilde{0}\rangle + \langle\tilde{0}|\delta\tilde{0}\rangle = 0. \quad (2.33)$$

The reference to the Q can be eliminated from Eq. (2.31) if we write the allowed variations $|\delta\tilde{0}\rangle$ as

$$|\delta\tilde{0}\rangle = |\delta\tilde{0}^{\perp}\rangle + i\delta\alpha|\tilde{0}\rangle, \quad (2.34)$$

where $|\delta\tilde{0}^{\perp}\rangle$ is orthogonal to $|\tilde{0}\rangle$, and $\delta\alpha$ is real according to Eq. (2.33). From the definition of Q in Eq. (2.27), we see that in Eq. (2.31) the contribution from variations along $|\tilde{0}\rangle$ vanish and we may thus write Eqs. (2.31) and (2.33) in the equivalent forms:

$$\left\langle \delta\tilde{0}^{\perp} \middle| H - i\frac{\partial}{\partial t} \middle| \tilde{0} \right\rangle = 0 \quad (2.35)$$

and

$$\langle \delta\tilde{0}^{\perp}|\tilde{0}\rangle = 0. \quad (2.36)$$

These equations are equivalent to those of Moccia [28]. If all variational parameters have independent real and imaginary orthogonal variations, we thus have an equation similar to Eq. (2.35) with the variation $i\langle \delta\tilde{0}^{\perp}|$. These equations are equivalent to the symmetrized form of Frenkel's variation principle:

$$Re\left\langle \delta\tilde{0} \middle| H - i\frac{\partial}{\partial t} \middle| \tilde{0} \right\rangle = 0, \quad (2.37)$$

where $\langle \delta\tilde{0}^{\perp}|$ may be substituted by $i\langle \delta\tilde{0}^{\perp}|$. Using that $i\alpha\langle\tilde{0}|H - i(\partial/\partial t)|\tilde{0}\rangle$ is purely imaginary, we can reintroduce $|\tilde{0}\rangle$ and write Eq. (2.37) as

$$Re\left\langle \delta\tilde{0} \middle| \left(H - i\frac{\partial}{\partial t} \right) \middle| \tilde{0} \right\rangle = 0, \quad (2.38)$$

without any explicit requirement of the variation to be orthogonal to $|\tilde{0}\rangle$, but only the normalization requirement Eq. (2.33). The discussion of the time evolution of $|\tilde{0}\rangle$ has up to this point followed closely the one of Olsen and Jørgensen [6]. Expanding Eq. (2.38), we obtain

$$\left\langle \delta\tilde{0} \middle| \left(H - i\frac{\partial}{\partial t} \right) \middle| \tilde{0} \right\rangle + \left\langle \left(H - i\frac{\partial}{\partial t} \right)\tilde{0} \middle| \delta\tilde{0} \right\rangle = 0, \quad (2.39)$$

which may be expressed in the form of Langhoff et al. [21]:

$$\delta\left\langle \tilde{0} \middle| \left(H - i\frac{\partial}{\partial t} \right) \middle| \tilde{0} \right\rangle + i\frac{\partial}{\partial t}\langle\tilde{0}|\delta\tilde{0}\rangle = 0. \quad (2.40)$$

In the time-independent limit, Eq. (2.35) corresponds to

$$\langle \delta\tilde{0}|H|\tilde{0}\rangle = 0, \tag{2.41}$$

while Eq. (40) becomes

$$\delta\langle\tilde{0}|H|\tilde{0}\rangle = 0. \tag{2.42}$$

In the time-independent limit, Eq. (2.40) thus corresponds to the usual variational criterion, while Eq. (2.35) corresponds to projected equations which may or may not be equivalent.

The above Eqs. (2.35), (2.38), and (2.40) for the time evolution are completely general and determine the same solution to the time-dependent Schrödinger equation for a sufficiently flexible trial function. Thus, they are obviously equivalent in exact theory. In approximate theories, Eqs. (2.40) and (2.35) may determine different time evolutions, depending on whether it holds that if $\langle \delta\tilde{0}^{\perp}|$ is an allowed variation then $i\langle \delta\tilde{0}^{\perp}|$ is an allowed variation [6, 29] [due to the step from Eq. (2.35) to Eq. (2.37)]. We are here seeking a formulation that is as closely related to the usual variational formulation in time-independent theory as possible. Equation (2.42) is obviously the variational condition for the energy, and in agreement with this, we thus choose Eq. (2.40) as the appropriate time-dependent variational principle. However, while Eq. (2.42) clearly corresponds to a variational criterion in the time-independent limit, Eq. (2.40) is not, in general, the stationary criterion of a functional. In particular, it is not equivalent to requiring that the time-dependent quasienergy is variational as is easily seen in writing Eq. (2.40) as

$$\delta Q(t) + i\frac{\partial}{\partial t}\langle\tilde{0}|\delta\tilde{0}\rangle = 0. \tag{2.43}$$

So far, we have thus accomplished to separate the determination of the phase factor from the equations that determine $|\tilde{0}\rangle$ and relate the time evolution of $|\tilde{0}\rangle$ to the time-dependent variational principle. Response functions may therefore be determined from the average value of an operator X as in Eq. (2.17) without any explicit reference to the time-dependent quasienergy. This procedure has often been used to identify response functions for variational wave functions.

For static perturbation, response functions can be obtained using variational perturbation theory by differentiation of an energy or Lagrangian function. Response equations and response functions are thus determined by differentiation on the same functional, and as a consequence, the response functions are in agreement with the $2n + 1$ rule. For variational wave functions, the static response functions obtained as energy derivatives are equivalent to the ones obtained from expansion of an expectation value [Eq. (2.17)]. This follows from the time-independent Hellmann–Feynman theorem:

$$\frac{dE}{d\varepsilon} = \frac{d\langle\tilde{0}|H|\tilde{0}\rangle}{d\varepsilon} = \left\langle\tilde{0}\left|\frac{\partial H}{\partial\varepsilon}\right|\tilde{0}\right\rangle, \tag{2.44}$$

which is a trivial consequence of the variational principle in Eq. (2.42). In time-dependent theory, a similar rigorous link between derivatives of some functional and the expansion of the expectation value in Eq. (2.17) is less straightforward. We shall here investigate such a connection.

From the time-dependent variation principle, we obtain straightforwardly the time-dependent Hellmann–Feynman theorem:

$$\begin{aligned}\frac{dQ}{d\varepsilon} &= \frac{d\left\langle\tilde{0}\left|\left(H - i\frac{\partial}{\partial t}\right)\right|\tilde{0}\right\rangle}{d\varepsilon} \\ &= \left\langle\tilde{0}\left|\frac{\partial H}{\partial\varepsilon}\right|\tilde{0}\right\rangle - i\frac{\partial}{\partial t}\left\langle\tilde{0}\left|\frac{d\tilde{0}}{d\varepsilon}\right.\right\rangle.\end{aligned} \tag{2.45}$$

Considering perturbations of the form in Eq. (2.3), we find that

$$\frac{\partial H}{\partial\varepsilon_x(\omega)} = X\exp(-i\omega t), \tag{2.46}$$

where ω is the frequency for a corresponding Fourier component that is yet arbitrary. For any wave function that satisfies the time-dependent variation principle, we thus have

$$\langle\tilde{0}|X|\tilde{0}\rangle\exp(-i\omega t) = \frac{dQ(t)}{d\varepsilon_x(\omega)} + i\frac{\partial}{\partial t}\left\langle\tilde{0}\left|\frac{d\tilde{0}}{d\varepsilon_x(\omega)}\right.\right\rangle. \tag{2.47}$$

The fundamental difference between time-dependent theory and time-independent theory is seen comparing the time-dependent equations [Eqs. (2.43) and (2.45)] and the time-independent ones [Eqs. (2.42) and (2.44)]. In the time-dependent equations, the time-dependent quasienergy Q has replaced the ordinary energy E. However, the

time-dependent equations contain, in addition, one extra term consisting of the derivative $i[\partial/(\partial t)]$ of the scalar product of the wave function and wave-function variations or wave-function responses. The extra term in Eqs. (2.43) and (2.47) shows that the time-dependent quasienergy does not straightforwardly take over the role of the energy in time-dependent theory. Langhoff et al. [21] showed that the last term in Eq. (2.43) vanishes if we take the time average of this equation. Sasagane et al. [7] demonstrated that in time-dependent theory the last term in Eq. (2.47) can be eliminated by a judicious choice of the frequency ω for periodic perturbations. We consider here a time-averaged approach where the last term in Eq. (2.47) as well as the last term in Eq. (2.43) vanishes. In this way, a close connection between time-independent and time-dependent theory is established, and it comes out naturally which frequency components $\varepsilon_x(\omega)$ are required in Eq. (2.47) to determine the response functions.

2.C. TIME-AVERAGED VARIATIONAL TIME-DEPENDENT PERTURBATION THEORY

Assume that the perturbation in Eq. (2.3) contains a finite set of frequencies and a least common multiple of periods T can be determined such that the Hamiltonian is periodic in time with the period T of the perturbation:

$$V^t(t+T) = V^t(t). \tag{2.48}$$

These criteria imply that the frequencies in Eq. (2.3) are an integer times a fundamental frequency: $\omega_i = n_i\omega$, where $\omega = (2\pi)/T$. Therefore, $\omega_i/\omega_j = n_i/n_j$. This is not strictly valid for two general physical frequencies but does not pose a practical problem as n_i and n_j can be any large integer. In any case, the procedure can be used to formally identify the expression for the response functions. Introducing the time average of a function $f(t)$,

$$\{f(t)\}_T = \frac{1}{T}\int_{-T/2}^{T/2} f(t)\,dt. \tag{2.49}$$

we obtain the time average of Eqs. (2.43) and (2.47) as

$$\delta\{Q(t)\}_T = 0, \tag{2.50}$$

$$\frac{d\{Q(t)\}_T}{d\varepsilon_x(\omega)} = \left\{\langle\tilde{0}|X|\tilde{0}\rangle\exp(-i\omega t)\right\}_T. \tag{2.51}$$

In Eqs. (2.50) and (2.51), we have used that the time average of a time-differentiated periodic function $Z(t)$ is zero:

$$\left\{\frac{\partial Z(t)}{\partial t}\right\}_T = 0. \tag{2.52}$$

Equations (2.50) and (2.51) are the time-averaged analogs of Eqs. (2.43)–(2.47). Equation (2.50) is the time-averaged variational condition that determines the time evolution of $|\tilde{0}\rangle$, and Eq. (2.51) is the time-averaged Hellmann–Feynman theorem, which may be used to relate the determination of response functions to the time-averaged quasienergy $\{Q(t)\}_T$, which we shall simply denote the quasienergy [33]. We shall examine Eqs. (2.50) and (2.51) in more detail since they are the fundamental equations of the Fourier component variational perturbation theory.

Given that we consider perturbations of the form in Eq. (2.3) with a periodicity as in Eq. (2.48), we find that a similar periodicity will enter in the $|\tilde{0}\rangle$ wave function. To see this, consider, for example, Eq. (2.40) in the form

$$\delta\left\langle\tilde{0}\middle|\left(H_0 - i\frac{\partial}{\partial t}\right)\middle|\tilde{0}\right\rangle + i\frac{\partial}{\partial t}\langle\tilde{0}|\delta\tilde{0}\rangle = -\delta\langle\tilde{0}|V|\tilde{0}\rangle. \tag{2.53}$$

To order n in the perturbation V, the right-hand side only contains contributions from the $(n-1)$th and lower-order wave function, while the left-hand side also contains reference to the nth-order wave function. To first order, the wave function has the form

$$|\tilde{0}^{(1)}(t)\rangle = \sum_{k_1}|\tilde{0}^{(1)}(\omega_{k_1})\rangle\exp(-i\omega_{k_1}t). \tag{2.54}$$

It now follows from induction that the higher-order wave function will have similar structures originating from products of sum over oscillations in accordance with the perturbation in Eq. (2.3):

$$|\tilde{0}^{(2)}(t)\rangle = \sum_{k_1,k_2}|\tilde{0}^{(2)}(\omega_{k_1},\omega_{k_2})\rangle \times\exp\left(-i(\omega_{k_1}+\omega_{k_2})t\right) \tag{2.55}$$

$$|\tilde{0}^{(m)}(t)\rangle = \sum_{k_1,k_2\cdots k_m}|\tilde{0}^{(m)}(\omega_{k_1},\omega_{k_2},\cdots\omega_{k_m})\rangle \times\exp\left(-i\sum_{n=1}^{m}\omega_{k_n}t\right). \tag{2.56}$$

Thus, the mth-order wave-function response $|\tilde{0}\rangle$ is a product of factors oscillating with frequencies corresponding to the form of the perturbation in Eq. (2.3). Since it is built from products of functions with the periodicity in Eq. (2.48), the mth-order response will also be periodic with period T. Note that $|\tilde{0}\rangle$ and not $|\bar{0}\rangle$ has this periodic behavior. Since $|\tilde{0}\rangle$ is periodic to all orders in V with a similar periodicity as V, it may be expanded in terms of Fourier components similar to the perturbation in Eq. (2.3). We may further separate the contributions from the time-dependent variational principle in Eq. (2.43) into a zero-phase part and an oscillating part. The zero-phase part is the time-averaged form in Eq. (2.50). The remainder vanish when we take the time average. This remainder is not necessary for determining the time evolution of $|\tilde{0}\rangle$. An order-by-order expansion of the zero-phase part will include to higher and higher order all the Fourier components of the perturbed wave function and is sufficient to uniquely determine these Fourier components. Since we showed above that $|\tilde{0}\rangle$ has the oscillatory form in Eqs. (2.54)–(2.56), we thus have that the time-averaged time-dependent variational condition is sufficient to determine the correct time evolution of $|\tilde{0}\rangle$ in the case of periodic perturbations. The time-dependent quasienergy can then be obtained from Eq. (2.27) and we have the complete solution to our problem.

Response functions are conveniently identified from Eq. (2.51) as we will now demonstrate. At this stage, it is appropriate to return to the discussion of the form of the perturbation in Eq. (2.3). As stated previously, we may include in the expansion perturbations that are convenient for the derivation of response functions. We therefore also include the field X with frequency ω_0 corresponding to the sum of a number of frequencies for the perturbations in Eq. (2.3). In this way, X may be treated with a similar basis at the other perturbations. Inserting expansion Eq. (2.17) that defines the response functions into Eq.(2.51) gives

$$\frac{d\{Q(t)\}_T}{d\varepsilon_x(\omega)} = \langle X \rangle + \sum_y \sum_{k_1} \langle\langle X; Y \rangle\rangle_{\omega_{k_1}} \times \varepsilon_y(\omega_{k_1})\delta(\omega + \omega_{k_1}) + \frac{1}{2}\sum_{y,z}\sum_{k_1,k_2} \langle\langle X; Y, Z \rangle\rangle_{\omega_{k_1},\omega_{k_2}} \times \varepsilon_y(\omega_{k_1})\varepsilon_z(\omega_{k_2})\delta(\omega + \omega_{k_1} + \omega_{k_2}) + \cdots, \tag{2.57}$$

where the symbol $\delta(\omega)$ means a factor of one, if $\omega = 0$ and zero otherwise. The response functions can thus be identified as derivatives of the quasienergy as follows:

$$\langle X \rangle = \frac{d\{Q\}_T}{d\varepsilon_x(0)}, \tag{2.58}$$

$$\langle\langle X; Y \rangle\rangle_{\omega_{k_1}} = \frac{d^2\{Q\}_T}{d\varepsilon_x(\omega_0)\, d\varepsilon_y(\omega_{k_1})}; \quad \omega_0 = -\omega_{k_1}, \tag{2.59}$$

$$\langle\langle X; Y, Z \rangle\rangle_{\omega_{k_1},\omega_{k_2}} = \frac{d^3\{Q\}_T}{d\varepsilon_x(\omega_0)\, d\varepsilon_y(\omega_{k_1})\, d\varepsilon_z(\omega_{k_2})}; \quad \omega_0 = -\omega_{k_1} - \omega_{k_2}, \tag{2.60}$$

$$\langle\langle X; Y, Z, \cdots \rangle\rangle_{\omega_{k_1},\omega_{k_2},\ldots} = \frac{d^{n+1}\{Q\}_T}{d\varepsilon_x(\omega_0)\, d\varepsilon_y(\omega_{k_1})\, d\varepsilon_z(\omega_{k_2})\cdots}; \quad \omega_0 = -\sum_{i=1}^{n} \omega_{k_i}. \tag{2.61}$$

We note that it is the time average of $\langle\tilde{0}|X|\tilde{0}\rangle \exp(-i\omega t)$ that provides us with the possibility to identify response functions from the quasienergy and dictates which frequency ω of $\varepsilon_x(\omega)$ can contribute to each order. If we instead had chosen to expand the time-averaged expectation value $\{\langle\tilde{0}|X|\tilde{0}\rangle\}_T$, we could not have obtained response functions with general frequency indices, but would have the restriction $0 = \sum_{i=1} \omega_{k_i}$ on the frequency indices for the response functions. The time average of $\langle\tilde{0}|X|\tilde{0}\rangle\exp(-i\omega t)$ gives the connection to the quasienergy through the time-dependent Hellmann–Feynman theorem. The physical interesting part of the time-dependent quasienergy, that is, the part that determines the response functions and thus all observables, is obtained to each order by taking the frequency ω of the ''measured'' response to be minus the sum of the ''external'' perturbations. To derive the nth-order response function describing the nth-order response of the expectation value of X, the appropriate choice of frequency ω of $\varepsilon_x(\omega)$ is

$$\omega_0 = -\sum_{i=1}^{n} \omega_{k_i}, \tag{2.62}$$

where ω_{k_i} is the frequency of the ith perturbation.

The derivative expressions for the response functions show that there exist permutational symmetry between operators and related frequencies. For the linear response function, Eq. (2.59) gives the symmetry relation

$$\langle\langle X, Y \rangle\rangle_{\omega} = \langle\langle Y, X \rangle\rangle_{-\omega}. \tag{2.63}$$

Similar symmetry relations hold for the higher-order response functions as a consequence of identifying the response functions by the differentiation's in Eqs. (2.59)–(2.61). For the quadratic response function,

$$\begin{aligned}
&\langle\langle X, Y, Z \rangle\rangle_{\omega_{k_1}, \omega_{k_2}} \\
&\quad = \langle\langle Z, X, Y \rangle\rangle_{-\omega_{k_1}-\omega_{k_2}, \omega_{k_1}} \\
&\quad = \langle\langle X, Z, Y \rangle\rangle_{\omega_{k_2}, \omega_{k_1}} \\
&\quad = \langle\langle Z, Y, X \rangle\rangle_{\omega_{k_1}, -\omega_{k_1}-\omega_{k_2}} \\
&\quad = \langle\langle Y, X, Z \rangle\rangle_{-\omega_{k_1}-\omega_{k_2}, \omega_{k_2}} \\
&\quad = \langle\langle Y, Z, X \rangle\rangle_{\omega_{k_2}, -\omega_{k_1}-\omega_{k_2}}.
\end{aligned} \tag{2.64}$$

In general, permutational symmetry exists between the operators and associated frequencies:

Operator:	X	Y	Z	U	$\cdots$
Frequency:	ω_0	ω_{k_1}	ω_{k_2}	ω_{k_3}	$\cdots$

Interchanging, for example, (X, ω_0) with (Y, ω_{k_1}) gives the same response function. It is cumbersome to obtain these underlying symmetry relations from the response functions when they are determined from the average value of X; see, for example, [6]. Identifying the response functions as derivatives of the quasienergy, we obtain these symmetry relations straightforwardly, and we see clearly how they arise as the Fourier component generalizations of the corresponding symmetry relations of time-independent theory.* The use of derivative expressions guarantees these symmetry relations for both exact response functions and for approximate models.

From Eqs. (2.23) and (2.57), it follows that the quasienergy can be written

$$\begin{aligned}
\{Q\}_T = E_0 &+ \sum_x \langle X \rangle \varepsilon_x(0) \\
&+ \frac{1}{2} \sum_{x,y} \sum_{k_1} \langle\langle X; Y \rangle\rangle_{\omega_{k_1}} \varepsilon_x(-\omega_{k_1}) \varepsilon_y(\omega_{k_1}) \\
&+ \frac{1}{6} \sum_{x,y,z} \sum_{k_1,k_2} \langle\langle X; Y, Z \rangle\rangle_{\omega_{k_1}, \omega_{k_2}} \\
&\times \varepsilon_x(-\omega_{k_1} - \omega_{k_2}) \varepsilon_y(\omega_{k_1}) \varepsilon_z(\omega_{k_2}) \\
&+ \cdots.
\end{aligned} \tag{2.65}$$

According to Eq. (2.25), the quasienergy is real for an exact state. If we take the complex conjugate of Eq. (2.65), we see that the real nature of the quasienergy is directly related to the symmetry relations of the response functions in Eqs. (2.19)–(2.22):

$$\begin{aligned}
\{Q^*\}_T = \{Q\}_T^* &= E_0 + \sum_x \langle X \rangle^* \varepsilon_x(0) \\
&+ \frac{1}{2} \sum_{x,y} \sum_{k_1} \langle\langle X; Y \rangle\rangle^*_{-\omega_{k_1}} \varepsilon_x(-\omega_{k_1}) \varepsilon_y(\omega_{k_1}) \\
&+ \frac{1}{6} \sum_{xyz} \sum_{k_1,k_2} \langle\langle X; Y, Z \rangle\rangle^*_{-\omega_{k_1}, \omega_{k_2}} \\
&\times \varepsilon_x(-\omega_{k_1} - \omega_{k_2}) \varepsilon_y(\omega_{k_1}) \varepsilon_z(\omega_{k_2}) \\
&+ \cdots \\
&= \{Q\}_T.
\end{aligned} \tag{2.66}$$

To obtain Eq. (2.66), we used Eqs. (2.6) and (2.7) and the symmetry relations in Eqs. (2.19)–(2.22). The symmetry relations in Eqs. (2.19)–(2.22) and the fact that the quasienergy is real are, of course, trivial in exact theory. However, they will not automatically be fulfilled in an approximate theory. Assume, for example, that we have the more general form for Q:

$$Q(t) = \frac{\left\langle \tilde{0}_1 \middle| \left(H - i\frac{\partial}{\partial t} \right) \middle| \tilde{0}_2 \right\rangle}{\langle \tilde{0}_1 | \tilde{0}_2 \rangle}. \tag{2.67}$$

This type of form is relevant for deriving response functions for CC and Møller–Plesset perturbation theory. When $0_1 = 0_2$ where the ''left wave function'' is equal to the ''right wave function,'' we obtain the usual expression Eq. (2.27), where we, in addition, explicitly have taken care of the normalization in Eq. (2.67). We note that when $0_1 = 0_2$ the imaginary part of the quasienergy can be written as

$$\mathrm{Im}[\,Q(t)] = -\frac{1}{2} \frac{\partial}{\partial t} \left(\ln \langle \tilde{0}_1 | \tilde{0}_1 \rangle \right). \tag{2.68}$$

*A point of interest in some special situations is that the symmetric form for the cubic and higher-order response functions may have extra poles at certain frequencies; see for example, the expressions for the cubic response functions in [6].

Thus, even if the wave function is not normalized as was assumed in deriving Eq. (2.25), the quasienergy is real:

$$\{Q(t)\}_T = \{\mathrm{Re}[Q(t)]\}_T. \tag{2.69}$$

In variational theories, $0_1 = 0_2$ and the quasienergy is real. The symmetry relations in Eqs. (2.19)–(2.22) are therefore fulfilled. For some nonvariational methods (not all), $0_1 \neq 0_2$ and we are not ensured that the quasienergy is real. This problem is not confined to time-dependent theory. For example, if we have complex functions in a time-independent theory, for example, due to magnetic perturbations, then the energy evaluated from Eq. (2.67) is not real even in the static limit. In time-dependent theory, this asymmetry, $0_1 \neq 0_2$, has, as a consequence, that the quasienergy is not necessarily real and that the fundamental symmetry relations in Eqs. (2.19)–(2.22) are not fulfilled. Since the symmetry relations are necessary to have a real expansion of the expectation value of a Hermitian operator, they are crucial for a meaningful identification of physical properties. (See also the discussion in Section 6.) We must therefore enforce these symmetry relations explicitly if they are not straightforwardly satisfied. This can be done in several ways: One way is simply to ignore this artifact in the derivation of response functions and identify the response functions as derivatives of the quasienergy as indicated up to this point. The expansion in Eq. (2.17) may then have a complex part while only the real part has a physical significance. Accordingly, the true response properties may be determined from the symmetrizations,

$$\langle X \rangle_0 \leftarrow \frac{1}{2}(\langle X \rangle_0 + \langle X \rangle_0^*), \tag{2.70}$$

$$\langle\langle X; Y \rangle\rangle_{\omega_{k_1}} \leftarrow \frac{1}{2}\left(\langle\langle X; Y \rangle\rangle_{\omega_{k_1}} + \langle\langle X; Y \rangle\rangle^*_{-\omega_{k_1}}\right), \tag{2.71}$$

$$\langle\langle X; Y, Z \rangle\rangle_{\omega_{k_1}, \omega_{k_2}} \leftarrow \frac{1}{2}\left(\langle\langle X; Y, Z \rangle\rangle_{\omega_{k_1}, \omega_{k_2}} + \langle\langle X; Y, Z \rangle\rangle^*_{-\omega_{k_1}, -\omega_{k_2}}\right), \tag{2.72}$$

$$\langle\langle X; Y, Z, \cdots \rangle\rangle_{\omega_{k_1}, \omega_{k_2}} \leftarrow \frac{1}{2}\left(\langle\langle X; Y, Z, \cdots \rangle\rangle_{\omega_{k_1}, \omega_{k_2} \cdots} + \langle\langle X; Y, Z \rangle\rangle^*_{-\omega_{k_1}, -\omega_{k_2}, \cdots}\right), \tag{2.73}$$

which are the analogs to what is done in the time-independent theory by taking only the real part of the energy

$$E \leftarrow \frac{1}{2}(E + E^*). \tag{2.74}$$

If a new quasienergy is constructed from Eq. (2.65) using these symmetrized response functions, this new quasienergy will be real. The symmetrizations of the response functions will in the state limit give properties that are consistent with the finite-field results of the symmetrized energy in Eq. (2.74).

An equivalent approach to obtain symmetrized response functions is to require the quasienergy to be real from the outset. Since the quasienergy is real in exact theory, this gives an equally valid analogy between exact theory and approximate theory. The fundamental equations become in this case

$$\delta\{\mathrm{Re}\, Q(t)\}_T = 0 \tag{2.75}$$

$$\frac{d\{\mathrm{Re}\, Q(t)\}_T}{d\varepsilon_x(\omega)} = \{\langle X \rangle(t)\exp(-i\omega t)\}_T. \tag{2.76}$$

This starting point automatically introduces the symmetrizations of the response functions in Eqs. (2.70)–(2.73). However, it also introduces many complex conjugate terms in the derivation, which has as only consequence to enforce the symmetrizations in Eqs. (2.70)–(2.73). It is also important to note that taking the real part does not mean taking the real part of each term since the response functions themselves do not have to be real in general. We wish to emphasize again that the lacking symmetries of the response functions are artifacts of our approximation and consequences of a different ''left wave function'' and ''right wave function.'' Although this, of course, is an indication of the inappropriateness of using the term ''wave function'' in this case, it may be convenient for the discussion of molecular properties first to determine the original asymmetric response functions. This corresponds to determining directly the expansion coefficients in the original expansion of the expectation value in Eq. (2.17). In obtaining the final expressions for the response properties, the appropriate symmetrization should then be applied. Although other theoretical work have used the explicitly enforced real quasienergy approach [21, 38–40], it is more standard to work with the

original expressions Eqs. (2.17) and (2.65). For these reasons, we shall continue to use the original form for the quasienergy in our derivations, but enforce the symmetrizations in Eqs. (2.70)–(2.73) when necessary.

We note that Eq. (2.65) is completely analogous with the energy expansion in time-independent perturbation theory. If we restrict the expansion in Eq. (2.3) to perturbations of zero frequencies, we obtain

$$\begin{aligned}\{Q\}_T = E_0 &+ \sum_x \langle X \rangle \varepsilon_x(0) \\ &+ \frac{1}{2} \sum_{x,y} \langle\langle X, Y \rangle\rangle_0 \varepsilon_x(0) \varepsilon_y(0) \\ &+ \frac{1}{6} \sum_{x,y,z} \langle\langle X, Y, Z \rangle\rangle_{0,0} \varepsilon_x(0) \varepsilon_y(0) \varepsilon_z(0) \\ &+ \cdots \end{aligned} \tag{2.77}$$

In this case, we have that

$$\{Q\}_T = Q = E(\varepsilon), \tag{2.78}$$

where $E(\varepsilon)$ is the usual energy depending on some frequency-independent strength parameters. In this case, it is obvious how the symmetry relations come about since they correspond to interchanges of the order of differentiation:

$$\langle\langle X; Y \rangle\rangle_0 = \frac{d^2E(\varepsilon)}{d\varepsilon_x(0)\, d\varepsilon_y(0)} = \frac{d^2E(\varepsilon)}{d\varepsilon_y(0)\, d\varepsilon_x(0)}. \tag{2.79}$$

The symmetries of the frequency-independent response function correspond to simple permutations of operators X, Y, Z, etc., and are special cases of the symmetry relations for frequency-dependent response functions, where the symmetries are generalized to permutations of operators and associated frequencies: (X, ω_0), (Y, ω_{k_1}), (Z, ω_{k_2}), etc. If only the operators are interchanged, a different frequency-dependent property is obtained. For example,

$$\langle\langle X; Y, Z \rangle\rangle_{\omega_{k_1}, \omega_{k_2}} \neq \langle\langle X; Z, Y \rangle\rangle_{\omega_{k_1}, \omega_{k_2}}, \tag{2.80}$$

when Y and Z are different operators and ω_{k_1} and ω_{k_2} are different frequencies. If this difference is neglected and the inequality is replaced by an equality, the response functions are assumed to have the so-called Kleinman symmetry. This approximation may be reasonably for very small frequencies but can, in general, not be recommended [6].

3. Response Theory for an Explicit Parameterization

In this section, we derive response functions for a model that depend explicitly on some parameters, but where the explicit dependency is not specified. The derivation is carried out at an abstract level to make apparent the similarities between different models, as well as the general differences between variational and nonvariational approaches. For the non-variational models, we use a Lagrangian technique similar to the one used by Helgaker and Jørgensen for obtaining energy-derivatives of nonvariational energies in time-independent theory [17, 18]. This allows variational and nonvariational models to be treated very similarly. The general expressions that we derive are used in the following sections to obtain expressions for response functions in exact theory and in SCF, CC, and MP2 theory. However, we emphasize that the obtained expressions can be used for any model that has a well-defined quasienergy and where the determination of the parameters is specified in a unique way.

2.A. FOURIER DECOMPOSITION OF PARAMETERS AND QUASIENERGY

We denote the parameters in our model commonly as λ and we assume that the time-dependent quasienergy ($Q(\lambda, \dot{\lambda})$) and the time-dependent equations [$e(\lambda, \dot{\lambda}) = 0$] are functions of these parameters and their time derivative. We introduce accordingly the time-dependent Lagrangian

$$L(\lambda, \dot{\lambda}, \bar{\lambda}) = Q(\lambda, \dot{\lambda}) + \bar{\lambda} e(\lambda, \dot{\lambda}), \tag{3.1}$$

where $\bar{\lambda}$ are time-dependent Lagrangian multipliers. Variational wave functions are treated as the special case where $\bar{\lambda} = 0$. A comment on the notation is in place. Throughout the remainder of this article, we use normal types for vectors, while bold face is preserved for matrices and supermatrices. We use a supermatrix notation where vectors and matrices are multiplied in order—thus, $\bar{\lambda}\mathbf{B}\lambda^1\lambda^2$ denotes the scalar $\sum_{ijk} \bar{\lambda}_i B_{ijk} \lambda^1_j \lambda^2_k$. We use bars to denote multiplier vectors. In accord with the discussion in the preceding sections, we proceed to the time-averaged formalism and derive the response functions using Fourier component varia-

tional perturbation theory. The parameters are expanded in orders of the periodic perturbation,

$$\lambda(t) = \lambda^{(0)} + \lambda^{(1)}(t) + \lambda^{(2)}(t) + \cdots, \quad (3.2)$$

$$\bar{\lambda}(t) = \bar{\lambda}^{(0)} + \bar{\lambda}^{(1)}(t) + \bar{\lambda}^{(2)}(t) + \cdots, \quad (3.3)$$

where the zeroth-order parameters do not depend on the perturbation. The higher-order parameters are expanded in the Fourier components of the perturbation in Eq. (2.3).

$$\lambda^{(1)}(t) = \sum_{k_1=-N}^{N} \exp(-i\omega_{k_1} t)\lambda^{(1)}(\omega_{k_1}), \quad (3.4)$$

$$\lambda^{(2)}(t) = \sum_{k_1, k_2=-N}^{N} \exp\left(-i(\omega_{k_1} + \omega_{k_2})t\right) \times \lambda^{(2)}(\omega_{k_1}, \omega_{k_2}), \quad (3.5)$$

and so on. The Fourier components depend on the perturbation-strength parameters,

$$\lambda^{(1)}(\omega_{k_1}) = \sum_x \varepsilon_x(\omega_{k_1})\lambda^X(\omega_{k_1}), \quad (3.6)$$

$$\lambda^{(2)}(\omega_{k_1}, \omega_{k_2}) = \frac{1}{2}\sum_{x,y} \varepsilon_X(\omega_{k_1})\varepsilon_Y(\omega_{k_2}) \times \lambda^{XY}(\omega_{k_1}, \omega_{k_2}). \quad (3.7)$$

Similar expressions are introduced for the multipliers. Instead of the Fourier decomposition in Eqs. (3.2)–(3.5), we may alternatively write the λ parameters as a sum over possible frequency combinations:

$$\lambda(t) = \sum_I \exp(-i\omega_I t)\lambda(\omega_I), \quad (3.8)$$

where

$$\lambda(\omega_I) = \sum_{k_1=-N}^{N} \lambda^{(1)}(\omega_{k_1})\delta(\omega_{k_1} - \omega_I) + \sum_{k_1, k_2=-N}^{N} \lambda^{(2)}(\omega_{k_1}, \omega_{k_2}) \times \delta(\omega_{k_1} + \omega_{k_2} - \omega_I) + \cdots \quad (3.9)$$

The Fourier coefficients $\lambda(\omega_I)$ do not explicitly refer to any specific order but only to the sum of the involved frequencies. This notation is convenient in some cases.

In variational perturbation theory for a time-independent perturbation, the change of variables from field-dependent variables $\lambda(\varepsilon)$ to the variables in each order of the perturbation $\lambda^{(1)}, \lambda^{(2)}, \lambda^{(3)} \cdots$, is carried out in one step. In Fourier component variational perturbation theory, the corresponding change of variables is carried out in two steps: First, the introduction of the time average implies a shift from the time-dependent variables and their derivatives with respect to time, $\lambda(t, \varepsilon)$, $\dot{\lambda}(t, \varepsilon)$, to the Fourier components $\lambda^{(1)}(\omega_1, \varepsilon)$, $\lambda^{(2)}(\omega_1, \omega_2, \varepsilon) \cdots$ [or the set of $\lambda(\omega_I, \varepsilon)$ parameters]. These parameters depend on the field strengths, here explicitly written out as a functional dependency of ε, and are the analogs to $\lambda(\varepsilon)$ in time-independent theory. Second, we introduce the parameter responses $\lambda^Y(\omega_1)$, $\lambda^{YZ}(\omega_1, \omega_2), \cdots$ to the specific perturbations. These parameters do not depend on the field strengths as they are defined as derivatives taken for zero-field strengths. They are, thus, the analogs to the $\lambda^{(1)}, \lambda^{(2)}, \lambda^{(3)}$ parameters of time-independent theory.

We now proceed to derive the response functions from Fourier component variational perturbation theory by carrying out an expansion of the quasienergy Lagrangian similar to the one just described for the parameters

$$L(t) = L^{(0)} + L^{(1)}(t) + L^{(2)}(t) + L^{(3)}(t) + L^{(4)}(t) + \cdots \quad (3.10)$$

We obtain the time-averaged quasienergy Lagrangian to each order as

$$\{L^{(0)}\}_T = L^{(0)}(0), \quad (3.11)$$

$$\{L^{(1)}\}_T = \sum_x \varepsilon_x(0)L^X(0), \quad (3.12)$$

$$\{L^{(2)}\}_T = \frac{1}{2}\sum_{k_1}\sum_{x,y} \varepsilon_X(\omega_0)\varepsilon_Y(\omega_{k_1})L^{XY}(\omega_0, \omega_{k_1}); \quad \omega_0 = -\omega_{k_1}, \quad (3.13)$$

$$\{L^{(3)}\}_T = \frac{1}{6}\sum_{k_1,k_2}\sum_{x,y,z} \varepsilon_X(\omega_0)\varepsilon_Y(\omega_{k_1})\varepsilon_Z(\omega_{k_2}) \times L^{XYZ}(\omega_0, \omega_{k_1}, \omega_{k_2}); \quad \omega_0 = -(\omega_{k_1} + \omega_{k_2}), \quad (3.14)$$

$$\{L^{(4)}\}_T = \frac{1}{24} \sum_{k_1,k_2,k_3} \sum_{x,y,z,u} \varepsilon_X(\omega_0)\varepsilon_Y(\omega_{k_1}) \times \varepsilon_Z(\omega_{k_2})\varepsilon_U(\omega_{k_3}) \times L^{XYZU}(\omega_0, \omega_{k_1}, \omega_{k_2}, \omega_{k_3}); \quad \omega_0 = -(\omega_{k_1} + \omega_{k_2} + \omega_{k_3}). \quad (3.15)$$

Note that the $L^{(n)}(t)$, in general, contain a summation over n frequencies and that this sum is reduced to a sum over $n-1$ frequencies when the time averaging is carried out. The parameter responses are determined from the variational criterion

$$\delta\{L\}_T = 0, \quad (3.16)$$

which in the Fourier component variational perturbation theory becomes variational criteria for the Fourier components of the quasienergy Lagrangians $L^{(0)}$, $L^X(0)$, $L^{XY}(\omega_0, \omega_{k_1})$, $L^{XYZ}(\omega_0, \omega_{k_1}, \omega_{k_2})$, and $L^{XYZU}(\omega_0, \omega_{k_1}, \omega_{k_2}, \omega_{k_3})$ with respect to variations in the parameter and multiplier responses. When the variational equations have been solved, the Fourier components of the quasienergy Lagrangian become equal to the response functions as is clear from Eqs. (2.57)–(2.61). The response functions are thus determined as derivatives of $\{L^{(n)}\}_T$ with respect to the field-strength variables $\varepsilon_y(\omega_Y)$; for example, the linear response functions become

$$\langle\langle X; Y \rangle\rangle_{\omega_{k_1}} = \frac{d^2\{L^{(2)}\}_T}{d\varepsilon_x(\omega_0)\, d\varepsilon_y(\omega_{k_1})}; \quad \omega_0 = -\omega_{k_1}. \quad (3.17)$$

The response functions can be obtained in a form that satisfies the $2n+1$ rule for the wave-function parameters λ and the $2n+2$ rule for the multipliers $\bar{\lambda}$. This is shown explicitly in a later subsection. We used the nomenclature $L^{(0)}$, $L^X(0)$, $L^{XY}(\omega_0, \omega_{k_1})$, etc., for the immediately obtained Fourier components of the quasienergy and where the simplifications due to $2n+1$ and $2n+2$ rules have not been introduced. In the final expressions for the response functions $\langle\langle X; Y, \cdots \rangle\rangle_{\omega_{k_1}, \cdots}$, we assume that the response equations have been solved and the $2n+1$ and $2n+2$ rules may then be used to simplify these expressions. In the following subsections, we demonstrate this for the low-order Lagrangians $\{L^{(0)}\}_T$, $\{L^{(1)}\}_T$, and $\{L^{(2)}\}_T$ and show how the physical content can be extracted: the energy from $\{L^{(0)}\}_T$, average values from $\{L^{(1)}\}_T$, and second-order molecular properties from $\{L^{(2)}\}_T$. We later prove the $2n+1$ and $2n+2$ rules for general frequency-dependent response functions.

3.B. THE ZEROTH-ORDER LANGRANGIAN

The zeroth-order Lagrangian becomes

$$L^{(0)}(\lambda^{(0)}, \bar{\lambda}^{(0)}) = E^{(0)}(\lambda^{(0)}) + \bar{\lambda}^{(0)} e^{(0)}(\lambda^{(0)}), \quad (3.18)$$

where we have used that in the zeroth-order limit the quasienergy reduces to the usual total energy $E^{(0)}$. The variational condition with respect to the zeroth-order Lagrangian multipliers gives the equation for the zeroth-order parameters $\lambda^{(0)}$:

$$0 = \frac{\partial L^{(0)}(\lambda^{(0)}, \bar{\lambda}^{(0)})}{\partial \bar{\lambda}^{(0)}} = e^{(0)}(\lambda^{(0)}). \quad (3.19)$$

This ensures that the usual energy is obtained in the zeroth-order limit. The variational condition for the $\lambda^{(0)}$ parameters determines the zeroth-order multipliers

$$0 = \frac{\partial L^{(0)}(\lambda^{(0)}, \bar{\lambda}^{(0)})}{\partial \lambda^{(0)}} = \frac{\partial E^{(0)}(\lambda^{(0)})}{\partial \lambda^{(0)}} + \bar{\lambda}^{(0)} \frac{\partial e^{(0)}(\lambda^{(0)})}{\partial \lambda^{(0)}}. \quad (3.20)$$

The unperturbed reference parameters $\lambda^{(0)}$ are required to calculate the energy and all other properties. The zeroth-order multipliers are required to calculate all ground-state properties except the energy. We do not need to calculate the unperturbed energy from Eq. (3.18), but may calculate it from $E^{(0)}(\lambda^{(0)})$. The use of the variational functional is a great advantage for all properties except the ground-state energy. The zeroth-order multipliers in the Lagrangian formalism are the analog of the so-called Z-vector in the interchange technique for calculation of analytical first derivatives of nonvariational energies [19, 20]. In the Lagrangian approach, the Z-vector arises automatically without resorting to the interchange technique.

Variational theory becomes the special case of the nonvariational theory where the second term in Eq. (3.20) vanishes. We obtain the standard variational criterion for the unperturbed parame-

ters $\lambda^{(0)}$:

$$0 = \frac{\partial E^{(0)}(\lambda^{(0)})}{\partial \lambda^{(0)}}. \tag{3.21}$$

Note that in a variational theory the equation that follows from differentiation of the quasienergy Lagrangian with respect to $\lambda^{(0)}$ now determines $\lambda^{(0)}$ and not $\bar{\lambda}^{(0)}$ as in non-variational theory. In the following, we treat the zeroth-order multipliers $\bar{\lambda}^{(0)}$ on equal footing with the zeroth-order parameters $\lambda^{(0)}$ and we will not refer explicitly to the dependency of these parameters.

3.C. THE FIRST-ORDER LAGRANGIAN

The first-order Lagrangian becomes

$$L^X(0) = \frac{d\{L^{(1)}\}_T}{d\varepsilon_X(0)} = \frac{\partial\{L^{(1)}\}_T}{\partial\varepsilon_X(0)} + \frac{\partial\{L^{(1)}\}_T}{\partial\lambda^{(1)}(0)}\lambda^X(0) + \bar{\lambda}^X(0)\frac{\partial\{L^{(1)}\}_T}{\partial\bar{\lambda}^{(1)}(0)}. \tag{3.22}$$

The variational criterion for the first-order multipliers gives an equation for the reference amplitudes, since

$$0 = \frac{\partial L^X(0)}{\partial\bar{\lambda}^X(0)} = \frac{\partial\{L^{(1)}\}_T}{\partial\bar{\lambda}^{(1)}(0)}. \tag{3.23}$$

This equation is, in fact, identical to the one obtained from $0 = [\partial\{L^{(0)}\}_T]/[\partial\bar{\lambda}^{(0)}]$ in Eq. (3.19) as we will see later. The variational criterion for the first-order parameters gives

$$0 = \frac{\partial L^X(0)}{\partial\lambda^X(0)} = \frac{\partial\{L^{(1)}\}_T}{\partial\lambda^{(1)}(0)}, \tag{3.24}$$

where we again note that this equation is identical to $0 = (\partial\{L^{(0)}\}_T)/(\partial\lambda^{(0)})$ in Eq. (3.20). From Eqs. (3.21)–(3.24), we obtain in accordance with the $2n + 1$ and $2n + 2$ rules the following expression for the first derivative that only depends on the zeroth-order parameters and multipliers:

$$\langle X \rangle = \frac{\partial\{L^{(1)}\}_T}{\partial\varepsilon_X(0)}. \tag{3.25}$$

This is the generalized Hellmann–Feynman theorem stating that all first-order properties including molecular gradients can be calculated from the zeroth-order parameters, $\lambda^{(0)}$ and $\bar{\lambda}^{(0)}$:

$$\langle X \rangle = \frac{\partial\{Q^{(1)}\}_T}{\partial\varepsilon_X(0)} + \bar{\lambda}^{(0)}\frac{\partial\{e^{(1)}\}_T}{\partial\varepsilon_X(0)}. \tag{3.26}$$

We note that for some nonvariational methods the symmetrization in Eq. (2.70) may be relevant—see the discussion in the previous section and the next subsection. In variational theory, the second term vanishes and the usual Hellmann–Feynman theorem expression is obtained:

$$\langle X \rangle = \frac{\partial\{Q^{(1)}\}_T}{\partial\varepsilon_X(0)}. \tag{3.27}$$

For standard wave functions, as, for example, in the SCF method, this becomes a simple expectation value of the operator X.

3.D. THE SECOND-ORDER LAGRANGIAN

The expression for the second derivative of the time-averaged second-order Lagrangian becomes

$$\begin{aligned}
L^{XY}(\omega_0, \omega_{k_1}) &= \frac{d^2\{L^{(2)}\}_T}{d\varepsilon_X(\omega_0)\, d\varepsilon_Y(\omega_{k_1})} \\
&= P\big(X(\omega_0), Y(\omega_{k_1})\big)\Bigg\{\frac{1}{2}\frac{\partial^2\{L^{(2)}\}_T}{\partial\varepsilon_X(\omega_0)\,\partial\varepsilon_Y(\omega_{k_1})} \\
&+ \frac{\partial^2\{L^{(2)}\}_T}{\partial\varepsilon_X(\omega_0)\,\partial\lambda^{(1)}(\omega_{k_1})}\lambda^Y(\omega_{k_1}) \\
&+ \frac{1}{2}\frac{\partial^2\{L^{(2)}\}_T}{\partial\lambda^{(1)}(\omega_0)\,\partial\lambda^{(1)}(\omega_{k_1})}\lambda^X(\omega_0)\lambda^Y(\omega_{k_1}) \\
&+ \bar{\lambda}^X(\omega_0)\frac{\partial^2\{L^{(2)}\}_T}{\partial\bar{\lambda}^{(1)}(\omega_0)\,\partial\varepsilon_Y(\omega_{k_1})} \\
&+ \bar{\lambda}^X(\omega_0)\frac{\partial^2\{L^{(2)}\}_T}{\partial\bar{\lambda}^{(1)}(\omega_0)\,\partial\lambda^{(1)}(\omega_{k_1})}\lambda^Y(\omega_{k_1}) \\
&+ \frac{1}{2}\bar{\lambda}^{XY}(\omega_0, \omega_{k_1})\frac{\partial\{L^{(2)}\}_T}{\partial\bar{\lambda}^{(2)}(\omega_0, \omega_{k_1})} \\
&+ \frac{1}{2}\frac{\partial\{L^{(2)}\}_T}{\partial\lambda^{(2)}(\omega_0, \omega_{k_1})}\lambda^{XY}(\omega_0, \omega_{k_1})\Bigg\},
\end{aligned} \tag{3.28}$$

where $P(X(\omega_0), y(\omega_{k_1}))$ is symmetric with respect to the interchange of X and Y and associated

frequencies,

$$P\big(X(\omega_0), Y(\omega_{k_1})\big) f^{XY}(\omega_0, \omega_{k_1}) = f^{XY}(\omega_0, \omega_{k_1}) + f^{YX}(\omega_{k_1}, \omega_0). \quad (3.29)$$

From the variational criteria for the second-order parameters and multipliers, we obtain again equations for the zeroth-order parameters:

$$0 = \frac{\partial L^{XY}(\omega_0, \omega_{k_1})}{\partial \bar{\lambda}^{XY}(\omega_0, \omega_{k_1})} = \frac{\partial \{L^{(2)}\}_T}{\partial \bar{\lambda}^{(2)}(\omega_0, \omega_{k_1})}, \quad (3.30)$$

$$0 = \frac{\partial L^{XY}(\omega_0, \omega_{k_1})}{\partial \lambda^{XY}(\omega_0, \omega_{k_1})} = \frac{\partial \{L^{(2)}\}_T}{\partial \lambda^{(2)}(\omega_0, \omega_{k_1})}. \quad (3.31)$$

The variational condition for the frequency-dependent first-order multipliers gives an equation for the first-order λ-parameters:

$$0 = \frac{\partial L^{XY}(\omega_0, \omega_{k_1})}{\partial \bar{\lambda}^{X}(\omega_0)} = \frac{\partial^2 \{L^{(2)}\}_T}{\partial \bar{\lambda}^{(1)}(\omega_0)\, \partial \varepsilon_Y(\omega_{k_1})} + \frac{\partial^2 \{L^{(2)}\}_T}{\partial \bar{\lambda}^{(1)}(\omega_0)\, \partial \lambda^{(1)}(\omega_{k_1})} \lambda^{Y}(\omega_{k_1}). \quad (3.32)$$

The variational criterion for the first-order parameters, in turn, determines the first-order multipliers:

$$0 = \frac{\partial L^{XY}(\omega_0, \omega_{k_1})}{\partial \lambda^{X}(\omega_0)} = \frac{\partial^2 \{L^{(2)}\}_T}{\partial \lambda^{(1)}(\omega_0)\, \partial \varepsilon_Y(\omega_{k_1})} + \frac{\partial^2 \{L^{(2)}\}_T}{\partial \lambda^{(1)}(\omega_0)\, \partial \lambda^{(1)}(\omega_{k_1})} \lambda^{Y}(\omega_{k_1}) + \bar{\lambda}^{Y}(\omega_{k_1}) \frac{\partial^2 \{L^{(2)}\}_T}{\partial \bar{\lambda}^{(1)}(\omega_{k_1})\, \partial \lambda^{(1)}(\omega_0)}. \quad (3.33)$$

Using the zeroth [Eqs. (2.30) and (2.31)] and the first [Eq. (3.32) and (3.33)]-order response equations to simplify the expression for the second-order quasienergy, we obtain the linear response function in accordance with the $2n + 1$ and $2n + 2$ rules as

$$\langle\langle X, Y \rangle\rangle_{\omega_{k_1}} = P\big(X(\omega_0), Y(\omega_{k_1})\big) \left\{ \frac{\partial^2 \{L^{(2)}\}_T}{\partial \varepsilon_X(\omega_0)\, \partial \lambda^{(1)}(\omega_{k_1})} \lambda^{Y}(\omega_{k_1}) + \frac{1}{2} \frac{\partial^2 \{L^{(2)}\}_T}{\partial \lambda^{(1)}(\omega_0)\, \partial \lambda^{(1)}(\omega_{k_1})} \times \lambda^{X}(\omega_0) \lambda^{Y}(\omega_{k_1}) \right\}. \quad (3.34)$$

Note that the first term in Eq. (3.28) vanishes because the Hamiltonian in Eq. (2.3) was restricted to terms first order in the perturbation strength parameters. We carried out the complete derivation up to this point in terms of quantities given explicitly as derivatives. It is convenient to define some of these derivatives as vectors and matrices. This is done in Table IV, and in Tables I–III, we give the linear, quadratic, and cubic response functions and related response equations in terms of the matrices for variational and non-variational theories. In analyzing and implementing these expressions, it is convenient to use a slightly simpler nomenclature where the connection between operators and related frequencies are introduced explicitly. We therefore denote ω_X for ω_0, ω_Y for ω_{k_1}, etc., in the tables and in the following.

At this point, it is relevant to return to the discussion in Section 2 concerning the symmetry of the response functions with respect to simultaneous change of sign of frequencies and complex conjugation [Eqs. (2.19)–(2.22)]. If the response functions do not satisfy these relations, we need to enforce them [Eqs. (2.70)–(2.73)]. This can most conveniently be done by introducing in Eqs. (3.26) and (3.34) the operator $C^{\pm\omega}$ that symmetrices with respect to simultaneous complex conjugation and inversion of the sign of the frequencies

$$C^{\pm\omega} f^{XY}(\omega_X, \omega_Y) = f^{XY}(\omega_X, \omega_Y) + (f^{XY}(-\omega_X, -\omega_Y))^*. \quad (3.35)$$

This operator is applied to the response functions in Table I, although, in some cases, it may be unnecessary.

3.E. THE $2n + 1$ AND $2n + 2$ RULES AND HIGHER-ORDER RESPONSE FUNCTIONS

The $2n + 1$ and $2n + 2$ rules for frequency-independent properties are well known (see [17, 18]

TABLE I
Response functions in a general nonvariational theory.[a]

Linear

$$\langle\langle X, Y \rangle\rangle_{\omega_Y} = \frac{1}{2} C^{\pm\omega} P(X(\omega_X), Y(\omega_Y)) \left\{ \eta^X + \frac{1}{2}\mathbf{F}(\omega_Y)\lambda^X(\omega_X) \right\} \lambda^Y(\omega_Y)$$

Quadratic

$$\langle\langle X, Y, Z \rangle\rangle_{\omega_Y, \omega_Z} = \frac{1}{2} C^{\pm\omega} P(X(\omega_X), Y(\omega_Y), Z(\omega_Z)) \left\{ \left[\frac{1}{2}\mathbf{F}^X + \frac{1}{6}\mathbf{G}(\omega_Y, \omega_Z)\lambda^x(\omega_X) \right] \lambda^Y(\omega_Y)\lambda^Z(\omega_Z) + \bar{\lambda}^X(\omega_X) \left[\mathbf{A}^Y + \frac{1}{2}\mathbf{B}(\omega_Y, \omega_Z)\lambda^Y(\omega_Y) \right] \lambda^Z(\omega_Z) \right\}$$

Cubic

$$\begin{aligned}\langle\langle X, Y, Z, U \rangle\rangle_{\omega_Y, \omega_Z, \omega_U} = {} & \frac{1}{2} C^{\pm\omega} P(X(\omega_X), Y(\omega_Y), Z(\omega_Z), U(\omega_U)) \\ & \left\{ \frac{1}{8}\mathbf{F}(\omega_Z + \omega_U)\lambda^{XY}(\omega_X, \omega_Y)\lambda^{ZU}(\omega_Z, \omega_U) + \frac{1}{2}\mathbf{F}^X\lambda^Y(\omega_Y)\lambda^{ZU}(\omega_Z, \omega_U) \right. \\ & + \frac{1}{4}\mathbf{G}(\omega_Y, \omega_Z + \omega_U)\lambda^X(\omega_X)\lambda^Y(\omega_Y)\lambda^{ZU}(\omega_Z, \omega_U) \\ & + \frac{1}{2}\bar{\lambda}^X(\omega_X)[\mathbf{A}^Y + \mathbf{B}(\omega_Y, \omega_Z + \omega_U)\lambda^Y(\omega_Y)]\lambda^{ZU}(\omega_Z, \omega_U) \\ & + \left[\frac{1}{6}\mathbf{G}^x + \frac{1}{24}\mathbf{H}(\omega_Y, \omega_Z, \omega_U)\lambda^X(\omega_X) \right] \lambda^Y(\omega_Y)\lambda^Z(\omega_Z)\lambda^U(\omega_U) \\ & \left. + \bar{\lambda}^X(\omega_X) \left[\frac{1}{2}\mathbf{B}^Y + \frac{1}{6}\mathbf{C}(\omega_Y, \omega_Z, \omega_U)\lambda^Y(\omega_Y) \right] \lambda^Z(\omega_Z)\lambda^U(\omega_U) \right\}\end{aligned}$$

[a]The appropriate matrices are defined in Table IV, and the response equations are given in Table III. The permutation operator P is defined in Eq. (3.29) and complex conjugation and the frequency sign inversion operator is defined in Eq. (3.35).

TABLE II
Response functions in a general variational theory.[a]

Linear

$$\langle\langle X, Y \rangle\rangle_{\omega_Y} = P(X(\omega_X), Y(\omega_Y)) \left\{ \eta^X + \frac{1}{2}\mathbf{F}(\omega_Y)\lambda^X(\omega_X) \right\} \lambda^Y(\omega_Y) = \eta^X\lambda^Y(\omega_Y)$$

Quadratic

$$\langle\langle X, Y, Z \rangle\rangle_{\omega_Y, \omega_Z} = P(X(\omega_X), Y(\omega_Y), Z(\omega_Z)) \left[\frac{1}{2}\mathbf{F}^X + \frac{1}{6}\mathbf{G}(\omega_Y, \omega_Z)\lambda^X(\omega_X) \right] \lambda^Y(\omega_Y)\lambda^Z(\omega_Z)$$

Cubic

$$\begin{aligned}\langle\langle X, Y, Z, U \rangle\rangle_{\omega_Y, \omega_Z, \omega_U} = {} & P(X(\omega_X), Y(\omega_Y), Z(\omega_Z), U(\omega_U)) \\ & \left\{ \frac{1}{8}\mathbf{F}(\omega_Z + \omega_U)\lambda^{XY}(\omega_X, \omega_Y)\lambda^{ZU}(\omega_Z, \omega_U) + \frac{1}{2}\mathbf{F}^X\lambda^Y(\omega_Y)\lambda^{ZU}(\omega_Z, \omega_U) \right. \\ & + \frac{1}{4}\mathbf{G}(\omega_Y, \omega_Z + \omega_U)\lambda^X(\omega_X)\lambda^Y(\omega_Y)\lambda^{ZU}(\omega_Z, \omega_U) \\ & \left. + \left[\frac{1}{6}\mathbf{G}^X + \frac{1}{24}\mathbf{H}(\omega_Y, \omega_Z, \omega_U)\lambda^X(\omega_X) \right] \lambda^Y(\omega_Y)\lambda^Z(\omega_Z)\lambda^U(\omega_U) \right\}\end{aligned}$$

[a]The appropriate matrices are defined in Table IV, and the response equations are given in Table III. The permutation operator P is defined in Eq. (3.29).

TABLE III
Response equations in a general response theory.[a]

Nonvariational theory	
Zeroth-order equations	$e^{(0)} = 0$
	$\bar{\lambda}^{(0)}\mathbf{A}(0) - \eta = 0$
First-order response equations	$\mathbf{A}(\omega_Y)\lambda^Y(\omega_Y) + \xi^Y = 0$
	$\bar{\lambda}^Y(\omega_Y)\mathbf{A}(-\omega_Y) + \eta^Y + \mathbf{F}(\omega_Y)\lambda^Y(\omega_Y) = 0$
Second-order response equations	$\mathbf{A}(\omega_Y + \omega_Z)\lambda^{YZ}(\omega_Y, \omega_Z)$
	$+P(Y(\omega_Y), Z(\omega_Z))\left\{\mathbf{A}^Y\lambda^Z(\omega_Z) + \frac{1}{2}\mathbf{B}(\omega_Y, \omega_Z)\lambda^Y(\omega_Y)\lambda^Z(\omega_Z)\right\} = 0$
	$\bar{\lambda}^{YZ}(\omega_Y, \omega_Z)\mathbf{A}(-\omega_Y - \omega_Z)$
	$+P(Y(\omega_Y), Z(\omega_Z))\left\{\mathbf{F}^Y\lambda^Z(\omega_Z) + \frac{1}{2}\mathbf{G}(\omega_Y, \omega_Z)\lambda^Y(\omega_Y)\lambda^Z(\omega_Z)\right.$
	$\left.+\frac{1}{2}\mathbf{F}(\omega_Y + \omega_Z)\lambda^{YZ}(\omega_Y, \omega_Z) + \bar{\lambda}^Y(\omega_Y)[\mathbf{A}^Z + \mathbf{B}(\omega_Z, \omega_X)\lambda^Z(\omega_Z)]\right\} = 0$
Variational theory	
Zeroth-order equations	$\eta = 0$
First-order response equations	$\eta^Y + \mathbf{F}(\omega_Y)\lambda^Y(\omega_Y) = 0$
Second-order response equations	$\mathbf{F}(\omega_Y + \omega_Z)\lambda^{YZ}(\omega_Y, \omega_Z)$
	$+P(Y(\omega_Y), Z(\omega_Z))\left\{\mathbf{F}^Y\lambda^Z(\omega_Z) + \frac{1}{2}\mathbf{G}(\omega_Y, \omega_Z)\lambda^Y(\omega_Y)\lambda^Z(\omega_Z)\right\} = 0$

[a]The appropriate matrices are defined in Table IV, and the permutation operator P is defined in Eq. (3.29).

and references therein). A $2n + 1$ rule was previously derived for monochromatic perturbations (see footnote 87 of [21]). We derive here the $2n + 1$ and $2n + 2$ rules for general frequency-dependent response functions.

To derive the $2n + 1$ and $2n + 2$ rules, it is convenient to introduce the not too short notations $L^N = L^{V_0, V_1, \cdots V_{n-1}}(\omega_0, \omega_1, \ldots, \omega_{n-1})$ for the Fourier components of the quasienergy Lagrangian and $\lambda^P = \lambda^{\bar{V}_1, \cdots \bar{V}_p}(\bar{\omega}_1, \ldots, \bar{\omega}_p)$ and $\lambda^Q = \lambda^{\tilde{V}_1, \cdots \tilde{V}_q}(\tilde{\omega}_1, \ldots, \tilde{\omega}_q)$ for the response amplitudes. Bars and tildes are used to distinguish the operators and frequencies in the response vectors from those of the Nth-order quasienergy derivative. The multipliers can be treated in an analogous way. The first derivative becomes

$$\frac{\partial L^N}{\partial \lambda^P} = \frac{\partial}{\partial \lambda^{\bar{V}_1, \cdots \bar{V}_p}(\bar{\omega}_1, \ldots, \bar{\omega}_p)} \times \frac{\partial^n \{L\}_T}{\partial \varepsilon_{V_0}(\omega_0)\partial \varepsilon_{V_1}(\omega_1) \cdots \partial \varepsilon_{V_{n-1}}(\omega_{n-1})}. \quad (3.36)$$

Introducing the frequency $\bar{\omega} = \sum_{i=1}^p \bar{\omega}_i$ and the $\lambda(\omega)$ notation of Eqs. (3.8) and (3.9), we obtain using the chain rule:

$$\begin{aligned}\frac{\partial L^N}{\partial \lambda^P} &= \frac{\partial}{\partial \varepsilon_{V_0}(\omega_0)\partial \varepsilon_{V_1}(\omega) \cdots \partial \varepsilon_{V_{n-1}}(\omega_{n-1})} \times \frac{\partial \lambda(\bar{\omega})}{\partial \lambda^{\bar{V}_1, \cdots \bar{V}_p}(\bar{\omega}_1, \ldots, \bar{\omega}_p)} \frac{\partial \{L\}_T}{\partial \lambda(\bar{\omega})} \\ &= \frac{\partial}{\partial \varepsilon_{V_0}(\omega_0)\partial \varepsilon_{V_1}(\omega_1) \cdots \partial \varepsilon_{V_{n-1}}(\omega_{n-1})} \times \prod_{i=1}^p \varepsilon_{\bar{V}_i}(\bar{\omega}_i) \frac{\partial \{L\}_T}{\partial \lambda(\bar{\omega})}. \end{aligned} \quad (3.37)$$

Introducing the grand symmetric $G_{(0, 1, \cdots n-1)}$ which generates all permutations of operators with associated frequencies, $V_i(\omega_i)$, $i = 0, n - 1$, and the heavy side step function $\theta(j) = 0$ for $j < 0$ and

TABLE IV
Vectors and matrices for general response functions.[a]

Quantity	Derivative expression
η^Y	$\frac{\partial^2\{L^{(2)}\}_T}{\partial\lambda^{(1)}(\omega_X)\,\partial\varepsilon_Y(\omega_Y)}$
ξ^Y	$\frac{\partial^2\{L^{(2)}\}_T}{\partial\bar{\lambda}^{(1)}(\omega_X)\,\partial\varepsilon_Y(\omega_Y)}$
$\mathbf{A}(\omega_Y)$	$\frac{\partial^2\{L^{(2)}\}_T}{\partial\bar{\lambda}^{(1)}(\omega_X)\,\partial\lambda^{(1)}(\omega_Y)}$
$\mathbf{B}(\omega_Y, \omega_Z)$	$\frac{\partial^3\{L^{(3)}\}_T}{\partial\bar{\lambda}^{(1)}(\omega_X)\,\partial\lambda^{(1)}(\omega_Y)\,\partial\lambda^{(1)}(\omega_Z)}$
$\mathbf{C}(\omega_Y, \omega_Z, \omega_U)$	$\frac{\partial^4\{L^{(4)}\}_T}{\partial\bar{\lambda}^{(1)}(\omega_X)\,\partial\lambda^{(1)}(\omega_Y)\,\partial\lambda^{(1)}(\omega_Z)\,\partial\lambda^{(1)}(\omega_U)}$
$\mathbf{F}(\omega_Y)$	$\frac{\partial^2\{L^{(2)}\}_T}{\partial\lambda^{(1)}(\omega_X)\,\partial\lambda^{(1)}(\omega_Y)}$
$\mathbf{G}(\omega_Y, \omega_Z)$	$\frac{\partial^3\{L^{(3)}\}_T}{\partial\lambda^{(1)}(\omega_X)\,\partial\lambda^{(1)}(\omega_Y)\,\partial\lambda^{(1)}(\omega_Z)}$
$\mathbf{H}(\omega_Y, \omega_Z, \omega_U)$	$\frac{\partial^4\{L^{(4)}\}_T}{\partial\lambda^{(1)}(\omega_X)\,\partial\lambda^{(1)}(\omega_Y)\,\partial\lambda^{(1)}(\omega_Z)\,\partial\lambda^{(1)}(\omega_U)}$
$\mathbf{A}^Z$	$\frac{\partial^3\{L^{(3)}\}_T}{\partial\bar{\lambda}^{(1)}(\omega_X)\,\partial\lambda^{(1)}(\omega_Y)\,\partial\varepsilon_Z(\omega_Z)}$
$\mathbf{B}^U$	$\frac{\partial^4\{L^{(4)}\}_T}{\partial\bar{\lambda}^{(1)}(\omega_X)\,\partial\lambda^{(1)}(\omega_Y)\,\partial\lambda^{(1)}(\omega_Z)\,\partial\varepsilon_U(\omega_U)}$
$\mathbf{F}^Z$	$\frac{\partial^3\{L^{(3)}\}_T}{\partial\lambda^{(1)}(\omega_X)\,\partial\lambda^{(1)}(\omega_Y)\,\partial\varepsilon_Z(\omega_Z)}$
$\mathbf{G}^U$	$\frac{\partial^4\{L^{(4)}\}_T}{\partial\lambda^{(1)}(\omega_X)\,\partial\lambda^{(1)}(\omega_Y)\,\partial\lambda^{(1)}(\omega_Z)\,\partial\varepsilon_U(\omega_U)}$
η	$\frac{\partial\{Q^{(0)}\}_T}{\partial\lambda^{(0)}}$

[a]Expressions for the matrices for a variational theory are obtained simply by replacing L with Q. Matrices referring to derivatives with respect to multipliers (e.g., $\mathbf{A}, \mathbf{B}\cdots$) are identical zero for variational methods. The sum of the frequencies occurring in the derivative expressions is zero; $\omega_X + \omega_Y = 0$, $\omega_X + \omega_Y + \omega_Z = 0$ or $\omega_X + \omega_Y + \omega_Z + \omega_U = 0$.

otherwise 1, we obtain

$$\frac{\partial L^N}{\partial\lambda^P} = G_{(0,1,\ldots,n-1)} \times \frac{\partial^{n-p}}{\partial\varepsilon_{V_0}(\omega_0)\,\partial\varepsilon_{V_1}(\omega_1)\cdots\,\partial\varepsilon_{V_{n-p-1}}(\omega_{n-p-1})} \times \frac{\partial\{L\}_T}{\partial\lambda(\bar{\omega})}\,\theta(n-p) \times \prod_{i=1}^{p}\delta_{\bar{V}_i V_{n-p-1+i}}\,\delta(\bar{\omega}_i - \omega_{n-p-1+i}). \quad (3.38)$$

Similarly, we obtain the second derivative as

$$\frac{\partial L^N}{\partial\lambda^P\,\partial\lambda^Q} = G_{(0,\ldots,n-1)} \times \frac{\partial^{n-p-q}}{\partial\varepsilon_{V_0}(\omega_0)\,\partial\varepsilon_{V_1}(\omega_1)\cdots\,\partial\varepsilon_{V_{n-p-q-1}}(\omega_{n-p-q-1})} \times \frac{\partial^2\{L\}_T}{\partial\lambda(\bar{\omega})\,\partial\lambda(\tilde{\omega})}\,\theta(n-p-q) \times \prod_{i=1}^{p}\delta_{V_i V_{n-p-1+i}}\,\delta(\bar{\omega}_i - \omega_{n-p-1+i}) \times \prod_{j=1}^{q}\delta_{\tilde{V}_j V_{n-p-q-1+j}}\,\delta(\tilde{\omega}_j - \omega_{n-p-q-1+j}), \quad (3.39)$$

where $\tilde{\omega} = \sum_{i=1}^{q}\tilde{\omega}_i$.

From Eq. (3.39), it is apparent that there exist relations between the derivatives of L^N with respect to λ^P and λ^Q for different n, p, and q and a different set of operators and frequencies. It is instructive here to compare them with the time-independent limit of Eq. (3.38) in the case where there is only one external perturbations X:

$$\frac{\partial L^N}{\partial\lambda^P} = G_{(0,1,\ldots,n-1)}\frac{\partial^{n-p}}{(\partial\varepsilon_X(0))^{n-p}}\frac{\partial L}{\partial\lambda_0}. \quad (3.40)$$

In the time-independent limit, it is obvious that the variational equations obtained from $(\partial L^N)/(\partial\lambda^P) = 0$ for all n and p are not all independent. The independent sets of equations are characterized only by the difference $n - p$. In other words, the same response equations are obtained straightforwardly in different orders, for example, $(\partial L^2)/(\partial\lambda^1) = 0$ and $(\partial L^3)/(\partial\lambda^2) = 0$ determine the same set of equations for the first-order responses, and, therefore, the same set of first-order responses is required for evaluating the linear and quadratic response function in the frequency-independent limit. This behavior is carried over to the frequency-dependent case, with only minor modifications. The essential sets of response equations are again not all independent as seen from Eq. (3.38)—again, the difference $n - p$ is characteristic of the set of independent equations. However, not only the operators, but both operators and fre-

quencies for the $n - p$ (remaining) perturbation strengths in Eq. (3.38) are required to be identical to give the same response equations. For the remaining p frequencies, the sum has to be the same to give exactly the same response function. This means that, overall, the same *forms* of the response equations are obtained in different order; however, the required set of *frequencies* for the responses may be slightly different for different order response functions.

For example, the equations for the zeroth-order amplitudes and multipliers found in the previous sections [Eqs. (3.19), (3.23), and (3.30)] are all equivalent as $n - p = 0$ and, therefore, obviously, $\bar{\omega} = 0$:

$$0 = \frac{\partial L^{(0)}}{\partial \bar{\lambda}^{(0)}} = \frac{\partial L^X(0)}{\partial \bar{\lambda}^X(0)} = \frac{\partial L^{XY}(-\omega_Y, \omega_Y)}{\partial \bar{\lambda}^{XY}(-\omega_Y, \omega_Y)} = e^{(0)}(\lambda^{(0)}). \tag{3.41}$$

The same comment also applies for the zeroth-order multiplier equations. The same form of equations for the first-order response equations are obtained to each order, for example, the equation for $\lambda^Y(\omega_Y)$ for a nonvariational method is determined from

$$0 = \frac{\partial L^{XY}(-\omega_Y, \omega_Y)}{\partial \bar{\lambda}^X(-\omega_Y)} = \frac{\partial L^{XYZ}(-\omega_Y - \omega_Z, \omega_Y, \omega_Z)}{\partial \bar{\lambda}^{XZ}(-\omega_Y - \omega_Z, \omega_Z)}. \tag{3.42}$$

Similarly, the same set of equations is seen to be obtained for $\lambda^Z(\omega_Z)$. For $\lambda^X(\omega_X)$, the only difference is due to the in general different frequency assigned to X in linear and quadratic response theory:

$$\frac{\partial L^{XY}(-\omega_Y, \omega_Y)}{\partial \lambda^Y(\omega_Y)} = \frac{\partial}{\partial \varepsilon_X(-\omega_Y)} \frac{\partial \{L\}_T}{\partial \lambda_{\omega_Y}}, \tag{3.43}$$

$$\frac{\partial L^{XYZ}(-\omega_Y - \omega_Z, \omega_Y, \omega_Z)}{\partial \lambda^{YZ}(\omega_Y, \omega_Z)} = \frac{\partial}{\partial \varepsilon_X(-\omega_Y - \omega_Z)} \frac{\partial \{L\}_T}{\partial \lambda_{\omega_Y + \omega_Z}}. \tag{3.44}$$

Thus, the form of the response equations is the same. A different frequency ω_X in $\lambda^X(\omega_X)$ is required in each order, unlike for the responses referring directly to the ''external'' perturbations $\lambda^Y(\omega_Y)$, $\lambda^Z(\omega_Z) \cdots$.

Our next task is to prove the $2n + 1$ and $2n + 2$ rules based on the above results. The characteristic order for the set of equations obtained from $(\partial L^N)/(\partial \lambda^P) = 0$ is $n - p$. We have from Eq. (3.39) that the second derivative is zero for $n > p + q$. Thus, L^N is linear in all λ^P collectively, where $p > Int(n/2)$. Since we require L^N to be stationary with respect to these λ^P parameters also, $(\partial L^N)/(\partial \lambda^P) = 0$, the coefficient for the λ^P parameters must be zero. Therefore, the final result—the stationary value—which we will denote the nth-order response function, does not depend on the parameters λ^P for $p > Int(n/2)$. In other words, the frequency-dependent parameter responses through nth order determine the frequency-dependent response functions through order $2n + 1$. This is the $2n + 1$ rule for frequency-dependent response functions. The above considerations are trivially extended to the treatment of both the λ parameters and the Lagrangian multipliers. However, for the Lagrangian multipliers, we can even strengthen the $2n + 1$ rule to a $2n + 2$ rule: To obtain the frequency-dependent response functions through order $2n + 2$, only the nth-order frequency-dependent responses to the Lagrangian multipliers are required.

The $2n + 2$ rule for the Lagrangian multipliers can be realized as follows: From the definition of the Lagrangian, the Lagrangian multipliers occur linear to every order. Consider now the $(2n + 2)$th-order Lagrangian. The terms including the $(n + 1)$th-order multiplier will depend on λ^P for $p = 0, 1, \cdots n, n + 1$ but not on higher-order responses than λ^{N+1}. Therefore, the use of the response equations to obtain an expression in accordance with the $2n + 1$ rules does not affect the terms linear in $\bar{\lambda}^{N+1}$, as the used response equations are obtained as derivatives of the Lagrangian with respect to $\lambda^P p > n + 1$ and $\bar{\lambda}^q q > n + 1$. We can therefore, without consequence for the reductions obtained in using the $2n + 1$ rule, use the variational criteria $(\partial L^{2N+2})/(\partial \bar{\lambda}^{N+1}) = 0$ to eliminate $\bar{\lambda}^{N+1}$. We thus obtain that we can evaluate $(2n + 2)$-order properties using only λ^P, $p \leq n + 1$ and $\bar{\lambda}^Q$, $q < n + 1$. Thus, we have proved the $2n + 2$ rule for the Lagrangian multiplier.

The use of the $2n + 1$ and $2n + 2$ rules have already been exemplified in the previous section by explicitly writing up the Lagrangian to a specific order and including all terms. After applying

the variational criteria, we used the resulting equations to eliminate the terms that were not in accord with the $2n + 1$ and $2n + 2$ rules. Having realized this, in general, we know a priori that these terms do not contribute. They can, thus, be safely ignored from the beginning of the derivation of the response functions to any order. The lower-order response equations can still be obtained according to the variational criteria for the required responses. The use of a variational Lagrangian and the $2n + 1$ and $2n + 2$ rules thus greatly simplify the derivation, as can be seen by reexamining the derivations in the previous subsections. We know, for example, a priori, that the average value for a molecular property in a nonvariational theory can be evaluated from zeroth-order parameters and multipliers, and we obtain straightforwardly Eq. (3.25) by simply ignoring all terms depending on first-order responses. Similarly, for the determination of frequency-dependent second-order properties, we can from the outset discard the response terms in Eq. (3.28) depending on second-order parameters and multipliers and obtain the linear response function directly in the form in Eq. (3.34).

3.F. SYMMETRY RELATIONS FOR THE RESPONSE FUNCTIONS

The reduction from the nonvariational method as given by Eqs. (3.30)–(3.34) to a variational method is obtained neglecting all terms containing $\bar{\lambda}$ and replacing L with Q. Equation (3.34) then becomes

$$\begin{aligned}\langle\langle X, Y \rangle\rangle_{\omega_Y} &= P(X(\omega_X), Y(\omega_Y)) \\ &\times \left\{ \frac{\partial^2 \{Q^{(2)}\}_T}{\partial \varepsilon_X(\omega_X)\, \partial \lambda^{(1)}(\omega_Y)} \lambda^Y(\omega_Y) \right. \\ &\left. + \frac{1}{2} \frac{\partial^2 \{Q^{(2)}\}_T}{\partial \lambda^{(1)}(\omega_X) \partial \lambda^{(1)}(\omega_Y)} \lambda^X(\omega_X) \lambda^Y(\omega_Y) \right\}. \end{aligned} \tag{3.45}$$

The response equation [Eq. (3.32)] is not defined in a fully variational theory, whereas Eq. (3.33) is replaced by

$$0 = \frac{\partial^2 \{Q^{(2)}\}_T}{\partial \lambda^{(1)}(\omega_X)\, \partial \varepsilon_Y(\omega_Y)} + \frac{\partial^2 \{Q^{(2)}\}_T}{\partial \lambda^{(1)}(\omega_X)\, \partial \lambda^{(1)}(\omega_Y)} \lambda^Y(\omega_Y). \tag{3.46}$$

Using the variational response equation in Eq. (3.46), a further simplification can be introduced in Eq. (2.45), such that the linear response functions can be written in a form requiring only the response parameters with respect to one of the operators X, Y. We thus obtain

$$\langle\langle X, Y \rangle\rangle_{\omega_Y} = \frac{\partial^2 \{Q^{(2)}\}_T}{\partial \varepsilon_X(\omega_X)\, \partial \lambda^{(1)}(\omega_Y)} \lambda^Y(\omega_Y). \tag{3.47}$$

We have thus rewritten the expression for the linear response function from a form explicitly exhibiting the symmetry of the linear response function with respect to the interchange of operators and related indices to a form that has built-in this symmetry implicitly and where the response function is evaluated in an asymmetric manner, requiring only the parameter responses with respect to the perturbation Y. The expressions given in Table II for response functions for variational wave functions are symmetrized explicitly, since they are obtained directly from Fourier component variational perturbation theory applied to the quasienergy. As stated above, the derivation of response functions from expansion of the expectation value gives expressions that do not explicitly show the symmetry between X and the remaining operators with corresponding frequencies. As a consequence, the expressions are less symmetric and the deviation is more complicated.

The practical advantage of using the asymmetric form is that in some cases fewer response equations need be solved as exemplified by the reduction above for the linear response function. On the other hand, when the symmetric form is used for evaluating the linear response function, the accuracy of the response function will be quadratic in the accuracy of the response vectors. A disadvantage of the asymmetric form is that the quadratic accuracy is lost and replaced by a linear scaling with the error in the response vector. See discussion in [17, 18, 41]. Rewriting the ''explicit symmetry form'' Eq. (3.45) in terms of the ''implicit symmetry form'' Eq. (3.47) is rather simple for the linear response functions, but less trivial for the higher-order response functions. For the quadratic response function, nothing is gained using an asymmetric form since a similar number of response equations are required in both cases. For the cubic response function, the number of second-order responses is different in the two cases as can be seen by comparing the expressions in

Table II with the expressions for SCF and MCSCF cubic response functions in, for example, [4, 42, 43]. The explicit symmetric form requires 10 response equations to be solved while the implicit symmetric form requires only seven. The difference is minor but may be relevant in some cases. Also, the issue of accuracy in the response property in terms of accuracy in the response vectors may be relevant in this context. The above considerations are rather specialized and different forms may be preferred for different purposes. For example, for calculating the full polarizability tensor, it is unimportant whether Eq. (3.45) or Eq. (3.47) is used since the numbers of X and Y perturbations are identical, whereas for calculation of nuclear magnetic shielding constants, the number of X perturbations (reflecting the number of different magnetic nuclei) may be considerably larger than the number of Y perturbations (reflecting the three components of the magnetic field) and the asymmetric form must be preferred.

For nonvariational models, the discussion is again different. The response of the parameters with respect to one of the perturbations cannot be removed without breaking the $2n + 2$ rule for the multipliers. For example, by eliminating the response $\lambda^X(\omega_X)$, we obtain the following form for the linear response function for a nonvariational model:

$$\langle\langle X, Y \rangle\rangle_{\omega_Y} = \frac{1}{2} C^{\pm\omega} \left\{ \frac{\partial^2 \{L^{(2)}\}_T}{\partial \varepsilon_X(\omega_X)\, \partial \lambda^{(1)}(\omega_Y)} \lambda^Y(\omega_Y) + \bar{\lambda}^Y(\omega_Y) \frac{\partial^2 \{L^{(2)}\}_T}{\partial \varepsilon_X(\omega_X)\, \partial \bar{\lambda}^{(1)}(\omega_Y)} \right\}. \quad (3.48)$$

Instead of $\lambda^X(\omega_X)$ and $\lambda^Y(\omega_Y)$, we thus need the response of both the wave-function parameters and the multipliers with respect to Y. We remember that a symmetrization with respect to the inversion of the sign of the frequency and complex conjugation of the response function may be relevant for some approximate models. This gives, in general, twice as many equations to be solved [$\lambda^Y(\omega_Y)$, $\bar{\lambda}^Y(\omega_Y)$, $(\lambda^Y(-\omega_Y))^*$, $(\bar{\lambda}^Y(-\omega_Y))^*$]. The asymmetric form may still be advantageous in some cases, where, again, nuclear magnetic shielding constants are the most obvious example [44], while when the number of X's and Y's are equal, in general, twice as many equations are required in the asymmetric form. Different strategies may thus be advantageous depending on the particular model and property under study [45]. However, in our opinion, the easiest derivation and the most convenient and general starting point for the analysis of computational efficient strategies are obtained by using a derivative approach as in the Fourier component variational perturbation theory where results in agreement with the $2n + 1$ and $2n + 2$ rules are obtained straightforwardly and then modify the obtained expressions according to the special needs.

4. Response Theory for Variational Wave Functions

4.A. RESPONSE FUNCTIONS IN A VARIATIONAL EXPONENTIAL PARAMETRIZATION

As a parametrization covering both the exact state and the class of approximate variational wave functions that can be described in terms of a single unitary transformation, we chose the exponential ansatz,

$$|\tilde{0}\rangle = \exp(\Lambda(t))|0\rangle, \quad (4.1)$$

where $\Lambda(t)$ is an anti-Hermitian operator. A self-consistent field (SCF) wave function can be described by the parametrization in Eq. (4.1) with the operator Λ as [3]

$$\Lambda(t) = \sum_m (\lambda_m(t) q_m^\dagger - \lambda_m^*(t) q_m), \quad (4.2)$$

where $(q_m^\dagger, q_m)$ are orbital rotation generators

$$q_m^\dagger = E_{pq} = a_{p\alpha}^\dagger a_{q\alpha} + a_{p\beta}^\dagger a_{q\beta}, \quad (4.3)$$

and where we require that $p > q$, such that $q_m^\dagger$ is an excitation operator and q_m is a deexcitation operator. For an exact state or a configuration interaction (CI) state,

$$\Lambda(t) = \sum_{m>0} (\lambda_m(t) R_m^\dagger - \lambda_m^*(t) R_m), \quad (4.4)$$

where R_m are state-transfer operators:

$$R_m^\dagger = |m\rangle\langle 0|. \quad (4.5)$$

For an approximate CI wave function, this parametrization describes an ''unrelaxed'' approach—the set of molecular orbitals used to build the relevant configurations is fixed. A ''relaxed''

CI approach can be described in terms of a double-exponential parametrization and an appropriate set of orbital constraints: for example, the SCF or multiconfigurational self-consistent field (MCSCF) equations. In this case, the wave function is nonvariational (in the orbital rotation parameters). SCF response functions have been derived in other contexts and implemented to high order [27, 28, 42, 46–53]. Response functions for MCSCF wave functions can be derived in an equivalent fashion using a double-exponential unitary transformation describing rotations in both the orbital and configuration spaces. Theory and implementation of MCSCF response functions have been described in detail in the literature in other contexts [43, 54–57].

Using a unified notation, Eqs. (4.2) and (4.4) may be expressed as

$$\Lambda(t) = \sum_{m>0} (\lambda_m(t) Q_m^\dagger - \lambda_m^*(t) Q_m) = \sum_m \lambda_m(t) O_m, \tag{4.6}$$

where we have absorbed the summations over excitation and deexcitation parts in one summation over both positive and negative m, such that the definition of λ_m is extended to

$$\lambda_m = \begin{cases} \lambda_m & m > 0 \\ -\lambda_m^* & m < 0 \end{cases} \tag{4.7}$$

and the operators O_m are defined,

$$O_m = \begin{cases} Q_m^\dagger & m > 0 \\ Q_m & m < 0. \end{cases} \tag{4.8}$$

The time-dependent quasienergy becomes according to Eq. (2.27)

$$Q(t) = \left\langle 0 \middle| \exp(-\Lambda(t)) \left(H - i\frac{\partial}{\partial t} \right) \exp(\Lambda(t)) \middle| 0 \right\rangle. \tag{4.9}$$

The determination of response functions and response equations follows now straightforwardly from the quasienergy $\{Q(t)\}_T$ in agreement with the expressions for the response functions, response equations, and matrices in Tables II–IV. We shall here exemplify the derivation and subsequent analysis through second order.

The starting point in the derivation is the Baker–Campbell–Hausdorf expansion

$$\begin{aligned} \exp(-\Lambda(t)) \left(H - i\frac{\partial}{\partial t} \right) \exp(\Lambda(t)) &= \left(H - i\frac{\partial}{\partial t} \right) + \left[\left(H - i\frac{\partial}{\partial t} \right), \Lambda(t) \right] \\ &\quad + \frac{1}{2} \left[\left[\left(H - i\frac{\partial}{\partial t} \right), \Lambda(t) \right], \Lambda(t) \right] + \cdots \end{aligned} \tag{4.10}$$

and the commutator relation

$$\left[\left(H - i\frac{\partial}{\partial t} \right), \Lambda(t) \right] = [H, \Lambda(t)] - i\dot{\Lambda}(t). \tag{4.11}$$

The zeroth-order quasienergy becomes simply the usual unperturbed stationary energy

$$Q^{(0)} = E_0 = \langle 0 | H_0 | 0 \rangle. \tag{4.12}$$

The variational requirement for the zeroth-order Lagrangian therefore becomes

$$0 = \eta_i = \frac{\partial \{Q^{(0)}\}_T}{\partial \lambda_i^{(0)}} = \langle 0 | [H_0, O_i] | 0 \rangle. \tag{4.13}$$

For an SCF state, Eq. (4.13) is the well-known Brillouin condition.

The first-order quasienergy is obtained by including all terms in the expansion Eq. (4.10) which are first order in V^t. However, as discussed in Section 3, we know a priori that only the terms that are in agreement with the $2n + 1$ rule are required. The first-order λ responses are therefore not needed to determine first-order properties. Accordingly, we limit ourselves to considering only

$${}^{2n+1}Q^{(1)}(t) = \langle 0 | V^t | 0 \rangle. \tag{4.14}$$

The $2n + 1$ form of the first-order quasienergy becomes

$$\left\{ {}^{2n+1}Q^{(1)}(t) \right\}_T = \langle 0 | V^{\omega=0} | 0 \rangle, \tag{4.15}$$

where V^0 is the zero-frequency part of the perturbation in Eq. (2.3). We obtain from Eq. (2.58) the expectation value

$$\langle X \rangle = \frac{\{Q^{(1)}(t)\}_T}{\partial \varepsilon_X(0)} = \langle 0 | X | 0 \rangle. \tag{4.16}$$

For determining the linear response function and the first-order response equations, it is similarly sufficient to consider the $2n + 1$ form of the sec-

ond-order quasienergy. We collect, accordingly, only the terms of the time-dependent quasienergy that are needed to obtain the time-averaged quasienergy in a form that satisfies the $2n + 1$ rule:

$$ {}^{2n+1}Q^{(2)}(t) = \left\langle 0 \middle| [\, V^t, \Lambda^{(1)}(t)] + \frac{1}{2}\Big[\Big[\, H_0, \Lambda^{(1)}(t)\Big] - i\dot{\Lambda}^{(1)}(t), \Lambda^{(1)}(t)\Big] \middle| 0 \right\rangle. \tag{4.17} $$

We now expand the perturbation in terms of Fourier components as in Eq. (2.3) and the parameters—and, thus, the Λ operator—as in Eqs. (3.4) and (3.5) and we obtain an expansion for ${}^{2n+1}Q^{(2)}(t)$ decomposed into Fourier components:

$$ \begin{aligned} {}^{2n+1}Q^{(2)}(t) = \sum_{k_1, k_2} \exp\big(-i(\omega_{k_1} + \omega_{k_2})t\big) & \left\langle 0 \middle| \Big[V^{\omega_{k_1}}, \Lambda^{(1)}(\omega_{k_2})\Big] \right. \\ & + \frac{1}{2}\Big[\Big[\, H_0, \Lambda^{(1)}(\omega_{k_1})\Big] \\ & \left. - \omega_{k_1}\Lambda^{(1)}(\omega_{k_1}), \Lambda^{(1)}(\omega_{k_2})\Big] \middle| 0 \right\rangle. \end{aligned} \tag{4.18} $$

We obtain, accordingly, the $2n + 1$ rule expression for the second-order quasienergy as

$$ \begin{aligned} \big\{{}^{2n+1}Q^{(2)}(t)\big\}_T = \sum_{k_1} \left\langle 0 \middle| \Big[V^{-\omega_{k_1}}, \Lambda^{(1)}(\omega_{k_i})\Big] \right. & \\ + \frac{1}{2}\Big[\Big[\, H_0, \Lambda^{(1)}(-\omega_{k_1})\Big] & \\ \left. + \omega_{k_1}\Lambda^{(1)}(-\omega_{k_1}), \Lambda^{(1)}(\omega_{k_1})\Big] \middle| 0 \right\rangle. & \end{aligned} \tag{4.19} $$

From the definitions in Table IV, we obtain (with $L = Q$)

$$ \eta_i^Y = \frac{\partial^2\{Q^{(2)}\}_T}{\partial\lambda_i^{(1)}(\omega_X)\,\partial\varepsilon_Y(\omega_Y)} = \langle 0|[\, Y, O_i]\,|0\rangle, \tag{4.20} $$

$$ \begin{aligned} F_{ij}(\omega_Y) = \frac{\partial^2\{Q^{(2)}\}_T}{\partial\lambda_i^{(1)}(\omega_X)\,\partial\lambda_j^{(1)}(\omega_Y)} & \\ = \frac{1}{2}P\big(O_i(\omega_X), O_j(\omega_Y)\big) & \\ \times\Big[\big\langle 0\big|\big[\,[\, H_0, O_i], O_j\big]\,\big|0\big\rangle & \\ + \omega_Y\big\langle 0|[\, O_i, O_j]\,|0\big\rangle\Big], & \end{aligned} \tag{4.21} $$

where we remember that $\omega_X + \omega_Y = 0$. The F matrix can be written in the following form:

$$ F_{ij}(\omega_Y) = -E_{ij}^{[2]} + \omega_Y S_{ij}^{[2]}, \tag{4.22} $$

where we have introduced the $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$ matrices

$$ E_{ij}^{[2]} = -\frac{1}{2}P(O_i, O_j)\big\langle 0\big|\big[\,[\, H_0, O_i], O_j\big]\,\big|0\big\rangle, \tag{4.23} $$

$$ S_{ij}^{[2]} = \big\langle 0|[\, O_i, O_j]\,|0\big\rangle. \tag{4.24} $$

Introducing the ordering where index j is ordered with excitation before deexcitation ($j > 0$ before $j < 0$) and i is ordered deexcitation before excitation ($i < 0$ before $i > 0$), we can write $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$ in the following form:

$$ \mathbf{E}^{[2]} = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix}, \tag{4.25} $$

$$ \mathbf{S}^{[2]} = \begin{pmatrix} \boldsymbol{\Sigma} & \boldsymbol{\Delta} \\ -\boldsymbol{\Delta}^* & -\boldsymbol{\Sigma}^* \end{pmatrix}. \tag{4.26} $$

The last equation implicitly defines $\mathbf{A}$, $\mathbf{B}$, $\boldsymbol{\Sigma}$, and Δ. (For $i, j > 0$: $A_{ij} = E_{-ij}^{[2]}$, $B_{ij} = E_{-i-j}^{[2]}$, $\Sigma_{ij} = S_{ij}^{[2]}$, $\Delta_{ij} = S_{-i-j}^{[2]}$.) Using the Jacobi identity, we may rewrite the $\mathbf{E}^{[2]}$ matrix:

$$ \begin{aligned} \big\langle 0\big|\big[\,[\, H_0, O_i], O_j\big]\,\big|0\big\rangle &= -\big\langle 0\big|\big[\,[\, O_i, O_j], H_0\big]\,\big|0\big\rangle \\ &\quad -\big\langle 0\big|\big[\,[\, O_j, H_0], O_i\big]\,\big|0\big\rangle \\ &= -\big\langle 0\big|\big[\, O_i, [\, H_0, O_j]\big]\,\big|0\big\rangle. \end{aligned} \tag{4.27} $$

To obtain the last equality, we have assumed that

$$ \begin{aligned} \langle 0|[\,[\, O_m, O_n], H_0]\,|0\rangle &= \sum_k c_k^{mn}\langle 0|[\, O_k, H_0]\,|0\rangle \\ &= 0. \end{aligned} \tag{4.28} $$

The sum over k in Eq. (4.28) may be over both redundant and nonredundant generators in configuration or orbital space for CI and SCF and is therefore an extension relative to the original manifold in Eq. (4.8). The identity in Eq. (4.28) is fulfilled for exact theory, approximate CI, and SCF, where the first equality follows from the form of the operators and the second follows from the

variational criteria. The matrices **A**, **B**, Σ, and Δ can now be written in the form

$$A_{ij} = \left\langle 0 \middle| \left[Q_i, \left[H_0, Q_j^\dagger \right] \right] \middle| 0 \right\rangle, \tag{4.29}$$

$$B_{ij} = \left\langle 0 \middle| \left[Q_i, \left[H_0, Q_j \right] \right] \middle| 0 \right\rangle, \tag{4.30}$$

$$\Sigma_{ij} = \left\langle 0 \middle| \left[Q_i, Q_j^\dagger \right] \middle| 0 \right\rangle, \tag{4.31}$$

$$\Delta_{ij} = \left\langle 0 \middle| \left[Q_i, Q_j \right] \middle| 0 \right\rangle. \tag{4.32}$$

It can be realized using the Brillouin condition [Eq. (4.13)] and the Jacobi identity that **A** and Σ are hermitian, **B** is symmetric, and Δ is antisymmetric and $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$ in Eqs. (4.25) and (4.26) are therefore Hermitian. To introduce the ordering of Eqs. (4.25) and (4.26) on the right-hand side of the linear response equations, we introduce the vector

$$g^Y = \begin{pmatrix} \eta^Y_{-i} \\ \eta^Y_i \end{pmatrix} = \begin{pmatrix} \langle 0 | [Y, Q_i] | 0 \rangle \\ \left\langle 0 \middle| \left[Y, Q_i^\dagger \right] \middle| 0 \right\rangle \end{pmatrix}. \tag{4.33}$$

The response equation for $\lambda^Y(\omega_Y)$,

$$\lambda^Y(\omega_Y) = -(\mathbf{F}(\omega_Y))^{-1} \eta^Y, \tag{4.34}$$

can thus be written as

$$\lambda^Y(\omega_Y) = (\mathbf{E}^{[2]} - \omega_Y \mathbf{S}^{[2]})^{-1} g^Y. \tag{4.35}$$

The linear response function becomes

$$\langle\langle X, Y \rangle\rangle_{\omega_Y} = \sum_{\pm i} \eta^X_i \lambda^Y_i(\omega_Y). \tag{4.36}$$

The derivations of the quadratic, cubic, and higher-order response functions proceed in a similar way. The relevant expressions for the linear, quadratic, and cubic response functions are listed in Tables II–V. In Table II, the expressions are given for the response functions in a variational theory in terms of λ responses and response matrices. The response equations determining the response vectors are given in the second part of Table III for the variational wave function. The matrices are defined in Table IV in general, and in Table V, the relevant matrices are specialized to a single-exponential variational ansatz. These expressions will be used for discussing the structures of the response functions for exact and approximate variational models.

4.B. RESPONSE FUNCTIONS FOR AN EXACT WAVE FUNCTION

In the case of exact theory, we assume that we have the complete set $|i\rangle$ of solutions to the time-independent Schrödinger equation

$$H_0 |i\rangle = E_i |i\rangle. \tag{4.37}$$

Using these states in the state-transfer operators in Eq. (4.5), we obtain expressions for the $\mathbf{S}^{[2]}$ and $\mathbf{E}^{[2]}$ matrices. For the $\mathbf{S}^{[2]}$ matrix, we find the elements

$$\Sigma^{[2]}_{ij} = \langle 0 | [| 0 \rangle \langle i |, | j \rangle \langle 0 |] | 0 \rangle = \delta_{ij} \tag{4.38}$$

TABLE V
Vectors and matrices for a single exponential parametrized variational wave function.[a]

Quantity	
η^Y_μ	$\langle 0 \| [Y, O_i] \| 0 \rangle$
$F_{ij}(\omega_Y)$	$\frac{1}{2} P(O_i(\omega_X), O_j(\omega_Y))[\langle 0 \| [[H_0, O_i], O_j] \| 0 \rangle + \omega_Y \langle 0 \| [O_i, O_j] \| 0 \rangle]$
$G_{ijk}(\omega_Y, \omega_Z)$	$\frac{1}{6} P(O_i(\omega_X), O_j(\omega_Y), O_k(\mathrm{u}_Z))[\langle 0 \| [[[H_0, O_i], O_j], O_k] \| 0 \rangle$ $+(\omega_Y + \omega_Z)\langle 0 \| [[O_i, O_j], O_k] \| 0 \rangle]$
$H_{ijkl}(\omega_Y, \omega_Z, \omega_U)$	$\frac{1}{24} P(O_i(\omega_X), O_j(\omega_Y), O_k(\omega_Z), O_l(\omega_U))[\langle 0 \| [[[[H_0, O_i], O_j], O_k], O_l] \| 0 \rangle$ $+(\omega_Y + \omega_Z + \omega_U)\langle 0 \| [[[O_i, O_j], O_k], O_l] \| 0 \rangle]$
F^Z_{ij}	$\frac{1}{2} P(O_i, O_j) \langle 0 \| [[Z, O_i], O_j] \| 0 \rangle$
G^U_{ijk}	$\frac{1}{6} P(O_i, O_j, O_k) \langle 0 \| [[[U, O_i], O_j], O_k] \| 0 \rangle$
η_i	$\langle 0 \| [H_0, O_i] \| 0 \rangle$

[a]The sum of the frequencies occurring in the derivative expressions is zero; $\omega_X + \omega_Y = 0$, $\omega_X + \omega_Y + \omega_Z = 0$ or $\omega_X + \omega_Y + \omega_Z + \omega_U = 0$.

and

$$\Delta_{ij} = \langle 0|[|0\rangle\langle i|, |0\rangle\langle j|]|0\rangle = 0. \quad (4.39)$$

For the $\mathbf{E}^{[2]}$ matrices, we find

$$A_{ij}^{[2]} = \langle 0|[|0\rangle\langle i|, [H_0, |j\rangle\langle 0|]]|0\rangle = (E_i - E_0)\delta_{ij} = \omega_i \delta_{ij} \quad (4.40)$$

and

$$B_{ij} = \langle 0|[|0\rangle\langle i|, [H_0, |0\rangle\langle j|]]|0\rangle = 0. \quad (4.41)$$

Finally, the g^Y vector becomes

$$g^Y = \begin{pmatrix} \eta_i^Y \\ \eta_i^Y \end{pmatrix} = \begin{pmatrix} -\langle i|Y|0\rangle \\ \langle 0|Y|i\rangle \end{pmatrix}. \quad (4.42)$$

The linear response equations therefore become

$$\begin{pmatrix} (\omega_i - \omega_Y)\lambda_{+i}^Y(\omega_Y) \\ (\omega_i + \omega_Y)\lambda_{-i}^Y(\omega_Y) \end{pmatrix} = \begin{pmatrix} -\langle i|Y|0\rangle \\ \langle 0|Y|i\rangle \end{pmatrix}. \quad (4.43)$$

Inserting these expressions in Eq. (4.33), we obtain the exact linear response functions in the usual sum-over-states representation:

$$\begin{aligned} \langle\langle X, Y \rangle\rangle_{\omega_Y} &= \sum_{i>0} \frac{\langle 0|X|i\rangle\langle i|Y|0\rangle}{\omega_Y - \omega_i} - \sum_{i>0} \frac{\langle 0|Y|i\rangle\langle i|X|0\rangle}{\omega_Y + \omega_i} \\ &= P(X(\omega_X), Y(\omega_Y)) \times \sum_{i>0} \frac{\langle 0|X|i\rangle\langle i|Y|0\rangle}{\omega_Y - \omega_i}. \end{aligned} \quad (4.44)$$

The parametrization in Eq. (4.5) may equally well describe a limited CI expansion with the corresponding approximate states entering the state-transfer operators. In the diagonal representation, the linear response function will thus also have the structure in Eq. (4.44). It is characteristic of a wave function that contains only state-transfer operators (in contrast to many-body operators; see discussion later) that the coupling of excitation and deexcitation operators through the **B** and **Δ** matrices vanishes. Another special feature of this type of wave function is that the **G** matrix (see Table V) vanishes since it contains an odd number of state-transfer operators. The form of the quadratic response function is easily obtained from the general expressions in the Table II and considerations similar to those above. An expression for the $\mathbf{F}^X$ matrix is obtained straightforwardly from the expression in Table V introducing the state-transfer operators. The quadratic response function becomes

$$\langle\langle X; Y, Z \rangle\rangle_{\omega_Y, \omega_Z} = -P(X(\omega_X), Y(\omega_Y), Z(\omega_Z)) \times \sum_{i,j>0} \frac{\langle 0|X|i\rangle\langle i|\bar{Y}|j\rangle\langle j|Z|0\rangle}{(\omega_X + \omega_i)(\omega_Z - \omega_j)}, \quad (4.45)$$

where

$$\bar{Y} = Y - \langle 0|Y|0\rangle. \quad (4.46)$$

The cubic response function becomes, in a similar way,

$$\begin{aligned} \langle\langle X; Y, Z, U \rangle\rangle_{\omega_Y, \omega_Z, \omega_U} &= P(X(\omega_X), Y(\omega_Y), Z(\omega_Z), U(\omega_U)) \\ &\times \left\{ - \sum_{i,j,k>0} \right. \\ &\times \frac{\langle 0|X|i\rangle\langle i|\bar{Y}|j\rangle\langle j|\bar{Z}|k\rangle\langle k|U|0\rangle}{(\omega_X + \omega_i)(\omega_Z + \omega_U - \omega_j)(\omega_U - \omega_k)} \\ &+ \sum_{i>0} \frac{\langle 0|CX|i\rangle\langle i|Y|0\rangle}{(\omega_X + \omega_i)(\omega_Y - \omega_i)} \\ &\times \left. \left(\sum_{j>0} \frac{\langle 0|Z|j\rangle\langle j|U|0\rangle}{(\omega_U - \omega_j)} \right) \right\}. \end{aligned} \quad (4.47)$$

4.C. RESIDUES OF EXACT RESPONSE FUNCTIONS

The exact linear response function has poles for ω_Y equal to plus or minus an excitation energy and only for these values. The residue at $\omega_Y = \omega_f$ is obtained from Eq. (4.44):

$$\lim_{\omega_Y \to \omega_f} (\omega_Y - \omega_f)\langle\langle X, Y \rangle\rangle_{\omega_Y} = T_{of}^X T_{fo}^Y = S_{X,Y}^{of}, \quad (4.48)$$

where we have introduced the transition strength matrix S_{XY}^{of} and the left and right first-order transition matrix elements

$$T_{fo}^Y = \langle f|Y|0\rangle, \quad (4.49)$$

$$T_{of}^X = \langle 0|X|f\rangle. \quad (4.50)$$

The left and right transition moments for a Hermitian operator are related to each other by a com-

plex conjugation: $T^Y_{of} = (T^Y_{fo})^*$. The residue for the linear response function at $\omega_Y = -\omega_f$ is easily obtained by interchanging the X and Y operators and related frequencies ω_Y and ω_X in Eq. (4.48):

$$\lim_{\omega_Y \to -\omega_f} (\omega_Y + \omega_f)\langle\langle X, Y \rangle\rangle_{\omega_Y} = -T^Y_{of}T^X_{fo} = -(S^{of}_{X,Y})^*. \quad (4.51)$$

The residues in Eqs. (4.48) and (4.51) are therefore related by complex conjugation and the change of sign. This is as expected since the exact response function should fulfill the symmetry relation $\langle\langle X, Y \rangle\rangle_{\omega_Y} = \langle\langle X, Y \rangle\rangle^*_{-\omega_Y}$. The transition strength matrix can be written in following form:

$$S^{of}_{XY} = T^X_{of}T^Y_{fo} = \frac{1}{2}\left[T^X_{of}T^Y_{fo} + \left(T^Y_{of}T^X_{fo}\right)^*\right], \quad (4.52)$$

where we now consider X and Y as indices. The transition strength matrix is Hermitian and thus has real eigenvalues. The diagonal elements of S can be written as $|\langle 0|X|f\rangle|^2$. The eigenvalues of the transition strength matrix are thus real and positive in exact theory. Since the diagonal elements represent transition probabilities for transitions between the states O and f, the above result is not surprising. The last equality in Eq. (4.52) is, of course, completely redundant in exact theory; however, it is relevant to establish these two different ways of writing the transition strength matrix for the later discussion of analogous forms in approximate theories.

The quadratic response function has poles where the absolute value of one of the two external frequencies is equal to an excitation energy, $\omega_Y = \pm\omega_f$, $\omega_Z = \pm\omega_f$, or their sum is equal to an excitation energy: $\omega_Y + \omega_Z = \pm\omega_i$. Substituting $-\omega_Y$ for ω_Y in the $\omega_Z = \omega_f$ residue, we obtain

$$\lim_{\omega_Z \to \omega_f} (\omega_Z - \omega_f)\langle\langle X; Y, Z \rangle\rangle_{-\omega_Y, \omega_Z} = -T^{XY}_{of}(-\omega_Y)T^Z_{fo}, \quad (4.53)$$

where we have introduced the second-order transition matrix elements

$$T^{XY}_{of}(-\omega_Y) = P(X(\omega_X), Y(\omega_Y)) \times \sum_{j>0} \frac{\langle 0|X|j\rangle\langle j|\overline{Y}|f\rangle}{\omega_j - \omega_X}, \quad (4.54)$$

where now $\omega_x = \omega_f - \omega_y$. When both ω_X and ω_Y are nonzero, we may write $T^{XY}_{of}(-\omega_Y)$ in the form

$$T^{XY}_{of}(-\omega_Y) = \sum_{j\geq 0} \frac{\langle 0|X|j\rangle\langle j|Y|f\rangle}{\omega_j - \omega_X} + \sum_{j\geq 0} \frac{\langle 0|Y|j\rangle\langle j|X|f\rangle}{\omega_j - \omega_Y}, \quad (4.55)$$

where we have used $\omega_X + \omega_Y = \omega_f$. The $\omega_Z = -\omega_f$ residue becomes

$$\lim_{\omega_Z \to -\omega_f} (\omega_Z + \omega_f)\langle\langle X; Y, Z \rangle\rangle_{\omega_Y, \omega_Z} = T^Z_{of}T^{XY}_{fo}(\omega_Y), \quad (4.56)$$

where

$$T^{XY}_{fo}(\omega_Y) = \left(T^{XY}_{of}(-\omega_Y)\right)^*. \quad (4.57)$$

The residues in Eqs. (4.53) and (4.56) are related as a consequence of the symmetry of the quadratic response function [Eq. (2.21)], giving Eq. (4.56) as minus the complex conjugate of Eq. (4.53). As for the residue of the linear response function, we may introduce a generalized transition strength matrix in a form which explicitly introduces the adjoint symmetry of the above residues:

$$S^{of}_{Z,XY}(\omega_Y) = T^Z_{of}T^{XY}_{fo}(\omega_Y) = \frac{1}{2}\left(T^Z_{of}T^{XY}_{fo}(\omega_Y) + \left(T^{XY}_{of}(-\omega_Y)T^Z_{fo}\right)^*\right). \quad (4.58)$$

The residues for ω_Y or ω_X equal to an excitation energy are trivially related to those of Eqs. (4.53) and (4.56) by permutation of operators and related frequencies. We note that the residues of the quadratic response functions in Eqs. (4.54) and (4.56) have poles when $\omega_Y = \omega_i$ or $\omega_X = \omega_i$. The first of these double residues becomes

$$\lim_{\omega_Y \to \omega_i} (\omega_Y - \omega_i) \times \left\{\lim_{\omega_Z \to -\omega_f} (\omega_Z + \omega_f)\langle\langle X; Y, Z \rangle\rangle_{\omega_Y, \omega_Z}\right\} = -T^Z_{of}T^X_{fi}T^Y_{fo}, \quad (4.59)$$

where

$$T^X_{fi} = \langle f|X|i\rangle - \delta_{fi}\langle 0|X|0\rangle. \quad (4.60)$$

The residue for $\omega_X = \omega_i$ is obtained by interchanging X and Y. The residue of Eq. (4.56) gives

similarly

$$\lim_{\omega_Y \to -\omega_i} (\omega_Y + \omega_i) \times \left\{ \lim_{\omega_Z \to \omega_f} (\omega_Z - \omega_f) \langle\langle X; Y, Z \rangle\rangle_{\omega_Y, \omega_Z} \right\} = -T^Y_{oi} T^X_{if} T^Z_{fo}. \quad (4.61)$$

These double residues of the quadratic response function are thus products of transition matrix elements between excited states and transition matrix elements between the ground state and an excited state. For $i \neq f$, we can thus find the transition strength matrix between states different from the reference state:

$$S^{of}_{XY} = T^X_{if} T^Y_{fi} = \frac{1}{2}\left[T^X_{if} T^Y_{fi} + \left(T^Y_{if} T^X_{fi} \right)^* \right], \quad (4.62)$$

where the second equality is again somewhat redundant in exact theory but will be useful for the discussion of approximate theories. For $i = f$, Eq. (4.60) contains information on the difference of first-order properties in the excited state and in the ground state:

$$\langle X \rangle_i = \langle X \rangle_o + T^X_{ii} = \frac{1}{2}(\langle X \rangle_o + \langle X \rangle^*_o) + \frac{1}{2}\left(T^X_{ii} + (T^X_{ii})^* \right). \quad (4.63)$$

Finally, we note that the residue search

$$\lim_{\omega_Y \to \omega_i} (\omega_Y - \omega_i) \left\{ \lim_{\omega_Z \to \omega_f} (\omega_Z - \omega_f) \langle\langle X; Y, Z \rangle\rangle_{\omega_Y, \omega_Z} \right\} = 0 \quad (4.64)$$

gives zero for an exact state (unless there exist a state j such that the difference in energy between states j and i is equal to the excitation energy for state f: $\omega_f = \omega_j - \omega_i$).

The cubic response function has poles where the absolute value of one of the three external frequencies is equal to an excitation energy, $\omega_Y = \pm\omega_f$, $\omega_Z = \pm\omega_f$, or $\omega_U = \pm\omega_f$, or when the sums of two or three of these frequencies are equal to an excitation energy. For later reference, we note that the following residue search in the cubic response function gives information on the cross section for second-order transitions:

$$\begin{aligned} \lim_{\omega_Z + \omega_U \to \omega_f} (\omega_Z + \omega_U - \omega_f) \langle\langle X; Y, Z, U \rangle\rangle_{-\omega_Y, \omega_Z, \omega_U} &= T^{XY}_{of}(-\omega_Y) T^{ZU}_{fo}(\omega_U) \\ &= \frac{1}{2}\Big(T^{XY}_{of}(-\omega_Y) T^{ZU}_{fo}(\omega_U) \\ &\quad + \left(T^{ZU}_{of} \right) T^{XY}_{fo}(\omega_Y)^* \Big) \\ &\equiv S^{of}_{XY,ZU}(\omega_Y, \omega_U). \end{aligned} \quad (4.65)$$

Other residues of the cubic response functions are related to third-order transition matrix elements and excited-state dynamic second-order properties, but will not be discussed here.

4.D. RESIDUES OF RESPONSE FUNCTIONS FOR A SINGLE EXPONENTIAL VARIATIONAL PARAMETRIZATION

The identification of molecular properties in response theory is based on analogy arguments. In the previous subsections, we developed the response functions for an exact state and found poles and residues of the exact response functions. In doing so, we identified expressions relating second- and higher-order frequency-dependent response properties, excitation energies, and transition properties to the linear, quadratic, and cubic response functions. In response theory, expressions for the evaluation of these properties for an approximate method is found from a development analogous to the one above for an exact wave function, and expressions for the evaluation of the molecular properties are inferred from analogy with the response function for the exact state.

The linear response function for an exact wave function has poles for ω^Y equal to plus or minus an excitation energy. In analogy with this, the poles of the response function for an approximate method determine the response theory excitation energies for this approximate method. From Eqs. (4.31)–(4.33), we see that for any variational model the response vectors and thus the response functions have poles when $\mathbf{F}(\omega_Y)^{-1}$ is singular. From Eq. (4.32), we find that the poles are determined from the generalized eigenvalue equation

$$\mathbf{E}^{[2]}\mathbf{U} = \mathbf{S}^{[2]}\mathbf{U}\boldsymbol{\Omega}, \quad (4.66)$$

where $\mathbf{U}$ contains the eigenvectors and $\boldsymbol{\Omega}$ is a diagonal matrix containing the eigenvalues. The generalized eigenvalue equation [Eq. (4.66)] has implicit a paired structure that is transparent when

the specific ordering of the excitation and deexcitation operators is used where the matrices $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$ have the structure in Eqs. (4.25), (4.26), and (4.29)–(4.32). The paired structure is thus obtained for a single exponential variational ansatz for the wave function for any kind of operator manifold.

The eigenvalue equation Eq. (4.66) only determines the eigenvector within a normalization. We require that the eigenvectors in $\mathbf{U}$ satisfy the normalization condition,

$$\mathbf{U}^{\dagger}\mathbf{S}^{[2]}\mathbf{U} = \boldsymbol{\sigma}, \tag{4.67}$$

where σ is a diagonal matrix with σ_i as diagonal elements. From Eqs. (4.66) and (4.67), we see that this representation simultaneously diagonalizes $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$, such that in addition to Eqs. (4.67) we obtain

$$\mathbf{U}^{\dagger}\mathbf{E}^{[2]}\mathbf{U} = \boldsymbol{\omega}, \tag{4.68}$$

where ω is a diagonal matrix with ω_i as diagonal elements. The existence of such a representation has been discussed elsewhere (see [4, 6] and references therein). We can relate the eigenvalues of the generalized eigenvalue equation in Eq. (4.66) to ω and σ:

$$\boldsymbol{\sigma}\boldsymbol{\Omega} = \boldsymbol{\omega}. \tag{4.69}$$

If we assume that the diagonal elements in σ are nonvanishing, we can scale the eigenvectors such that the σ_i elements have absolute value 1. With $\sigma_i = \pm 1$, we obtain that the linear response function has poles for $\omega_Y = \pm\omega_i$. We chose to order the eigenvectors with $\sigma_j = +1$ with a positive index and $\sigma_{-j} = -1$ with a negative index. We denote in the following the eigenvector with excitation energy ω_f as U^f. From Eqs. (4.25)–(4.26) and (4.66), it is seen that if $U^f = \binom{v_1}{v_2}$ is an eigenvector with excitation energy ω_f then $U^{-f} = \binom{v_2^*}{v_1^*}$ is an eigenvector to Eq. (4.66) with eigenvalue $\Omega_{-f} = -\omega_f$.

Using Eqs. (4.67)–(4.69), we find

$$(\mathbf{E}^{[2]} - \omega_Y\mathbf{S}^{[2]})^{-1} = \mathbf{U}(\boldsymbol{\omega} - \omega_Y\boldsymbol{\sigma})^{-1}\mathbf{U}^{\dagger}. \tag{4.70}$$

From Eq. (4.70) and the linear response equation in Eq. (4.32), we see that the linear response vectors have poles for plus and minus the eigenvalues with the following residues:

$$\lim_{\omega_Y \to \omega_f} (\omega_Y - \omega_f)\lambda^Y(\omega_Y) = U^f {}^v T^Y_{fo}, \tag{4.71}$$

$$\lim_{\omega_Y \to -\omega_f} (\omega_Y + \omega_f)\lambda^Y(\omega_Y) = {}^v T^Y_{of} U^{-f}, \tag{4.72}$$

where we have introduced

$${}^v T^Y_{fo} = -\sum_{\pm i} U_i^{-f}\eta_i^Y, \tag{4.73}$$

$${}^v T^Y_{of} = \sum_{\pm i} \eta_i^Y U_i^f. \tag{4.74}$$

The residues of the linear response function becomes

$$\lim_{\omega_Y \to \omega_f} (\omega_Y - \omega_f)\langle\langle X, Y \rangle\rangle_{\omega_Y} = {}^v T^X_{of} {}^v T^Y_{fo}, \tag{4.75}$$

$$\lim_{\omega_Y \to -\omega_k} (\omega_Y + \omega_k)\langle\langle X, Y \rangle\rangle_{\omega_Y} = -{}^v T^Y_{of} {}^v T^X_{fo}. \tag{4.76}$$

By comparing with the corresponding exact theory in Eqs. (4.52), we are led to identify the transition strength matrix in variational theory:

$${}^v S^{of}_{XY} = {}^v T^X_{of} {}^v T^Y_{fo} = \frac{1}{2}\left[{}^v T^X_{of} {}^v T^Y_{fo} + \left({}^v T^Y_{of} {}^v T^X_{fo}\right)^*\right]. \tag{4.77}$$

This is the expression for calculation of transition properties in variational theory. We note that variational theory has several features in common with exact theory: The left and right transition moments in Eqs. (4.73) and (4.74) are adjoint. The transition strength matrix is Hermitian and we may choose between the simple product of a left and a right transition matrix element or the explicitly symmetrized expression in Eq. (4.77). From the residues, we can, in principle, only determine the transition matrix elements within a sign: however, only the product of transition matrix elements as given by the transition strength matrix in Eq. (4.77) is required to calculate the physical observable. We also note that this is not different from exact theory where transition matrix elements only are determined up to a complex phase factor, since the wave functions only are determined up to a phase factor.

We now investigate the poles of the quadratic response function in variational theory. The quadratic response function has residues for $\omega_Y = \pm\omega_f$ or $\omega_Z = \pm\omega_f$ or when the sum of these two frequencies is equal to an excitation energy, in

accord with exact theory. We obtain the residues

$$\lim_{\omega_Z \to \omega_f} (\omega_Z - \omega_f)\langle\langle X; Y, Z \rangle\rangle_{-\omega_Y, \omega_Z} = -{}^v T_{of}^{XY}(-\omega_Y)\, {}^v T_{fo}^{Z}, \tag{4.78}$$

$$\lim_{\omega_Z \to -\omega_f} (\omega_Z + \omega_f)\langle\langle X; Y, Z \rangle\rangle_{\omega_Y, \omega_Z} = {}^v T_{of}^{Z}\, {}^v T_{fo}^{XY}(\omega_Y), \tag{4.79}$$

where we have introduced the second-order transition matrix elements,

$$\begin{aligned} {}^v T_{of}^{XY}(-\omega_Y) &= -P(X(\omega_X), Y(\omega_Y)) \\ &\quad \times \left[\mathbf{F}^X + \frac{1}{2}\mathbf{G}(-\omega_Y, \omega_f)\lambda^X(-\omega_X)\right] \\ &\quad \times \lambda^Y(-\omega_Y)U^f, \end{aligned} \tag{4.80}$$

$$\begin{aligned} {}^v T_{fo}^{XY}(\omega_X, \omega_Y) &= P(X(\omega_X), Y(\omega_Y)) \\ &\quad \times \left[\mathbf{F}^X + \frac{1}{2}\mathbf{G}(\omega_Y, -\omega_f)\lambda^X(\omega_X)\right] \\ &\quad \times \lambda^Y(\omega_Y)U^{-f}, \end{aligned} \tag{4.81}$$

where, again, $\omega_X = \omega_f - \omega_Y$. These are the analogs of Eqs. 4.54) and (4.57) for a variational theory. The residue of the quadratic response functions in Eqs. (4.78) and (4.79) have poles when $\omega_Y = \pm\omega_i$. The residue becomes

$$\lim_{\omega_Y \to \omega_i} (\omega_Y - \omega_i) \times \left\{ \lim_{\omega_Z \to -\omega_f} (\omega_Z + \omega_f)\langle\langle X; Y, Z \rangle\rangle_{\omega_Y, \omega_Z} \right\} = -{}^v T_{of}^{Z}\, {}^v T_{fi}^{X}\, {}^v T_{io}^{Y}, \tag{4.82}$$

$$\lim_{\omega_Y \to -\omega_i} (\omega_Y + \omega_i) \times \left\{ \lim_{\omega_Z \to \omega_f} (\omega_Z - \omega_f)\langle\langle X; Y, Z \rangle\rangle_{\omega_Y, \omega_Z} \right\} = -{}^v T_{oi}^{Y}\, {}^v T_{if}^{X}\, {}^v T_{fo}^{Z}, \tag{4.83}$$

where

$${}^v T_{if}^{X} = \left(\mathbf{F}^X + \mathbf{G}(-\omega_i, \omega_f)\lambda^X(\omega_i - \omega_f)\right)U^{-i}U^f. \tag{4.84}$$

This provides us with the means to calculate the transition strength between excited states. The special case $i = f$ is particularly interesting since this is related to the evaluation of an excited-state expectation value. We discuss this in the next subsection.

Finally, we note that the residue search in Eq. (4.64) that gives zero for an exact quadratic response function in general gives a nonvanishing result for an approximate variational approach. This is related to the fact that the **G** matrix is nonvanishing, while it vanishes for an exact state.

4.E. EXCITED-STATE PROPERTIES FROM RESIDUES OF RESPONSE FUNCTIONS

The evaluation of excited-state properties such as expectation values, molecular gradients, and Hessians are interesting, as they are the key to the characterization of excited states in the same way as for the ground state where they have long been calculated efficiently. The analytical evaluation of the molecular gradients for excited states are important for an efficient optimization of excited-state geometries. The second-derivative matrix allows for analytical calculation of excited-state harmonic frequencies. Higher-order derivatives can be used to investigate the anharmonic force field. Therefore, we give particular attention to the calculation of excited-state properties in light of the results derived in the previous section. In particular, we discuss the use of Eq. (4.84) for the evaluation of excited-state first-order properties.

In the previous sections of this article, we used Fourier component variational perturbation theory with emphasis on obtaining response functions in a form consistent with the $2n + 1$ and $2n + 2$ rules. Therefore, computationally tractable expressions are obtained for second- and higher-order frequency-dependent properties. The question is whether similar computational tractable expressions are obtained for properties determined as residues of the response functions. For $i = f$, we obtain Eq. (4.84) in the following form:

$$\langle Y \rangle_f - \langle Y \rangle_0 = {}^v T_{ff}^{Y} = \left(\mathbf{F}^Y + \mathbf{G}(-\omega_f, \omega_f)\lambda^Y(0)\right)U^{-f}U^f. \tag{4.85}$$

To evaluate expectation values for excited states, we thus have to solve one set of equations for each property according to Eq. (4.85). This is not in agreement with a $2n + 1$ rule for the *excited state*, but we have to remember that our response func-

tion and the $2n + 1$ rules refer to the ground-state properties. In response theory, the excited state is obtained not from a variational calculation on the excited state, but from a variational calculation on the ground state followed by a solution for the appropriate root in a generalized eigenvalue equation. The excited states as described by response theory for a variational model for the ground state are not variational. While the expressions for transition properties obtained directly from the residues appears to be computationally efficient, those for calculations of properties in the excited state are not. We will here investigate this issue a bit further. It seems natural to take the energy of the excited state to be

$$E_f = E_o + \omega_f. \tag{4.86}$$

As usual, our approach is based on an analogy with exact theory where the sum of the excitation energy and the ground-state energy is trivially equal to the excited-state energy. The parametrization in Eq. (4.1) with the chosen set of operators, along with the variational principle, determine first of all the ground-state energy in a usual variational calculation. The excitation energies are determined, in turn, through response theory. Finally, Eq. (4.86) defines the excited-state total energy and thus all static properties in the excited state that can be obtained as energy derivatives.

We strictly use the analogy argument above to determine the excited-state properties. The first step is thus to construct a variational Lagrangian that gives the correct total energy. For this purpose, it is convenient to write the excitation energy as

$$\omega_f = (U^f)^\dagger \mathbf{E}^{[2]} U^f, \tag{4.87}$$

where U^f is the eigenvector with excitation energy ω_f and where we have assumed that the U^f vector satisfies the normalization, $(U^f)^\dagger \mathbf{S}^{[2]} U^f = 1$. $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$ are defined in Eqs. (4.23) and (4.24). The ground state is constrained to fulfill the variational condition in Eq. (4.13), which we can write as $\eta = 0$. The total ground-state energy is obtained according to Eq. (4.12) as $E_0 = \langle 0|H_o|0\rangle$. The Lagrangian representing Eq. (4.86) therefore becomes

$$L_f = E_o + (U^f)^\dagger \mathbf{E}^{[2]} U^f + \bar{\alpha}\left((U^f)^\dagger \mathbf{S}^{[2]} U^f - 1\right) + \bar{\lambda}^f \eta, \tag{4.88}$$

where $\bar{\alpha}$ and $\bar{\lambda}^f$ are Lagrangian multipliers. All matrices in this expression are defined for zero-field strength in the previous subsections. To be useful in this context, we need to extend the definition of the Lagrangian to arbitrary values of the field strength. We do so by replacing H_0 with H, the reference state $|0\rangle$ with $\exp(\Lambda)|0\rangle$, and, finally, the operators O_i with $\exp(\Lambda)O_i \exp(-\Lambda)$. This allows us to use Eq. (4.88) to calculate energy derivatives of the excited-state surface for general perturbations—dipole operators, geometrical perturbations, and so on. We require the Lagrangian to be variational in all parameters $-(U^f)^\dagger$, U^f, λ, $\bar{\alpha}$, and $\bar{\lambda}^f$ and obtain

$$0 = \frac{dL_f}{d\bar{\lambda}^f} = \eta, \tag{4.89}$$

$$0 = \frac{dL_f}{d\bar{\alpha}} = (U^f)^\dagger \mathbf{S}^{[2]} U^f - 1, \tag{4.90}$$

$$0 = \frac{dL_f}{d(U^f)^\dagger} = \mathbf{E}^{[2]} U^f + \bar{\alpha}\mathbf{S}^{[2]} U^f, \tag{4.91}$$

$$0 = \frac{dL_f}{dU^f} = (U^f)^\dagger \mathbf{E}^{[2]} + \bar{\alpha}(U^f)^\dagger \mathbf{S}^{[2]}, \tag{4.92}$$

and

$$0 = \frac{dL_f}{d\lambda} = \frac{dE_0}{d\lambda} + (U^f)^\dagger \frac{d\mathbf{E}^{[2]}}{d\lambda} U^f + \bar{\alpha}(U^f)^\dagger \frac{d\mathbf{S}^{[2]}}{d\lambda} U^f + \bar{\lambda}^f \frac{d\eta}{d\lambda}. \tag{4.93}$$

The variational condition for the $\bar{\lambda}^f$ multipliers gives the constraint that ensures that the ground state satisfies the Brillouin condition and is variational. The variational condition for the $\bar{\alpha}$ multiplier Eq. (4.89) give back the normalization condition on the excitation vectors. We have treated U^f and $(U^f)^\dagger$ as independent variables. Since $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$ are Hermitian, the variational condition for $(U^f)^\dagger$ [Eq. (4.91)] is satisfied if U^f is an eigenvector of the generalized eigenvalue problem and $\bar{\alpha}$ is chosen as the excitation energy. The variational condition for U^f [Eq. (4.92)] is the Hermitian adjoint of Eq. (4.91) and thus fulfilled under the same assumptions. The variational condition for λ [Eq. (4.93)] determines the $\bar{\lambda}$ multipliers.

In agreement with the $2n + 1$ and $2n + 2$ rules, we obtain the following expression for the first

derivative of the excited-state total energy:

$$\frac{dL}{d\varepsilon_X(0)} = \frac{\partial E_0}{\partial \varepsilon_X(0)} + (U^f)^\dagger \frac{\partial \mathbf{E}^{[2]}}{\partial \varepsilon_X(0)} U^f + \bar{\lambda}^f \frac{\partial \eta}{\partial \varepsilon_X(0)}, \tag{4.94}$$

where it is understood that the derivatives are taken for zero-field strength. Note that $[\partial \mathbf{S}^{[2]}]/[\partial \varepsilon_Y(0)] = 0$. At zero field, the equations for the zeroth-order multipliers are found from Eq. (4.93) as

$$\bar{\lambda}\mathbf{E}^{[2]} = -(U^f)^\dagger \frac{d\mathbf{E}^{[2]}}{d\lambda} U^f, \tag{4.95}$$

where we have used that at the optimal point $(dE_0)/(d\lambda) = 0$ and $(d\eta)/(d\lambda) = \mathbf{E}^{[2]}$, using Eq. (4.27). Furthermore, we have used that $(d\mathbf{S}^{[2]})/(d\lambda) = 0$.

We may write this in a form more easily compatible with Eq. (4.84) [using $(U^f)^\dagger(\partial \mathbf{E}^{[2]})/(\partial \varepsilon_X(0)) = \mathbf{F}^X U^{-f}$]:

$$\langle X \rangle_f = \langle X \rangle_0 + \mathbf{F}^X U^{-f} U^f + \bar{\lambda}^f \eta^X. \tag{4.96}$$

We see that the G term of Eq. (4.84) was replaced by a Lagrangian multiplier term in Eq. (4.96). This could also easily be obtained from Eq. (4.84) directly by interchange techniques. We find the above procedure more general as higher-order properties of the excited state can easily be obtained and in a form that fulfills the $2n + 1$ and $2n + 2$ rules. Also, it is illustrative that a variational functional exists for the excited-state total energy, although the excited state is not variationally optimized. Similarly, the expression [Eq. (4.84)] for evaluating the transition probability between excited states can be rewritten in a form requiring only the solution of one additional set of equations for the evaluation of the transition probability for all operators X.

The property evaluated in Eq. (4.84) is the derivative of the excitation energy with respect to the strength of the perturbation Y. we are thus, in fact, evaluating the derivative of a property already determined from a simpler response function—namely, as the poles of the linear response function. We showed above that this property is more efficiently evaluated by using the derivative expression together with a variational Lagrangian than by using Eq. (4.84) obtained from the residues and it is similar for the second derivatives. An expression for these can be derived from the second residue of the cubic response function, which will depend on both first- and second-order λ responses. A similar second derivative expression of the Lagrangian in Eq. (4.88) depends only on first-order λ responses, but will now instead depend on first-order responses to U^f. This suggests that for the evaluation of properties that formally can be described as derivatives of low-order properties it may be advantageous to evaluate these as derivatives of the low-order property rather than from the expressions for higher-order residues. This statement obtains even more weight when we later discuss the similar aspects for nonvariational methods.

It is important here to note the limitations of the analogy with the exact theory used above. In exact theory, the excited-state wave functions are eigenvectors of the Hamiltonian problem Eq. (4.37). In response theory, the excitation energies are obtained by solving the response theory generalized eigenvalue equations. For an exact state, we have seen that the excitation energies obtained as poles of the response functions are just the ordinary energy differences. However, in general, the excitation energies obtained from the response theory generalized eigenvalue equations are both conceptually and numerically quite different from the result obtained by diagonalizing a Hamiltonian matrix. For (orbital unrelaxed) CI calculations, the two approaches become equivalent and we indirectly have an explicit representation of the excited states in terms of eigenvectors of a CI matrix. This is not true for SCF and MCSCF response functions where it is not possible to generate an explicit representation of the excited-state wave function from the excitation vector and the SCF or MCSCF reference function. For the SCF response function —also commonly denoted RPA—there has been some discussion on how to determine a reference state that is consistent with the basic assumptions of the RPA approximation [58–60]. The present approach does not solve this problem. Although it is important to note that the analogy with exact theory is not complete in all respects, it is also worth noting that response theory does not rely on an explicit representation of the excited states, and the response theory representation of the ground and excited state (though not a wave-function representation) is joined together by the fact that the ground state and the response function follow from the same parametrization. All physical properties of the excited states are obtained in a consistent way either from residues of higher-order response

functions or by differentiation of the total energy of the excited state as described previously in this subsection.

5. Response Theory for Nonvariational Wave Functions: Coupled Cluster Response Theory

Some of the simplest and most widespread methods for treating dynamical electron correlation are nonvariational. In this section, we will discuss various aspects of response theory for single-reference coupled cluster (CC) theory to demonstrate some of the most important considerations that are required for developing response theory for nonvariational methods. Different strategies for the evaluation of molecular properties in CC theory have been proposed [40, 44, 45, 61–77]. Our recent implementations of CC response functions [67–71] are based on the approach advocated here. We discuss the determination of response properties in CC theory without and with orbital relaxation. Expressions for frequency-dependent polarizabilities in the context of second-order Møller–Plesset perturbation theory were derived recently [22, 38] using also quasienergy Lagrangians, but a more complicated formulation of the intermediates. We briefly discuss how in the present approach frequency-dependent response properties in Møller–Plesset perturbation theory can be obtained as approximations to orbital relaxed CC response properties.

5.A. THE CC QUASIENERGY LAGRANGIAN

The time-dependent CC state is parametrized as

$$\begin{aligned}|\overline{CC}(t)\rangle &= \exp(-iF(t))|\widetilde{CC}(t)\rangle \\ &= \exp(-iF(t))\exp(T(t))|R\rangle, \quad (5.1)\end{aligned}$$

where the reference $|R\rangle$ typically is the SCF state. In this subsection, we consider the ''unrelaxed'' approach where the reference R is fixed and not time-dependent. $F(t)$ is a function of time and $T(t)$ is the time-dependent cluster operator consisting of single, double, . . . , and up to m-tuple excitations:

$$T(t) = T_1(t) + T_2(t) + \cdots T_m(t). \quad (5.2)$$

In the case where $m = N =$ the number of electrons, the exponential CC parametrization is an alternative representation of the exact state in the chosen one-particle basis set—the FCI state. The cluster operators can be written in shorthand notation:

$$T(t) = \sum_{i=1}^{m} T_i(t) = \sum_{i,\,\mu_i} t_{\mu_i}(t)\tau_{\mu_i}. \quad (5.3)$$

The summation is over both excitation levels i and excitations τ_{μ_i} within this excitation level.

We will in the following derivations assume several properties for the τ_{μ_i} excitation operators to be fulfilled. We assume they commute

$$[\tau_{\mu_i}, \tau_{\nu_j}] = 0 \quad (5.4)$$

and satisfy the killer condition

$$\langle R|\tau_{\mu_i} = 0. \quad (5.5)$$

Furthermore, it is convenient in the derivation to use a biorthonormal representation. This implies that we have defined the excitation (τ_{μ_i}) and deexcitation ($\tau_{\mu_i}^{\dagger}$) operators such that the metric matrix **S** is equal to the unit matrix:

$$S_{\mu_i\nu_j} = \langle \mu_i|\tau_{\nu_j}|R\rangle = \langle R|\tau_{\nu_i}^{\dagger}\tau_{\nu_j}|R\rangle = \delta_{\mu_i\nu_j} = \delta_{ij}\delta_{\mu\nu}. \quad (5.6)$$

The deexcitation operators are not necessarily the adjoint of the excitation operators, but are often chosen as a linear combination of the adjoint of the excitation operators with scaling coefficients chosen to satisfy Eq. (5.6). Equations (5.4)–(5.6) are not crucial to derive response functions in the approach we take here; however, they are important in closed-shell single-reference CC theory as they simplify the derivation significantly and further make the theory much more computationally tractable. In the case of the closed-shell CC ansatz, the above assumptions appear rather natural and are no restriction. To develop response theory for a more general CC ansatz, the criteria can be relaxed without fundamental consequences except for an increased complexity of the equations.

Introducing the ansatz Eq. (5.3) into the time-dependent Schrödinger equation and transforming with $\exp(-T(t))$, we obtain

$$\exp(-iF(t))\exp(-T(t))\left(H - i\frac{\partial}{\partial t} - \dot{F}(t)\right)|\widetilde{CC}(t)\rangle = 0. \quad (5.7)$$

Projection onto the reference determines the time-dependence of F:

$$Q(t) = \dot{F}(t) = \left\langle R \middle| \left(H - i\frac{\partial}{\partial t} \right) \middle| \widetilde{CC}(t) \right\rangle = \langle R|H|\widetilde{CC}(t)\rangle. \quad (5.8)$$

We denote $Q(t)$ as the CC time-dependent quasienergy. Projecting Eq. (5.7) onto $\langle \mu_i| = \langle R|\tau_{\mu_i}^{\dagger}$, we obtain the time-dependent cluster amplitude equations

$$\left\langle \mu_i \middle| \exp(-T(t)) \left(H - i\frac{\partial}{\partial t} \right) \middle| \widetilde{CC}(t) \right\rangle = 0. \quad (5.9)$$

The time-dependent cluster amplitudes are obtained without reference to $Q(t)$. When the cluster amplitudes have been found, $Q(t)$ can be obtained from Eq. (5.8). It is noted that in the time-independent limit Eq. (5.9) reduces to the usual cluster amplitude equations

$$\Omega_{\mu_i} = \langle \mu_i|\exp(-T)\, H \exp(T)|R\rangle = 0 \quad (5.10)$$

and Eq. (5.8) becomes the usual CC ground-state energy

$$E_0 = \langle R|H \exp(T)|R\rangle. \quad (5.11)$$

We may express the time-dependent quasienergy in Eq. (5.8) with the time-dependent constraints in Eq. (5.9) in terms of a time-dependent CC quasienergy Lagrangian [67]:

$$L = \langle R|H \exp(T(t))|R\rangle + \sum_{i,\mu_i} \bar{t}_{\mu_i}(t) \left\langle \mu_i \middle| v \exp(-T(t)) \left(H - i\frac{\partial}{\partial t} \right) \times \exp(T(t)) \middle| R \right\rangle. \quad (5.12)$$

From this point, the determination of the CC response functions and response equations is a simple application of the theory developed in the preceding sections. For approximate CC models, response functions are simply obtained by introducing the corresponding approximated CC equations as constraints in the Lagrangian. The above procedure can be applied to any CC model with a well-defined quasienergy and with well-defined time-dependent amplitude equations. This is crucial for using the theory for, for example, the CC2 and CC3 models as discussed before [67, 68].

From the considerations in Section 2 [in particular, the discussion following Eqs. (2.67)–(2.69)], it is clear that the CC quasienergy is not necessarily real. We should have this in mind and ensure that the expressions for molecular properties satisfy the symmetry relations in Eqs. (2.19)–(2.22). We thus have to apply the symmetrization procedure in Eqs. (2.70)–(2.73) using the symmetrization operator $C^{\pm\omega}$ in Eq. (3.35).

5.B. CC RESPONSE FUNCTIONS

The zeroth-order Lagrangian becomes

$$L^{(0)} = \langle \Lambda|H_0|CC\rangle, \quad (5.13)$$

where we from the zeroth-order amplitudes and multipliers have defined the unperturbed CC wave function:

$$|CC\rangle = \exp(T^{(0)})|R\rangle, \quad (5.14)$$

as well as the auxiliary combination of the projection onto the reference state and the transformed excited configurations:

$$\langle \Lambda| = \left(\langle R| + \sum_{i,\mu_i} \bar{t}_{\mu_i}^{(0)} \langle \mu_i| \right) \exp(-T^{(0)}). \quad (5.15)$$

The variational condition with respect to the zeroth-order Lagrangian multipliers gives the cluster amplitude equations

$$0 = \frac{\partial L^{(0)}}{\partial \bar{t}_{\mu_i}^{(0)}} = \langle \mu_i|\exp(-T^{(0)})\, H_0 \exp(T^{(0)})|HF\rangle, \quad (5.16)$$

and the variational condition for the amplitudes determines the zeroth-order multipliers

$$0 = \frac{\partial L^{(0)}}{\partial t_{\nu_j}^{(0)}} = \left\langle \Lambda \middle| \left[H_0, \tau_{\nu_j} \right] \middle| CC \right\rangle = \left(\langle R| + \sum_{i,\mu_i} \bar{t}_{\mu_i}^{(0)} \langle \mu_i| \right) \exp(-T^{(0)}) \times \left[H_0, \tau_{\nu_j} \right] |CC\rangle. \quad (5.17)$$

When the cluster amplitude equations Eq. (5.16) are solved, the zeroth-order Lagrangian is variational with respect to the zeroth-order multipliers and the Lagrangian gives the usual CC energy.

Equation (5.17) ensures that the Lagrangian is variational with respect to the cluster amplitudes, thereby giving an equation for the multipliers.

Following the outline in Section 3 for nonvariational methods, we obtain the standard expressions for an expectation value in CC theory:

$$\langle X \rangle = \frac{\partial \{L^{(1)}(t)\}_T}{\partial \varepsilon_X^{(0)}} = \langle \Lambda | X | CC \rangle. \quad (5.18)$$

Equation (5.18) requires only the zeroth-order amplitudes and multipliers for the determination of all first-order properties. The form of the energy in Eq. (5.13) and first-order properties in Eq. (5.18) show that a real energy and real expectation value are not guaranteed. In modern electronic structure theory, the unperturbed solution to the molecular Schrödinger equation is most often obtained using real arithmetic. For most practical purposes, this is therefore not a problem that needs to be considered. However, the expressions for the first-order property in Eq. (5.18), in principle, also gives a nonzero contribution even if X is a purely imaginary Hermitian operator and the wave function is real. This means that the standard expression used in CC theory in some sense is unphysical; however, usually, we do not ask for such an expectation value since its value is zero in exact theory. In any case, this artifact is corrected for when the symmetrization in Eq. (2.70) is carried out:

$$\begin{aligned} \langle X \rangle &= \frac{1}{2} C^{\pm\omega} \langle \Lambda | X | CC \rangle \\ &= \frac{1}{2} (\langle \Lambda | X | CC \rangle + \langle \Lambda | X | CC \rangle^*). \end{aligned} \quad (5.19)$$

Consider the case where the reference wave function is purely real. For a one-electron operator, the expectation value in the form in Eq. (5.18) can be written in terms of a real asymmetric density matrix D:

$$D_{pq} = \langle \Lambda | E_{pq} | CC \rangle. \quad (5.20)$$

Denoting the integrals of the one-electron operator as X_{pq}, we obtain the following expression for the first-order property from Eq. (5.18):

$$\langle X \rangle = \sum_{pq} D_{pq} X_{pq}, \quad (5.21)$$

while Eq. (5.19) becomes

$$\begin{aligned} \langle X \rangle &= \sum_{pq} D_{pq} \frac{1}{2} (X_{pq} + X_{pq}^*) \\ &= \sum_{pq} \frac{1}{2} (D_{pq} + D_{qp}) X_{pq}. \end{aligned} \quad (5.22)$$

For a real Hermitian operator and a set of real orbitals, Eqs. (5.21) and (5.22) are equivalent due to the symmetry properties of the integrals. For a purely imaginary Hermitian operator, the symmetry properties are different and only Eq. (5.22) gives the correct zero result. The conclusion of this discussion is that the standard expression Eq. (5.21) is valid for real operators; however, Eq. (5.22) is, in general, more appropriate. Expressions of the type in Eq. (5.18) have often been denoted generalized Hellmann–Feynman theorems. It is, however, clear that Eq. (5.18) is fundamentally different from a Hellmann–Feynman theorem since $\langle \Lambda |$ is not the adjoint of $|\mathrm{CC}\rangle$, but only an auxiliary state that contains the Lagrangian multipliers. This is further substantiated by Eq. (5.19), showing that the physical expectation value appears in a somewhat different form than as the usual expectation value in the Hellmann–Feynman theorem. Care should therefore be exercised in using Eq. (5.18) as a generalized Hellmann–Feynman theorem. Only when the symmetrized form in Eq. (5.19) is replacing Eq. (5.18) in the derivation of [53] is the same result obtained as in the present derivation. Using the Lagrangian technique, the concept of a generalized Hellmann–Feynman theorem becomes somewhat redundant as Eqs. (5.18) and (5.19) are just the lowest-order realization of the $2n + 1$ and $2n + 2$ rules and the difference between Eq. (5.19) and Eq. (5.18) becomes a matter of imposing the symmetrizations of Eqs. (2.70)–(2.73) or not. A similar discussion holds for the higher-order response properties. In contrast to our previous derivation [67], we will impose the symmetrization $C^{\pm\omega}$ explicitly here.

From the expression above, we see that for the calculation of all first-order properties only the solution of one additional set of parameters is required: the zeroth-order multipliers. We can write the equation for the zeroth-order multipliers [Eq. (5.17)] as

$$\bar{t}^{(0)} \mathbf{A} = -\boldsymbol{\eta}, \quad (5.23)$$

where **A** is the nonsymmetric CC Jacobian,

$$A_{\mu_i\nu_j} = \left\langle \mu_i \middle| \exp(-T^{(0)}) \left[H_0, \tau_{\nu_j} \right] \middle| CC \right\rangle, \quad (5.24)$$

and the vector η is

$$\eta_{\nu_j} = \left\langle R \middle| \left[H_0, \tau_{\nu_j} \right] \middle| CC \right\rangle. \quad (5.25)$$

The second-order quasienergy becomes

$$\begin{aligned} \{^{2n+1}L^{(2)}(t)\}_T &= \left\langle \left\langle \Lambda \middle| [V^t, T^{(1)}(t)] \right. \right. \\ &\quad + \frac{1}{2} \left[\left[H_0, T^{(1)}(t) \right], T^{(1)}(t) \right] \middle| CC \Big\rangle \\ &\quad - i \sum_{i,\mu_i} \tilde{t}^{(1)}_{\mu_i}(t) \dot{t}^{(1)}_{\mu_i}(t) \\ &\quad \left. + \sum_{i,\mu_i} \bar{t}^{(1)}_{\mu_i}(t) \langle \bar{\mu}_i | V^t + \left[H_0, T^{(1)}(t) \right] | CC \rangle \right\rangle. \end{aligned} \quad (5.26)$$

In Eq. (5.26), we have introduced

$$\langle \bar{\mu}_i | = \langle \mu_i | \exp(-T^{(0)}). \quad (5.27)$$

As discussed in Section 3 we only need to consider the $2n + 1$ form. We could also have neglected the terms depending on the first-order multipliers by applying the $2n + 2$ rule. We have kept these terms in the derivation at this point since they allow us in a simple way to derive the first-order response equations and expressions for relevant matrices. Note that this exemplifies that the $2n + 1$ rule can be applied without affecting the $(n + 1)$th-order multiplier terms, but if we used the $2n + 2$ rule for the multipliers, we remove terms linear in the first-order it responses, and, therefore, the $2n + 2$ form cannot be used to derive the nth-order response equations. Only terms where frequencies are equal in magnitude but of opposite sign can contribute to the time average:

$$\begin{aligned} \{^{2n+1}L^{(2)}(t)\}_T &= \sum_{k=-n}^{n} \left[\left\langle \Lambda \middle| \left[V^{-\omega_k}, T^{(1)}(\omega_k) \right] \right. \right. \\ &\quad + \frac{1}{2} \left[\left[H_0, T^{(1)}(-\omega_k) \right], T^{(1)}(\omega_k) \right] \middle| CC \Big\rangle \\ &\quad - \sum_{\mu_i} \bar{t}^{(1)}_{\mu_i}(-\omega_k) \left[\omega_k t^{(1)}_{\mu_i}(\omega_k) \right] \\ &\quad + \sum_{\mu_i} \bar{t}^{(1)}_{\mu_i}(-\omega_k) \langle \bar{\mu}_i | V^{\omega_k} \\ &\quad \left. + \left[H_0, T^{(1)}(\omega_k) \right] | CC \rangle \right]. \end{aligned} \quad (5.28)$$

From the expression in Table III, we obtain

$$A_{\mu_i\nu_j}(\omega_Y) = \frac{\partial^2 \{L^{(2)}\}_T}{\partial \bar{t}^{(1)}_{\mu_i}(\omega_X) \partial t^{(1)}_{\nu_j}(\omega_Y)} = A_{\mu_i\nu_j} - \omega_Y \delta_{\mu_i\nu_j}, \quad (5.29)$$

where **A** (without frequency argument) is again the nonsymmetric CC Jacobian. The CC linear response equations become

$$(\mathbf{A} - \omega_Y \mathbf{I}) t^Y(\omega_Y) + \xi^Y = 0, \quad (5.30)$$

for the first-order amplitude responses and

$$\bar{t}^Y(\omega_Y)(\mathbf{A} + \omega_Y \mathbf{I}) + \eta^Y + \mathbf{F} t^Y(\omega_Y) = 0. \quad (5.31)$$

for the first-order multipliers. We have here introduced the CC vectors ξ^Y and η^Y and the matrix **F**. They arise naturally from the derivative expressions in Table IV and specialized expressions for CC theory are compiled in Table VI. We note that the expressions in Table VI are valid for models where the cluster expansion has been truncated, but do not apply for models where, in addition, approximations have been introduced in the ground-state CC amplitude equations. Thus, they are adequate for CCS, CCSD, and CCSDT, but, for example, not strictly valid for CC2 and CC3 [67, 68]. Note that this is not due to restrictions in the theory, but a limitation of the notation introduced for the sake of conciseness. For models like CC2 and CC3, the appropriate expressions are easily obtained by returning to the derivative definitions in Table IV and tracing the approximations introduced in the cluster equations to the relevant matrices. The present approach is thus well defined for any iterative CC model.

The linear response functions for any iterative CC model can be written in the common form

TABLE VI
Vectors and matrices for CC response functions.[a]

η^Y_μ	$\langle \Lambda\|[Y, \tau_\mu]\|CC\rangle$
ξ^Y_μ	$\langle \mu\|Y\|CC\rangle$
$A_{\mu\nu}$	$\langle \overline{\mu}\|[H_0, \tau_\nu]\|CC\rangle$
$B_{\mu\nu\sigma}$	$\langle \overline{\mu}\|[[H_0, \tau_\nu], \tau_\sigma]\|CC\rangle$
$C_{\mu\nu\sigma\delta}$	$\langle \overline{\mu}\|[[[H_0, \tau_\nu], \tau_\sigma], \tau_\delta]\|CC\rangle$
$F_{\mu\nu}$	$\langle \Lambda\|[[H_0, \tau_\mu], \tau_\nu]\|CC\rangle$
$G_{\mu\nu\sigma}$	$\langle \Lambda\|[[[H_0, \tau_\mu], \tau_\nu], \tau_\sigma]\|CC\rangle$
$H_{\mu\nu\sigma\delta}$	$\langle \Lambda\|[[[[H_0, \tau_\mu], \tau_\nu], \tau_\sigma], \tau_\delta]\|CC\rangle$
$A^Z_{\mu\nu}$	$\langle \overline{\mu}\|[Z, \tau_\nu]\|CC\rangle$
$B^U_{\mu\nu\sigma}$	$\langle \overline{\mu}\|[[U, \tau_\nu], \tau_\sigma]\|CC\rangle$
$F^Z_{\mu\nu}$	$\langle \Lambda\|[[Z, \tau_\mu], \tau_\nu]\|CC\rangle$
$G^U_{\mu\nu\sigma}$	$\langle \Lambda\|[[[U, \tau_\mu], \tau_\nu], \tau_\sigma]\|CC\rangle$
η_ν	$\langle R\|[H_0, \tau_\nu]\|CC\rangle$

[a]Here, τ_{ν_j} denotes a j-fold excitation operator indexed by ν for brevity. R is the reference state for the CC parametrization. $|CC\rangle = \exp(T^{(0)})|R\rangle$ denotes the zeroth-order reference CC wave function. $\langle \overline{\mu}_i| = \langle R|\tau^\dagger_{\mu_i} \exp(-T^{(0)})$, where the deexcitation operators $\tau^\dagger_{\mu_i}$ are the biorthogonal left manifold corresponding to τ_{ν_j} satisfying $\langle R|\tau^\dagger_{\nu_i}\tau_{\nu_j}|R\rangle = \delta_{\mu_i\nu_j}$. Furthermore, the auxiliary combination Λ is defined: $\langle \Lambda| = \langle R| + \sum_{i,\mu_i} t^{(0)}_{\mu_i}\langle \mu_i \exp(-T^{(0)})$. Note that relations exist between **F** and **B**, **G** and **C**, and so on: $F_{\mu_i\nu_j} = \langle R|[[H_0, \tau_{\mu_i}], \tau_{\nu_j}]|R\rangle \delta_{i1}\delta_{j1} + \sum_{k,\rho_k} \tilde{t}^{(0)}_{\rho_k} B_{\rho_k\mu_i\nu_j}$, $G_{\mu_i\nu_j\sigma_k} = \sum_{l,\rho_l} \tilde{t}^{(0)}_{\rho_l} C_{\rho_l\mu_i\nu_j\sigma_k}, \cdots$. These expressions cover CC models that are truncated in the cluster approximation, but where the CC amplitude equations have not been further approximated. Thus, for example, CCS, CCSD, and CCSDT are straightforwardly obtained by limiting the operator manifold to $i, j, k = 1$ for CCS, 1 and 2 for CCSD, and 1, 2, and 3 for CCSDT. The expressions are not adequate for, for example, the CC2 and CC3 models where the zeroth-order CC equations are approximated in addition to the cluster expansion being truncated. For models where approximations have been introduced in the cluster equations, the corresponding terms should also be neglected in the matrix definitions, in accord with the original derivative definitions in Table IV. Note that for closed-shell CC theory the commutator expressions in the tables vanish for more than four commutators since the Hamiltonian is a two-electron operator. Thus, higher-derivative matrices than **H** do not exist, and $\mathbf{G}^U$ and $\mathbf{H}^U$ are vanishing if U is a one-electron operator.

using also the $2n + 2$ rule for the multipliers:

$$\langle\langle X, Y\rangle\rangle_{\omega_Y} = \frac{1}{2} C^{\pm\omega} P(X(\omega_X), Y(\omega_Y)) \times \left[\eta^X + \frac{1}{2}\mathbf{F} t^X(\omega_X)\right] t^Y(\omega_Y). \quad (5.32)$$

The $C^{\pm\omega}$ symmetrizer of Eq. (3.35) is used for ensuring that the appropriate symmetry relations are fulfilled. The response functions will contain this symmetrizer in the rest of this section. We note that in CC theory the **F**-matrix becomes independent of the frequencies. This follows from the fact that the excitation operators commute and, therefore, terms like $[T^{(1)}(t), \dot{T}^{(1)}(t)]$ vanish identically. All matrices defined using two or more differentiations with respect to the cluster amplitudes on the CC quasienergy do not contain any frequency dependence. This is the case for the **F**, **G**, **H** and **B**, **C**, **D** matrices. Therefore, the quadratic CC response function can be written in the following rather compact form using the expressions in Table I:

$$\langle\langle X, Y, Z\rangle\rangle_{\omega_Y,\omega_Z} = \frac{1}{2} C^{\pm\omega} P(X(\omega_X), Y(\omega_Y), Z(\omega_Z)) \times \left\{\left[\frac{1}{2}\mathbf{F}^X + \frac{1}{6}\mathbf{G} t^X(\omega_X)\right] t^Y(\omega_Y) + \bar{t}^X(\omega_X)\left[\mathbf{A}^Y + \frac{1}{2}\mathbf{B} t^Y(\omega_Y)\right]\right\} t^Z(\omega_Z). \quad (5.33)$$

The cubic and higher-order response functions are obtained in a similar way. Several implementations of CC linear response theory have been reported [65, 66, 69, 72]. Our most recent one is based on the formulas in this article [69]. We describe in detail the theory and the first implementation of frequency-dependent quadratic and cubic response functions for CCS, CC2, and CCSD in [70, 71].

5.C. POLES AND RESIDUES OF CC RESPONSE FUNCTIONS

Excitation energies and transition moments are obtained as poles and residues of the response function. The nonsymmetric CC Jacobian can be diagonalized:

$$\mathbf{LAR} = \mathbf{\Omega}; \qquad \Omega_{ij} = \omega_i \delta_{ij}. \quad (5.34)$$

The columns of **R** thus contain the right eigenvectors of **A**, and the rows of **L** contain the left eigenvectors. When the eigenvectors span the complete space $\mathbf{L} = \mathbf{R}^{-1}$, we will denote single eigenvectors with eigenvalue ω_f as R^f and L^f: $R^f_{\mu_i} = R_{\mu_i f}$, $L^f_{\mu_i} = L_{f\mu_i}$. Transformation to the representation where the Jacobian is diagonal [Eq. (5.34)] implies a transformation of the right operator manifold—the excitation operators—to the diagonal

representation as follows:

$$ {}^{d}\tau_k = \sum_{i,\,\mu_i} \tau_{\mu_i} R^k_{\mu_i} \tag{5.35} $$

and similarly for the left operator manifold—the deexcitation operators:

$$ {}^{d}\tau^{\dagger}_k = \sum_{i,\,\mu_i} L^k_{\mu_i} \tau^{\dagger}_{\mu_i}. \tag{5.36} $$

Greek indices refer to the elementary basis, and roman, to the diagonal basis. This determines unambiguously the transformation of all relevant matrices and vectors to the diagonal representation (${}^{d}t^{Y} = \mathbf{L}t^{Y}$, ${}^{d}\xi^{Y} = \mathbf{L}\xi^{Y}$, ${}^{d}\eta^{X} = \eta^{X}\mathbf{R}$, ${}^{d}\mathbf{F} = \mathbf{FRR}$, etc.). In the diagonal representation, we obtain the following form of the first-order CC amplitude response equations [Eq. (5.30)]:

$$ (\omega_Y - \omega_k)\,{}^{d}t^{Y}_k(\omega_Y) = {}^{d}\xi^{Y}_k. \tag{5.37} $$

We can thus write the response function in Eq. (5.32) in the diagonal representation as

$$ \langle\langle X, Y\rangle\rangle_{\omega_Y} = \frac{1}{2} C^{\pm\omega} P(X(-\omega_Y), Y(\omega_Y)) \times \left(\sum_k \frac{{}^{d}\eta^{X}_k\,{}^{d}\xi^{Y}_k}{\omega_Y - \omega_k} + \frac{1}{2} \sum_{kn} \frac{{}^{d}\xi^{X}_k\,{}^{d}F_{kn}\,{}^{d}\xi^{Y}_n}{(\omega_Y + \omega_k)(\omega_Y - \omega_n)} \right). \tag{5.38} $$

It is evident from Eq. (5.38) that the CC linear response function has poles when $\omega_Y = \pm\omega_k$, where ω_k is one of the eigenvalues of the CC Jacobian. We note that relative to the exact linear response function in the diagonal representation in Eq. (4.44) the CC linear response function has an additional term—the F matrix term. As discussed in Section 3, this term can be eliminated for variational theories (and thus also exact theory) while this is only possible in nonvariational theory at the expense of introducing the first-order response of the Lagrangian multipliers. However, we observe that in the case of the CC linear response function as derived from the Lagrangian in Eq. (5.12) the extra F term does not give additional poles and that the poles are only first order. As we will discuss later in this section, this is not so for many other nonvariational approaches, and these response functions thus do not have a correct pole structure that can be used for an unambiguous identification of excitation energies and transition properties. The pole structure of the CC linear response function is in agreement with the one of the exact response functions, and the F term causes no ambiguity in the determination of the poles and residues of the CC linear response function. Rather, the F matrix term in the linear response function arises naturally because of the nonvariational exponential parametrization in exactly the same way as it enters ordinary time-independent energy derivatives.

From the usual response theory analogy arguments, we identify the CC excitation energies as the poles of the CC linear response function. To determine CC excitation energies, we need to solve for the eigenvalues of the CC Jacobian from either the right

$$ \mathbf{A}R^f = \omega_f R^f \tag{5.39} $$

or the left

$$ L^f\mathbf{A} = \omega_f L^f, \tag{5.40} $$

where the vectors are chosen to fulfill the biorthonormality condition

$$ L^m R^n = \delta_{mn}. \tag{5.41} $$

For determining the excitation energies, we only need to solve for either the left or the right eigenvectors. However, when we wish to determine other properties, for example, one- or two-photon transition probabilities or excited-state properties, we need both the left and the right eigenvectors.

Another comment applies to the determination of excitation energies in the CC response theory. Since the Jacobian is nonsymmetric, it may have complex eigenvalues. Complex eigenvalues and thus complex excitation energies are unphysical and an artifact of the way the approximations are introduced. In all cases where the CC approximation is a good approximation for the reference state, it may be expected that these complex eigenvalues do not pose a problem. This is in agreement with our previous experience, although no rigorous relationship exists that ensures the CC excitation energies of Eq. (5.39) are real.

In the following, we will identify expressions for the residues and discuss the analogy with exact theory. To obtain the residues of the response functions, we will not use a strategy where the response functions are expressed in the diagonal representation as done in Eq. (5.38) since this may lead to the misconception that a complete diagonalization should be carried out, even though it, of

course, is trivial to back transform the residues to the original basis of excitation and deexcitation operators. We will instead take a route where we first determine the residues of the response vectors, and subsequently use those to determine the residues of the response functions. This gives a more transparent structure of the equations and expresses the equations in the original basis of excitation and deexcitation operators where the calculations are carried out. Let us initially introduce the scalar quantities

$$ {}^{cc}T^{Y}_{fo} = {}^{d}\xi^{Y}_{f} = (L^{f}\xi^{Y}), \tag{5.42} $$

$$ \begin{aligned} {}^{cc}T^{Y}_{of} &= {}^{d}\left[\boldsymbol{\eta}^{Y} + \mathbf{F}t^{Y}(-\omega_f)\right]_f \\ &= \left(\left[\boldsymbol{\eta}^{Y} + \mathbf{F}t^{Y}(-\omega_f)\right]R^{f}\right). \end{aligned} \tag{5.43} $$

The reason for the notation will soon become apparent. Furthermore, we introduce the auxiliary vector

$$ \overline{M}^{f}(\omega_f) = -(\mathbf{F}R^{f})(\omega_f\mathbf{1} + \mathbf{A})^{-1}. \tag{5.44} $$

Using the definitions in Eqs. (5.42)–(5.44), we obtain the following residue vectors of the amplitude and multiplier first-order response vectors from Eqs. (5.30) and (5.31):

$$ \lim_{\omega_Y \to \omega_f} (\omega_Y - \omega_f)t^{Y}(\omega_Y) = R^{f\,cc}T^{Y}_{fo}, \tag{5.45} $$

$$ \lim_{\omega_Y \to -\omega_f} (\omega_Y + \omega_f)t^{Y}(\omega_Y) = 0, \tag{5.46} $$

$$ \lim_{\omega_Y \to \omega_f} (\omega_Y - \omega_f)\bar{t}^{Y}(\omega_Y) = {}^{cc}T^{Y}_{fo}\overline{M}^{f}(\omega_f), \tag{5.47} $$

$$ \lim_{\omega_Y \to -\omega_f} (\omega_Y + \omega_f)\bar{t}^{Y}(\omega_Y) = -{}^{cc}T^{Y}_{of}(\omega_f)L^{f}. \tag{5.48} $$

Assume that a function $a(\omega_1, \omega_2)$ has first-order residues $f_1(\omega_2)$ for $\omega_1 = +\omega_i$ and a residue $-f_2(\omega_2)$ for $\omega_1 = -\omega_i$, where all ω_i are real and positive. If we define the function $b(\omega_1, \omega_2) = (a(-\omega_1, -\omega_2))^*$, then $b(\omega_1, \omega_2)$ has residues $(f_2(-\omega_2))^*$ for $\omega_1 = +\omega_i$ and $(-f_1(-\omega_2))^*$ for $\omega_1 = -\omega_i$. The function $1/2(a(\omega_1, \omega_2) + b(\omega_1, \omega_2))$ therefore has residues $1/2(f_1(\omega_2) + (f_2(-\omega_2))^*)$ for $\omega_1 = +\omega_i$ and $-1/2(f_2(\omega_2) + (f_1(-\omega_2))^*)$ for $\omega_1 = -\omega_i$. It is instructive to have this in mind when taking the residues of the CC response functions.

The residues of the linear response function become

$$ \begin{aligned} \lim_{\omega_Y \to \omega_f} &(\omega_Y - \omega_f)\langle\langle X, Y\rangle\rangle_{\omega_Y} \\ &= \frac{1}{2}\left({}^{cc}T^{X}_{of}{}^{cc}T^{Y}_{fo} + \left({}^{cc}T^{Y}_{of}{}^{cc}T^{X}_{fo}\right)^*\right) = {}^{cc}S^{of}_{XY}, \end{aligned} \tag{5.49} $$

$$ \begin{aligned} \lim_{\omega_Y \to \omega_f} &(\omega_Y + \omega_f)\langle\langle X, Y\rangle\rangle_{\omega_Y} \\ &= -\frac{1}{2}\left({}^{cc}T^{Y}_{of}{}^{cc}T^{X}_{fo} + \left({}^{cc}T^{X}_{of}{}^{cc}T^{Y}_{fo}\right)^*\right) \\ &= -({}^{cc}S^{of}_{XY})^*, \end{aligned} \tag{5.50} $$

where the second residue is trivially related to the first residue by interchanging X and Y and a change of sign. At this point, it is interesting to note the similarities and differences relative to exact theory. The obvious difference is that ${}^{cc}T^{Y}_{of} \neq {}^{cc}T^{Y}_{fo}{}^*$. This is connected to the asymmetry of the CC quasienergy leading to the necessity of introducing the symmetrization with respect to complex conjugation and sign reversal of the frequencies [Eq. (3.35)]. When this symmetrization was carried out, we obtained that the two residues in Eqs. (5.49) and (5.50) are adjoint with the exception of an overall sign. Furthermore, the CC transition strength matrix is Hermitian as are the exact transition strength matrix. Thus, the transition strengths in the diagonal representation are real. However, in CC theory where there exists an inherent difference between ''left and right'' due to the projection approach, and we cannot argue as in Section 4.C for exact theory that in the diagonal representation the CC transition strengths equal the squared norm of some transition matrix elements. This means, for example, that we cannot prove that the CC transition strengths are positive! The arguments are the same as for possible imaginary excitation energies: We do not expect and have not found this to be a problem in any sensible calculation. However, a word of caution is proper to the extent that in any approximate theory certain relations that are fulfilled in exact theory are not ensured in the approximate theory and this may, in principle, lead to unphysical results.

We now pass on to the residues of the quadratic response functions. First, we note that the quadratic response function has poles when $\omega_Y = \pm\omega_f$, $\omega_Z = \pm\omega_f$, where the poles for the positive sign originate from both amplitude and multiplier responses, while the one for the negative sign origi-

nate exclusively from the poles of the first-order multipliers. Since $\omega_X = -\omega_Y - \omega_Z$, the CC quadratic response function also has poles when $\omega_Y + \omega_Z = \pm\omega_f$. This is in agreement with the exact quastatic response function. The $\omega_Z = \omega_f$ residue of the CC quadratic response function becomes (substituting $-\omega_Y$ for ω_Y)

$$\lim_{\omega_Z \to \omega_f} (\omega_Z - \omega_f)\langle\langle X; Y, Z \rangle\rangle_{-\omega_Y, \omega_Z} = -\frac{1}{2}\left({}^{cc}T_{of}^{XY}(-\omega_Y)\,{}^{cc}T_{fo}^{Z} + \left({}^{cc}T_{of}^{Z\,cc}T_{fo}^{XY}(\omega_Y)\right)^*\right), \tag{5.51}$$

while the $\omega_Z = -\omega_f$ residue becomes

$$\lim_{\omega_Z \to -\omega_f} (\omega_Z + \omega_f)\langle\langle X; Y, Z \rangle\rangle_{\omega_Y, \omega_Z} = \frac{1}{2}\left({}^{cc}T_{of}^{Z\,cc}T_{fo}^{XY}(\omega_Y) + \left({}^{cc}T_{of}^{XY}(-\omega_Y)\,{}^{cc}T_{fo}^{Z}\right)^*\right). \tag{5.52}$$

We have introduced here the second-order transition matrix element,

$${}^{cc}T_{fo}^{XY}(\omega_Y) = -P(X(\omega_X), Y(\omega_Y))L^f \times\left(\left[\mathbf{A}^X + \frac{1}{2}\mathbf{B}t^X(\omega_X)\right]t^Y(\omega_Y)\right), \tag{5.53}$$

$$\begin{aligned}{}^{cc}T_{of}^{XY}(-\omega_Y) &= -P(X(\omega_X), Y(\omega_Y)) \\ &\times\left\{\left(\left[\mathbf{F}^X + \frac{1}{2}\mathbf{G}t^X(-\omega_X)\right]t^Y(-\omega_Y) \right.\right. \\ &\left. + \bar{t}^X(-\omega_X)\left[\mathbf{A}^Y + \mathbf{B}t^Y(-\omega_Y)\right]\right)R^f \\ &\left. + \overline{M}^f(\omega_f)\left[\mathbf{A}^X + \frac{1}{2}\mathbf{B}t^X(-\omega_X)\right]t^Y(-\omega_Y)\right\},\end{aligned} \tag{5.54}$$

where $\omega_X = \omega_f - \omega_Y$. As for the linear response functions, the residues do, in principle, not allow for a determination of transition matrix elements; however, the structure is suggestive—we have different left and right transition matrix elements and expect again that the correct expression for the molecular property is obtained by an appropriate symmetrization. We will see this confirmed when taking the residue of the cubic response function in the next subsection. We note that the residues of the quadratic response functions in Eqs. (5.51) and (5.52) have poles when, respectively, $\omega_Y = -\omega_i$ or $\omega_X = \omega_i$. The first of these double residues becomes

$$\lim_{\omega_Y \to -\omega_i} (\omega_Y + \omega_i) \times\left\{\lim_{\omega_Z \to \omega_f} (\omega_Z - \omega_f)\langle\langle X; Y, Z \rangle\rangle_{\omega_Y, \omega_Z}\right\} = -\frac{1}{2}\left({}^{cc}T_{oi}^{Y\,cc}T_{if}^{X\,cc}T_{fo}^{Z} + \left({}^{cc}T_{of}^{Y\,cc}T_{fi}^{X\,cc}T_{io}^{Z}\right)^*\right), \tag{5.55}$$

where

$${}^{cc}T_{if}^{X} = L^i\left(\mathbf{A}^X + \mathbf{B}t^X(\omega_i - \omega_f)\right)R^f. \tag{5.56}$$

In agreement with exact theory and the symmetry properties of the response functions, we obtain that the $\omega_Z = -\omega_f$, $\omega_Y = \omega_i$ residue is the complex conjugate of the $\omega_Z = \omega_f$, $\omega_Y = -\omega_i$ residue in Eq. (5.55).

We introduce the symmetrized transition strength between two excited states $i \neq f$ as

$${}^{cc}S_{XY}^{if} = \frac{1}{2}\left[{}^{cc}T_{if}^{X\,cc}T_{fi}^{Y} + \left({}^{cc}T_{if}^{Y\,cc}T_{fi}^{X}\right)^*\right], \tag{5.57}$$

in analogy with the explicitly symmetrized expressions of exact theory [Eq. (4.62)]. Note that this expression has the Hermitian property $({}^{cc}S_{XY}^{if})^* = {}^{cc}S_{YX}^{if}$, while this is not true for the primitive produce $({}^{cc}T_{if}^{X\,cc}T_{fi}^{Y})^* \neq {}^{cc}T_{if}^{Y\,cc}T_{fi}^{X}$.

Finally, we note the residue search of the quadratic response function

$$\lim_{\omega_Y \to \omega_i} (\omega_Y - \omega_i) \times\left\{\lim_{\omega_Z \to \omega_f} (\omega_Z - \omega_f)\langle\langle X; Y, Z \rangle\rangle_{\omega_Y, \omega_Z}\right\} \neq 0. \tag{5.58}$$

Thus, there exists a residue search that gives identically zero for the exact quadratic response function but a nonvanishing result for the CC quadratic response function. This is similar to SCF (see Section 4).

5.D. ALTERNATIVE EXPRESSIONS FOR RESPONSE FUNCTIONS AND RESIDUES IN CC THEORY

In this subsection, we discuss alternative forms of the response functions and residues with emphasis on the differences in structure and computational requirements. The CC linear response in Eq. (5.32) can be rewritten in an asymmetric form requiring only response equations with respect to the perturbation Y to be solved:

$$\langle\langle X, Y\rangle\rangle_{\omega_Y} = \frac{1}{2} C^{\pm\omega}\left[\eta^X t^Y(\omega_Y) + \bar{t}^Y(\omega_Y)\xi^X\right]. \tag{5.59}$$

As discussed in Section 3.F, Eq. (5.59) may be advantageous relative to Eq. (5.32) in some cases. Since the linear response function in the form Eq. (5.59) is a reformulation of the one used in the residue analysis in the previous subsection, an alternative but equivalent residue is obtained from Eq. (5.59). Using Eq. (5.59), we obtain again the equations Eqs. (5.49) and (5.50); however, the ${}^{\mathrm{cc}}T^Y_{of}$ element now has a slightly different form:

$${}^{\mathrm{cc}}T^Y_{of} = \eta^Y R^f + \overline{M}^f(\omega_f)\xi^Y. \tag{5.60}$$

Using the interchange technique, the two different forms of ${}^{\mathrm{cc}}T^Y_{of}$ in Eqs. (5.43) and (5.61) are seen to be equivalent [$\overline{M}^f(\omega_f)\xi^Y = -\mathbf{F}R^f(\omega_f\mathbf{1}+\mathbf{A})^{-1}\times\xi^Y = \mathbf{F}R^f t^Y(-\omega_f) = \mathbf{F}t^Y(-\omega_f)R^f$]. Consider now the calculation of the transition strength using Eq. (5.49) together with either Eqs. (5.42) and (5.43) or Eq. (5.42) in combination with Eq. (5.60). Using the first set of equations, we need to solve for R^f, L^f, $t^Y(-\omega_f)$, and $(t^X(-\omega_f))^*$ to calculate ${}^{\mathrm{cc}}S^{of}_{XY}$; while using the latter, we need to solve for R^f, L^f, and $\overline{M}^f$. The latter form thus requires only the solution of one set of equations for $\overline{M}^f$ to determine ${}^{\mathrm{cc}}S^{of}_{XY}$ for all operator sets, while the first requires the solution of first-order response equations for each different operator X or Y. Thus, $\overline{M}^f$ has the role of a Lagrangian multiplier. For $X = Y$ = a real operator, the same number of equations must be solved using either of the two approaches; in all other cases, the approach utilizing the $\overline{M}^f$ vector is the most efficient. The apparent paradox is therefore that the $2n+1$ and $2n+2$ rule expressions for the linear response function give first-order transition matrix elements that are not in accord with the $2n+1$ rule, while the expression that does not fulfill the $2n+2$ rule for the multiplier responses gives first-order transition matrix elements that satisfy the $2n+1$ rule. The $2n+1$ rule for transition matrix elements refers to that the $(2n+1)$th-order transition matrix elements can be calculated from only nth-order response vectors. The above paradox is simply a consequence of the fact the $2n+1$ and $2n+2$ rules refer to the derivatives of the quasienergy functional—and these rules are not transferable to the transition matrix elements that are not derivatives of the quasienergy Lagrangian. In fact, we have already seen this for variational theory (see Section 4). This is thus a feature common for response theory both for variational and nonvariational wave functions and not a speciality of the nonvariational theories.

Next, we will discuss the evaluation of the two-photon transition matrix elements and two-photon transition strengths. According to exact theory, the two-photon transition matrix elements can be found from the residue of the quadratic response function [Eqs. (5.51)–(5.54)], while the two-photon transition strength itself is obtained as a residue of the cubic response functions [Eq. (4.65)]. The residue of the cubic response function in the $2n+1$ and $2n+2$ rule form in Table I becomes

$$\begin{aligned}\lim_{\omega_Z+\omega_U\to\omega_f} &(\omega_Z+\omega_U-\omega_f)\langle\langle X;Y,Z,U\rangle\rangle_{-\omega_Y,\omega_Z,\omega_U}\\ &= \frac{1}{2}\Big({}^{\mathrm{cc}}T^{XY}_{\mathrm{of}}(-\omega_Y)\,{}^{\mathrm{cc}}T^{ZU}_{f\mathrm{o}}(\omega_U)\\ &\quad + \left({}^{\mathrm{cc}}T^{ZU}_{of}(-\omega_U)\,{}^{\mathrm{cc}}T^{XY}_{f\mathrm{o}}(\omega_Y)\right)^*\Big).\end{aligned} \tag{5.61}$$

${}^{\mathrm{cc}}T^{XY}_{f\mathrm{o}}(\omega_Y)$ is found in the same form as in Eq. (5.53), while ${}^{\mathrm{cc}}T^{XY}_{of}(-\omega_Y)$ becomes

$$\begin{aligned}{}^{\mathrm{cc}}&T^{XY}_{of}(-\omega_Y)\\ &= -P(X(\omega_X),Y(\omega_Y))\\ &\quad\times\Big\{\Big(\Big[\mathbf{F}^X + \frac{1}{2}\mathbf{G}t^X(-\omega_X)\Big]t^Y(-\omega_Y)\\ &\quad + \bar{t}^X(-\omega_X)\left[\mathbf{A}^Y + \mathbf{B}t^Y(-\omega_Y)\right]\Big)R^f\\ &\quad + \mathbf{F}t^{XY}(-\omega_X,-\omega_Y)R^f\Big\}.\end{aligned} \tag{5.62}$$

This expression differs from Eq. (5.54) in that it contains a term depending on the second-order amplitude responses. The expression from the quadratic response residue in Eq. (5.54) is thus

preferable since it does not involve the second-order response and instead the $\overline{M}^f(\omega_f)$ vector is required. We find again consistency between the two expressions as is easily checked by using the interchange technique since

$$\begin{aligned}
&\mathbf{F}t^{XY}(-\omega_X,-\omega_Y)R^f \\
&\quad=\mathbf{F}R^f t^{XY}(-\omega_X,-\omega_Y) \\
&\quad=-(\mathbf{F}R^f)(\mathbf{A}+(\omega_X+\omega_Y)\mathbf{1})^{-1} \\
&\qquad\times\left[\mathbf{A}^X+\frac{1}{2}\mathbf{B}t^X(-\omega_X)\right]t^Y(-\omega_Y) \\
&\quad=\overline{M}^f(\omega_X+\omega_Y)\left[\mathbf{A}^X+\frac{1}{2}\mathbf{B}t^X(-\omega_X)\right] \\
&\qquad\times t^Y(-\omega_Y). \qquad (5.63)
\end{aligned}$$

We note that $\omega_X+\omega_Y=\omega_f$ for the evaluation of the second-order transition moment and the $\overline{M}^f(\omega_f)$ vector are thus required only for this one frequency to calculate all two-photon processes for different X and Y and different related frequencies.

The residues obtained from the CC response functions have the structure $\frac{1}{2}[T_L^A T_R^B+(T_L^B T_R^A)^*]$. In a rigorous sense, this has as a consequence that we cannot identify the individual transition matrix elements since we do not have a simple product of the transition matrix elements, but a more general structure. However, in Section 4.C, we wrote the residues of the exact response function in a fashion that is consistent with this form, suggesting that in CC we have to work with different left and right transition matrix elements and that the final expression for molecular properties must be appropriately symmetrized. This is confirmed in the sense that the definitions of the left and right transition matrix elements are consistent. We have seen this above for the one- and two-photon transition strengths for the transition between the ground state and an excited state, where the residues of the linear, quadratic, and cubic response functions have different meaning, but give equivalent left and right transition matrix elements. We have used this picture of a left and right generalization with confidence in Eqs. (5.56) and (5.57).

The expression for ${}^{cc}T_{if}^X$ that is required for evaluating the transition strength between excited states can be rewritten using the interchange technique:

$$\begin{aligned}
{}^{cc}T_{if}^X &= L^i\left(\mathbf{A}^X+\mathbf{B}t^X(\omega_i-\omega_f)\right)R^f \\
&= L^i\mathbf{A}^X R^f-(L^i\mathbf{B}R^f)\left(\mathbf{A}+(\omega_f-\omega_i)\mathbf{1}\right)\xi^X \\
&= L^i\mathbf{A}^X R^f+\overline{N}^{if}O(\omega_i,\omega_f)\xi^X, \qquad (5.64)
\end{aligned}$$

where

$$\overline{N}^{if}(\omega_i,\omega_f)\left(\mathbf{A}+(\omega_f-\omega_i)\mathbf{1}\right)+L^i\mathbf{B}R^f=0. \qquad (5.65)$$

For $i=f$, ${}^{cc}T_{if}^X$ is related to the evaluation of excited-state first-order properties. We will discuss this in more detail in the next subsection.

In this section, we have seen how it in some cases may be advantageous to manipulate the residue expressions to obtain computationally tractable expressions. This is a consequence of the fact that the $2n+1$ and $2n+2$ rules for the response functions do not carry over to the residues, but only hold for the response functions themselves that are obtained as derivatives of the carrier quasienergy functional. A closer analysis is required to obtain the computational most efficient expressions for properties determined as residues, leading ultimately to rules of the $2n+1$ and $2n+2$ type for the properties determined from the residues as demonstrated above. In the next subsection, we exemplify another approach where we derive the expressions for molecular properties from a property-oriented carrier functional, here specialized to excited-state properties. Similar carrier or property-oriented Lagrangians can, in principle, be constructed for other molecular properties, in some cases requiring a generalization to time- or frequency-dependent properties, but we defer further examinations of this subject to another publication [78].

5.E. EXCITED-STATE PROPERTIES FROM CC RESPONSE THEORY

In this section, we consider the calculation of molecular properties for excited states. In particular, we determine the molecular gradient since the gradient is required for an efficient calculation of excited-state geometries and properties. The investigation of excited states in CC response theory proceed through several steps. First, the reference

state is determined. Usually, the Hartree–Fock (HF) state is chosen as the reference state. Thus, we require that

$$0 = e_{mn}(\kappa) = \langle \mathrm{HF}|[\, E_{mn}, H_0\,]|\mathrm{HF}\rangle \quad (5.66)$$

for the nonredundant orbital rotation operators denoted by E_{mn}. Next, the ground-state amplitudes of the CC wave function is obtained by solving the cluster amplitude equations [Eq. (5.10)]. The excitation energy and the excitation vectors are then obtained by solving the CC response eigenvalue equations [Eqs. (5.39) and (5.40)], and from the expressions for the residues given in the previous subsections, we can evaluate various transition properties and excited-state properties. In this subsection, we will derive expressions for excited-state properties in an alternative but formally equivalent way as derivatives of the excited-state total energy. We also discuss various aspects related to the evaluation of excited-state properties as well as aspects of response theory for non-variational wave functions. We denote the amplitude constraint by $\Omega_{\mu_i}(t, \kappa)$, where t and κ refer to the dependency on the CC amplitudes and the orbital rotation parameters. When the left and right eigenvectors satisfy the biorthonormality constraint in Eq. (5.41), the excitation energy can be written as

$$\omega_f = L^f \mathbf{A}(t, \kappa) R^f. \quad (5.67)$$

The Lagrangian for the total energy $E_f = E_0 + \omega_f$ of the excited state becomes

$$\begin{aligned} L_f(t, \bar{t}^f, \kappa, \bar{\kappa}^f, L^f, R^f, \bar{\alpha}) &= E_0(t, \kappa) + L^f \mathbf{A}(t, \kappa) R^f \\ &\quad + \sum_{i, \mu_i} \bar{t}^f_{\mu_i} \Omega_{\mu_i}(t, \kappa) \\ &\quad + \bar{\alpha}(L^f R^f - 1) + \sum_{mn} \bar{\kappa}^f_{mn} e_{mn}(\kappa). \end{aligned} \quad (5.68)$$

Requiring the Lagrangian to be variational in all parameters, $t, \bar{t}^f, \kappa, \bar{\kappa}^f, L^f, R^f$, and $\bar{\alpha}$, we obtain the following equations:

$$0 = \frac{dL_f}{d\bar{\alpha}} = L^f R^f - 1, \quad (5.69)$$

$$0 = \frac{dL_f}{dL^f} = \mathbf{A}(t, \kappa) R^f + \bar{\alpha} R^f, \quad (5.70)$$

$$0 = \frac{dL_f}{dR^f} = L^f \mathbf{A}(t, \kappa) + \bar{\alpha} L^f, \quad (5.71)$$

$$0 = \frac{dL_f}{d\bar{t}^f_{\mu_i}} = \Omega_{\mu_i}(t, \kappa), \quad (5.72)$$

$$0 = \frac{dL_f}{dt_{\nu_j}} = \frac{dE_o(t, \kappa)}{dt_{\nu_j}} + L^f \frac{d\mathbf{A}(t, \kappa)}{dt_{\nu_j}} R^f + \sum_{i, \mu_i} \bar{t}^f_{\mu_i} \frac{d\Omega_{\mu_i}(t, \kappa)}{dt_{\nu_j}}, \quad (5.73)$$

$$0 = \frac{dL_f}{d\bar{\kappa}^f_{mn}} = e_{mn}(\kappa), \quad (5.74)$$

$$0 = \frac{dL_f}{d\kappa_{mn}} = \frac{dE_o(t, \kappa)}{d\kappa_{mn}} + L^f \frac{d\mathbf{A}(t, \kappa)}{d\kappa_{mn}} R^f + \sum_{i, \mu_i} \bar{t}^f_{\mu_i} \frac{d\Omega_{\mu_i}(t, \kappa)}{d\kappa_{mn}} + \sum_{pq} \bar{\kappa}^f_{pq} \frac{de_{pq}(\kappa)}{d\kappa_{mn}}. \quad (5.75)$$

Equation (5.69) is the biorthonormality condition for the excited-state vectors, Equations (5.70) and (5.71) are satisfied with $\bar{\alpha}$ being the excitation energy, and L^f and R^f, the corresponding left and right eigenvectors. Equations (5.72) is the ground-state CC equations. Equation (5.73) is the equation for the amplitude multipliers. Equation (5.74) ensures that the orbitals of the reference states are optimized, while Eq. (5.75)a determines the orbital multipliers for the excited-state Lagrangian. When these equations are fulfilled, the Lagrangian gives the total energy of the excited state as the sum of the CC ground-state energy and the CC response theory excitation energy. Neglecting all terms depending on L^f and R^f, the Lagrangian in Eq. (5.68) reduces to the ground-state energy Lagrangian.

The gradient for the excited state becomes in accordance with the $2n + 1$ and $2n + 2$ rules

$$\frac{dL_f}{d\varepsilon_X} = \frac{1}{2} C^{\pm\omega} \left(\frac{\partial E_o(t, \kappa)}{\partial \varepsilon_X} + L^f \frac{\partial \mathbf{A}(t, \kappa)}{\partial \varepsilon_X} R^f + \sum_{i, \mu_i} \bar{t}^f_{\mu_i} \frac{\partial \Omega_{\mu_i}(t, \kappa)}{\partial \varepsilon_X} + \sum_{mn} \bar{\kappa}^f_{mn} \frac{\partial e_{mn}(\kappa)}{\partial \varepsilon_X} \right)$$

$$= \frac{1}{2} C^{\pm\omega} \left(\frac{\partial E_o(t,\kappa)}{\partial \varepsilon_X} + L^f \mathbf{A}^X R^f + \sum_{i,\mu_i} \bar{t}^f_{\mu_i} \xi^X_{\mu_i} + \sum_{mn} \bar{\kappa}^f_{mn} \frac{\partial e_{mn}(\kappa)}{\partial \varepsilon_X} \right), \quad (5.76)$$

where $\mathbf{A}^X$ and ξ^X_μ are identical to the ones defined in Table V. We will now discuss some of the implications of the above analysis. Neglecting the orbital relaxation contribution, we obtain

$$\frac{dL_f}{d\varepsilon_X} = \frac{1}{2} C^{\pm\omega} \left(\frac{\partial E_o(t,\kappa)}{\partial \varepsilon_X} + L^f \mathbf{A}^X R^f + \sum_{\mu_i} \bar{t}^f_{\mu_i} \xi^X_{\mu_i} \right). \quad (5.77)$$

The expression Eq. (5.77) is equivalent to the expression obtained by adding the ground-state first-order property [Eq. (5.19)] to the expression found [Eq. (5.56) with $i = f$] from the residue of the quadratic response function if we apply the $C^{\pm\omega}$ symmetrizations in Eq. (4.63):

$$\begin{aligned} \langle X \rangle_f &= \langle X \rangle_0 + \langle X - \bar{X} \rangle_f \\ &= \frac{1}{2} C^{\pm\omega} \left(\frac{\partial E_o(t,\kappa)}{\partial \varepsilon_X} + \bar{t}^{(0)} \xi^X + L^f \mathbf{A}^X R^f + L^f \mathbf{B} t^X R^f \right) \\ &= \frac{1}{2} C^{\pm\omega} \left(\frac{\partial E_o(t,\kappa)}{\partial \varepsilon_X} + L^f \mathbf{A}^X R^f + (\bar{t}^{(0)} - L^f \mathbf{B} R^f \mathbf{A}^{-1}) \xi^X \right), \end{aligned} \quad (5.78)$$

where $\bar{t}^{(0)}$ are the ground-state zeroth-order multipliers. Since Eq. (5.73) can be expressed as

$$\bar{t}^f = \bar{t}^{(0)} - L^f \mathbf{B} R^f \mathbf{A}^{-1} = -(\eta + L^f \mathbf{B} R^f) \mathbf{A}^{-1}, \quad (5.79)$$

it is seen that Eq. (5.78) is equivalent to Eq. (5.77). In the case where we do not include orbital relaxation in the Lagrangian in Eq. (5.68), the two derivsations thus agree as they should in a consistent theory. We note that the structure of Eq. (5.77) is similar to the one obtained in variational theory, Eq. (4.94).

We may summarize the above discussion as follows: For calculation of excited-state first-order properties, it is advantageous to consider the derivative of the excited-state energy as defined by the ground state plus the excitation energy. The excited-state properties may then be obtained using linear response theory, rather than from the residue of the quadratic response function as was done previously. The advantages of this approach are twofold: (1) A more computational advantageous expression that satisfies the $2n + 1$ and $2n + 2$ rules is obtained straightforwardly. (2) The derivative approach allows us to turn on or off the orbital relaxation term in a simple way, where the orbital relaxation terms also satisfy the $2n + 1$ and $2n + 2$ rules. This observation may be generalized as follows: When possible, it is advantageous to use derivatives of expressions for the low-order residues to identify higher-order transition properties and/or excited-state properties rather than to identify the expressions from residues of even higher-order response functions. A derivative approach better facilitates the use of the $2n + 1$ and $2n + 2$ rules, and orbital relaxation can be introduced at will.

Expressions for the CC excited-state gradients have been derived before in other contexts [34, 36] and the first implementation for CCSD was reported by Stanton and Gauss [35] and was recently extended to CC2 [79]. It has proven highly successful for the calculation of excited-state equilibrium geometries and (through numerical differentiation of the analytical gradient) excited-state harmonic frequencies. The present formalism exhibits in a simple and illustrative way the basic structure of the theory. For example, it is found that to calculate the excited-state molecular gradient we need to solve only *one* set of additional CC equations in addition to the ground-state amplitude equations and the left and right eigenvalue equations. Besides giving computational expressions where the number of equations that needs to be solved is minimized, the Lagrangian technique introduces the concept of Lagrangian multipliers for the excited state. Thus, $\bar{t}^f$ of Eq. (5.79) is the excited-state analog of the ground-state multipliers in Eq. (5.23) and ensures that the functional in Eq. (5.68) is variational. Furthermore, the Lagrangian technique allows us to include orbital relaxation in the functional, giving results for the orbital rotations in accord with the $2n + 1$ and $2n + 2$ rules without having to resort to using several cumbersome steps of an interchange technique.

Higher-order derivatives can be found easily by taking the second derivative of the excited-state Lagrangian in Eq. (5.68) and allows for an analytical calculation of second-order (static) properties in the excited state—most notable, the molecular Hessian.

The procedure that we have used in this section exemplifies the generality of the Lagrangian technique. If we know how to calculate some property including the equations that must be solved, we can construct a property-oriented Lagrangian, allowing all derivatives of this property to be obtained easily and in a form that satisfies the $2n + 1$ and $2n + 2$ rules. In this case, the property is the excited-state energy obtained from the linear response eigenvalue equation in combination with the ground-state energy. The excited-state Lagrangian [Eq. (5.69)] is the carrier functional for the determination of static excited-state properties.

5.F. ORBITAL RELAXED CC RESPONSE THEORY AND SECOND-ORDER MøLLER–PLESSET PERTURBATION THEORY

We may include orbital relaxation explicitly in the time-dependent CC quasienergy Lagrangian, modifying the Lagrangian in Eq. (5.12) to

$$\begin{aligned} L_{\mathrm{cc}} = {} & \left\langle \mathrm{HF} \middle| \exp(-\kappa(t)) \left(H - i\frac{\partial}{\partial t} \right) \exp(\kappa(t)) \right. \\ & \left. \times \exp(T(t)) \middle| \mathrm{HF} \right\rangle \\ & + \sum_{\mu_i} \bar{t}_{\mu_i}(t) \left\langle \mu_i \middle| \exp(-T(t)) \exp(-\kappa(t)) \right. \\ & \left. \times \left(H - i\frac{\partial}{\partial t} \right) \exp(\kappa(t)) \exp(T(t)) \middle| \mathrm{HF} \right\rangle \\ & + \sum_{mn} \bar{\kappa}_{mn}(t) \left\langle \mathrm{HF} \middle| \left[E_{mn}, \exp(-\kappa(t)) \right. \right. \\ & \left. \left. \times \left(H - i\frac{\partial}{\partial t} \right) \exp(\kappa(t)) \right] \middle| \mathrm{HF} \right\rangle. \end{aligned} \tag{5.80}$$

The summation pair indices (mn) runs over all nonredundant orbital rotations. The last term introduces the time-dependent HF equations as constraints, and the reference state is an HF state. The derivation of frequency-dependent properties follows the same strategy as demonstrated in the last section and we therefore give no details. The resulting linear response function can be written as

$$\begin{aligned} & \langle\langle X; Y \rangle\rangle_{\omega_Y} \\ & \quad = \left. \frac{\partial^2 \{L\}_T}{\partial \varepsilon_X(\omega_X)\, \partial \varepsilon_Y(\omega_Y)} \right|_{\varepsilon = 0} \\ & \quad = \frac{1}{2} C^{\pm\omega} P(X(\omega_X), Y(\omega_Y)) \\ & \qquad \times \left[\left\langle \Lambda \middle| I^{XY}(\omega_X, \omega_Y) \right. \right. \\ & \qquad + \left[I^X(\omega_X), T^Y(\omega_Y) \right] \middle| \mathrm{CC} \right\rangle \\ & \qquad + \frac{1}{2} \left\langle \Lambda \middle| \left[\left[H_0, T^X(\omega_X) \right], T^Y(\omega_Y) \right] \middle| \mathrm{CC} \right\rangle \\ & \qquad \left. + \sum_{mn} \bar{\kappa}^{(0)}_{mn} \left\langle \mathrm{HF} \middle| \left[E_{mn}, I^{XY}(\omega_X, \omega_Y) \right] \middle| \mathrm{HF} \right\rangle \right], \end{aligned} \tag{5.81}$$

where we have introduced

$$I^Y(\omega_Y) = Y + \left[H_0, \kappa^Y(\omega_Y) \right] - \omega_Y \kappa^Y(\omega_Y), \tag{5.82}$$

$$\begin{aligned} & I^{XY}(\omega_X, \omega_Y) \\ & \quad = \frac{1}{2} P(X(\omega_X), Y(\omega_Y)) \left(\left[X, \kappa^Y(\omega_Y) \right] \right. \\ & \qquad + \frac{1}{2} \left[\left[H_0, \kappa^X(\omega_X) \right], \kappa^Y(\omega_Y) \right] \\ & \qquad \left. + \frac{\omega_Y}{2} \left[\kappa^X(\omega_X), \kappa^Y(\omega_Y) \right] \right). \end{aligned} \tag{5.83}$$

The equation determining the first-order clusters parameters is equivalent to Eq. (5.30) with the only modification that the right-hand side of the cluster amplitude response equation is modified to

$$\xi^Y_{\mu_i}(\omega_Y) = \langle \mu_i | \exp(-T) I^Y(\omega_Y) \exp(T) | \mathrm{HF} \rangle. \tag{5.84}$$

In addition to the CC equations, we need to solve first-order HF response equations. The orbital multipliers are determined from

$$\begin{aligned} & \langle \Lambda | [H_0, E_{mn}] | \mathrm{CC} \rangle \\ & \quad + \sum_{pq} \bar{\kappa}_{pq} \left\langle \mathrm{HF} \middle| \left[E_{pq}, [H_0, E_{mn}] \right] \middle| \mathrm{HF} \right\rangle = 0. \end{aligned} \tag{5.85}$$

We can now discuss some structural differences between the orbital relaxed form in Eq. (5.81) and

the CC linear response function in Eq. (5.32). First, we note that by setting all the orbital rotations to zero we obtain

$$\begin{aligned}\langle\langle X;Y\rangle\rangle_{\omega_Y} &= \frac{1}{2}C^{\pm\omega}P(X(\omega_X),Y(\omega_Y)) \\ &\times\Big[\big\langle\Lambda\big|\big[X,T^Y(\omega_Y)\big]\big|\mathrm{CC}\big\rangle \\ &+\frac{1}{2}\big\langle\Lambda\big|\big[\big[H_0,T^X(\omega_X)\big],T^Y(\omega_Y)\big]\big|\mathrm{CC}\big\rangle\Big],\end{aligned} \tag{5.86}$$

which is equivalent to Eq. (5.32), since $\langle\Lambda\|[X, T^Y(\omega_Y)]\|\mathrm{CC}\rangle = \eta^X t^Y(\omega_Y)$ and $\langle\Lambda\|[[H_0, T^X(\omega_X)], T^Y(\omega_Y)]\|\mathrm{CC}\rangle = \mathbf{F}t^X(\omega_X)t^Y(\omega_Y)$. In the relaxed form [Eq. (5.81)], we have replaced Y with I^Y relative to Eq. (5.32) and additional terms enter originating from the second-order terms in the expansion of $\exp(-\kappa(t))(H - i[\partial/(\partial t)])\exp(\kappa(t))$.

In the diagonal representation, the sum over the HF states runs over both positive and negative excitation energies, meaning that the response vectors $\kappa^Y(\omega)$ have poles ω equal to either plus or minus an excitation energy. As a consequence, products of first-order response vectors contain second-order poles, for example, $[[H_0, \kappa^X(-\omega)], \kappa^Y(\omega)]$ contain second-order poles at ω equal to an HF eigenvalues. For a nonvariational nonlinear parametrization, products of first-order responses will occur in the expressions for second-order frequency-dependent properties obtained as quasienergy derivatives, as seen from Eq. (3.34). This may lead to second-order poles when a paired structure similar to the one in HF is present. Since only excitation operators are included in the CC parametrization, we do not have a paired structure in the CC diagonal representation. Hence, in the CC linear response function in Eq. (5.32) where orbital relaxation is not included, we only have first-order CC poles as also found in the previous subsections. Introducing orbital relaxation, we arrive at the form in Eq. (5.81), where both correlated CC poles and uncorrelated HF poles are present and, furthermore, the HF poles are of second order. There is, in this way, a major structural difference between the two cases. The orbital relaxed case is a two-step approach; first, an HF step and, then, a CC step. This gives us two sets of constraints and two sets of parameters and therefore two sets of poles in the linear response functions. In the orbital unrelaxed case, we assume that the orbitals are fixed during the calculation. From the CC unrelaxed linear response function given by Eq. (5.32), we may therefore straightforwardly identify excitation energies and transition moments, since the pole structure is consistent with the pole structure of the exact response function. In the orbital relaxed case, the pole structure is not consistent with the one of exact theory and underlying HF poles cause spurious divergencies. In this context, it is important to realize that excited states represented by the HF poles are already represented at the correlated level by the CC poles. Indeed, it is questionable at all to use the term response function about Eq. (5.81), and we reserve the term CC linear response function to the unrelaxed form in Eq. (5.32).

In CC theory, the deexcitation manifold is introduced in an indirect way. The parametrization is described exclusively in terms of excitation operators, while the coupling to the deexcitation manifold is due to the left projection manifold. As a consequence, we do not have a direct coupling of the excitation and deexcitation spectrum in the first-order response equations. This is important as it is this coupling between the excitation and deexcitation manifold that causes second-order poles in the expressions for the frequency-dependent polarizabilities. We do not have these problems in the unrelaxed CC approach even though we have products of first-order responses. Restricting ourselves to consider excitation operators only, we have avoided these types of problems. A special feature of CC theory is also that the $\exp(-T_1)$ part of the CC expansion mimics the orbital relaxations to the extent that it can be described with the use of excitation operators only.

The derivation and analysis of the relaxed CC response function show the following: (1) If the model is a two-step approach, this gives rise to a pole structure from each of the two ''steps'' and may ultimately lead to a pole structure of the linear response function that is not in accord with the one of the exact response functions. (2) If the nonvariational nonlinear model has a paired structure where the first-order responses have poles both for plus and minus the excitation energies, then the linear response function may have second-order poles. The determination of transition strengths based on the linear response function is therefore not possible.

On the basis of the analysis above, it is also obvious that the response function for the well-re-

nowned CCSD(T) method will be even more dubious. In CCSD(T), a perturbational correction for the effect of triples excitations is added to the CCSD energy. The perturbational correction is defined assuming HF orbitals and thus requires orbital relaxation to be included. A CCSD(T) linear response property will thus have both SCF and CCSD poles (where the SCF poles are of second-order nature) as well as poles corresponding to the triples excitations. Even if the orbital constraint could be relaxed, the poles would still be of CCSD quality: Only iterative models can give response functions with a pole structure that is consistent with exact theory. It is, of course, possible to define perturbational corrections to, for example, CCS or CCSD excitation energies [80]; however, it should be emphasized that the excitation energies obtained in such an approach are not the poles of any response function. Thus, there will always formally be a lack of consistency between the ground-state energy and the excitation energy in such an approach. Each is defined using a procedure that is independent of the other.

As another example, we discuss briefly the Brueckner coupled cluster (BCC) theory. In the CC theory, the cluster parameters and the orbital rotation parameters are treated at equal footing in a one-step approach:

$$|\tilde{\mathrm{BCC}}(t)\rangle = \exp(\kappa(t))\exp(T(t))|R\rangle, \quad (5.87)$$

where κ refers to the orbital rotation operators in the form of Eq. (4.4) and T is the CC operator in Eq. (5.2) excluding singles excitations T_1 from the cluster expansion. In BCC, the deexcitation manifold is incorporated directly into the parametrization, and we therefore obtain a structure having features in common with HF namely, a paired structure with coupling of the excitation and deexcitation manifolds of the type given by the **B** and Δ matrices of Eqs. (4.25) and (4.26). As a consequence of the one-step approach, only one set of poles is present in the linear response function. However, since BCC is nonvariational and nonlinear, the products of first-order responses will be present in the linear response function and the linear response function therefore contains second-order poles, as was previously observed in [39]. This prevents us from calculating transition properties in BCC. Thus, the product of first-order response vectors that is harmless in unrelaxed CC theory is fatal for BCC because of the paired structure of the BCC response theory. We thus conclude that the pole structure of BCC response functions are not in accord with the one of the exact response functions. The BCC approach is therefore not a solution to the problems inherent in the orbital relaxed CC approach, although in the limit of vanishing cluster amplitudes, the HF response functions are obtained from the parametrization in Eq. (5.87). Only the original orbital unrelaxed CC approach leads to response functions with a pole structure consistent with that of the exact response functions.

Another commonly used method in the molecular quantum chemistry is the Møller–Plesset perturbation theory. Several attempts have been made to derive expressions for second-order Møller–Plesset (MP2) frequency-dependent properties. The discussion seems now to be settled with the work of Hättig and Heß [38] using an approach in line with the one of Aiga et al. [22]. In the formalism of this article, the MP2 time-dependent quasienergy Lagrangian is most easily found as the second-order approximation to the relaxed CC quasienergy Lagrangian, where order in this context refers to order in the fluctuation potential of Møller–Plesset perturbation theory:

$$\begin{aligned} L_{\mathrm{MP2}} = {} & \left\langle \mathrm{HF} \middle| \exp(-\kappa(t)) \left(H - i\frac{\partial}{\partial t} \right) \exp(\kappa(t)) \right. \\ & \left. \times (1 + T_2(t)) \middle| \mathrm{HF} \right\rangle \\ & + \sum_{\mu_2} \bar{t}_{\mu_2}(t) \left\langle \mu_2 \middle| \exp(-\kappa(t)) \left(H - i\frac{\partial}{\partial t} \right) \right. \\ & \left. \times \exp(\kappa(t)) \middle| \mathrm{HF} \right\rangle \\ & + \sum_{\mu_2} \bar{t}_{\mu_2}(t) \left\langle \mu_2 \middle| \left[\exp(-\kappa(t)) \left(F - i\frac{\partial}{\partial t} \right) \right. \right. \\ & \left. \left. \times \exp(\kappa(t)), T_2(t) \right] \middle| \mathrm{HF} \right\rangle \\ & + \sum_{mn} \bar{\kappa}_{mn}(t) \left\langle \mathrm{HF} \middle| \left[E_{mn}, \exp(-\kappa(t)) \right. \right. \\ & \left. \left. \times \left(H - i\frac{\partial}{\partial t} \right) \exp(\kappa(t)) \right] \middle| \mathrm{HF} \right\rangle \end{aligned} \quad (5.88)$$

F is the Fock operator. The approximations of Eq. (5.88) can be traced in the derivatives such that the MP2 linear response function becomes the second-order approximation to the relaxed CCSD

response function in Eq. (5.81). Other expressions that are more symmetric in $\bar{t}_{\mu_2}$ and t_{μ_2} may be more optimal for MP2 in practical use. These have already been discussed in several places in the literature and will not be described here in more detail. We give a few comments on MP2 response theory in line with the above discussion. First, MP2 is a two-step approach consisting of an HF step and a second-order MP2 step. Thus, expressions for response properties will have poles at the HF poles and at the MP2 poles (which are the double-excitation poles described to zeroth-order in the fluctuation potential). Next, similar to the relaxed CCSD approach, the nonvariational nonlinear nature leads to products of first-order orbital responses, and the HF poles are thus second-order poles. Hence, for several reasons, the MP2 response function does not have a pole structure that is consistent with the one of the exact linear response function as observed in [22]. Finally, we note that one of the errors that has been made in the derivation of the MP2 response functions is the neglect of the time derivative of the T_2 term. We see that this term automatically is included in the present approach, defining the MP2 time-dependent Lagrangian as an approximation to the relaxed CCSD Lagrangian.

Other ''second-order'' models exist that unlike MP2 do give response functions with a pole structure consistent with exact theory. One is the CC2 model [68], which is an iterative second-order approximation to CCSD and thus represented by response functions of the unrelaxed CC approach as discussed in the previous Subsections 5.A–E. The second-order polarization propagator approximation [81] is another example of a second-order approach that also gives a correct pole structure. This approach is based on a somewhat different philosophy for obtaining response functions and will not be discussed further here.

6. Summary

For exact theory, many different routes may be taken to derive abstract expressions for the determination of molecular properties. However, for approximate theories, considerably more care is needed since many relations that are trivially fulfilled in exact theory are no longer satisfied. Furthermore, with actual calculations in mind, it also becomes crucial to minimize the number of equations to be solved as well as having a simple and well-structured theory. In approximate theory, some strategies for obtaining molecular properties are therefore better than others.

The calculation of energy derivatives in time-independent theory is by now a well-established, highly mature field. Crucial for this status is that the techniques for obtaining correct and computationally tractable expressions are well known and straightforward. These techniques rely on the variational principle in the broad sense, including the Lagrangian technique for expressing nonvariational energies in a variational form. Due to the absence of a well-defined energy function, the calculation of molecular properties in time-dependent theory is a more complicated and less developed field. While, indeed, progress has taken place in the field of response theory for determining molecular properties for approximate models, there has been some confusion concerning the correct time-dependent variational principles and, in particular, which procedure should be used to derive the response functions. Furthermore, there has in many cases been a substantial difference in the methodologies and concepts that are used in time-dependent and time-independent theory.

In this article, we built a bridge between the time-independent techniques for determining static molecular properties and the response function formalism for determining frequency-dependent molecular properties and transition properties. The time-dependent quasienergy $Q(t)$ and the (time-averaged) quasienergy $\{Q(t)\}_T$ are central in establishing this link:

$$Q(t) = \left\langle \tilde{0} \middle| \left(H - i\frac{\partial}{\partial t} \right) \middle| \tilde{0} \right\rangle. \tag{6.1}$$

In time-dependent theory, the generalized variational principle and the generalized Hellmann–Feynman theorem can be written in terms of the time-dependent quasienergy:

$$\delta Q(t) + i\frac{\partial}{\partial t}\langle \tilde{0} | \delta \tilde{0} \rangle = 0 \tag{6.2}$$

and

$$\langle \tilde{0} | X | \tilde{0} \rangle \exp(-i\omega t) = \frac{\partial Q(t)}{\partial \varepsilon_x(\omega)} + i\frac{\partial}{\partial t}\left\langle \tilde{0} \middle| \frac{\partial \tilde{0}}{\partial \varepsilon_x(\omega)} \right\rangle. \tag{6.3}$$

Equation (6.2) is the fundamental time-dependent equation for the quantum mechanical system and

is equivalent to the time-dependent Schrödinger equation for sufficiently flexible trial functions. This time-dependent variation principle can therefore, for example, be used directly to obtain the dynamical equations for the system [82]. In our case we have, however, a different goal, namely, the derivation of response functions for periodic perturbations.

The essential difference between Eqs. (6.2) and (6.3) and the time-independent analogs is the second term in Eqs. (6.2) and (6.3), demonstrating that the time-dependent quasienergy cannot be interpreted as a usual energy functional from which response functions and response equations can be determined by straightforward differentiation. At first sight, this appears to hinder the use of the techniques of time-independent theory in the determination of molecular properties in time-dependent theory.

However, for periodic perturbation, time-averaging overcomes this problem. Thus, the time-averaged variational principle and the time-averaged Hellmann–Feynman theorem,

$$\delta\{Q(t)\}_T = 0 \tag{6.4}$$

$$\frac{\partial\{Q(t)\}_T}{\partial\varepsilon_x(\omega)} = \left\{\langle\tilde{0}|X|\tilde{0}\rangle\exp(-i\omega t)\right\}_T, \tag{6.5}$$

does exactly remove the last term in Eqs. (6.2) and (6.3).

We have shown that the variational criteria for the (time-averaged) quasienergy is sufficient for determining the time-evolution of $|\tilde{0}\rangle$. Furthermore, we have seen that the Hellmann–Feynman theorem for the quasienergy leads automatically to an expansion allowing us to determine response functions to any order and with general frequency indices as derivative of the quasienergy. We therefore conclude that the quasienergy contains all the information that we need for the determination of the response functions.

We thus have a generalized energy functional, the quasienergy, from which both the wave-function parameters and the response functions can be determined by differentiation. The determination of response functions and response equations are simply generalized to Fourier components in a well-defined way, giving a natural extension of standard energy derivative techniques to the case of time-dependent periodic perturbations. It is therefore obvious that this strategy benefits from the advantages of ordinary energy derivative techniques. Response functions in agreement with the $2n + 1$ and $2n + 2$ are obtained immediately. Additional reductions and manipulations may in some particular cases give computationally more advantageous expressions; however, we believe that the $2n + 1$ and $2n + 2$ rule expressions should be the starting point of any such investigation. Thus, we advocate the determination of response functions from a Fourier component variational perturbation theory applied to the time-averaged quasienergy as the natural bridge between the response theory formalism and the energy derivative formalism.

We have used the Fourier component variational perturbation theory to consider general variational and nonvariational parametrizations, and we have specialized this to particular examples: exact, self-consistent field (SCF), and coupled cluster (CC) wave functions. We have also briefly discussed the development of response theory for multiconfigurational self-consistent field (MCSCF), Brueckner coupled cluster (BCC), and second-order Møller–Plesset (MP2) theory. The SCF properties derived in this article are formally equivalent to those obtained previously, although the present formalism gives slightly different structures of the response functions. The CC response functions that we obtain are slightly different from those previously presented. A closer inspection of some previous CC response theory calculations of frequency-dependent polarizabilities and oscillator strengths shows that the tensors considered in these works were diagonal due to symmetry, and since only real arithmetic and real operators (dipole) operators were considered, the results of these calculations are identical to those obtained in the present formalism. However, in general (for nondiagonal tensors, hyperpolarizabilities, and imaginary operators), different properties are obtained. The expressions given in this article were derived with emphasis on preserving as many as possible of the symmetry relations satisfied in exact theory.

We have furthermore described how the Lagrangian technique can be used not only to determine the response functions, but also for more detailed analysis of the expressions that can be determined from the response functions and their poles and residues. We have shown for the example of excited-state properties how a property-oriented carrier Lagrangian can be defined, where the properties in question are obtained as derivatives of this carrier Lagrangian. Since the Lagrangian is variational in all parameters and the properties are determined as derivatives, this leads to expres-

sions satisfying the $2n + 1$ and $2n + 2$ type of rules. On the basis of this analysis, we have suggested expressions for the calculation of excited-state properties and transition properties in SCF, MCSCF, and CC theory that are in accord with the $2n + 1$ and $2n + 2$ rules and thus computationally advantageous relative to previous SCF, MCSCF, and CC response theory developments. In particular, this is important in connection with the calculation of excited-state molecular gradients. Using the techniques derived in this article, we have derived and implemented response functions, transition moments, and excited-state properties for several CC models: Calculations of excitation energies, [67, 68] transition moments, [69] frequency-dependent polarizabilities, [69] Cauchy moments [83], and frequency-dependent first and second hyperpolarizabilities [70, 71] have been reported recently; implementations of the quartic and pentic response functions and of two- and three-photon transition moments are in progress and will be the subjects of forthcoming publications.

For the above reasons, we recommend the use of the general and computational tractable expressions derived in this article in future response theory studies of nonlinear properties and in studies of excited states. We also believe that the general sections together with the following more specialized discussions can be paradigmatic for the derivation and analysis of response functions for other and future approximate methods.

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