Paper I

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Abstract

A general method is presented for the calculation of molecular properties to arbitrary order at the Kohm-Sham density functional level of theory. The quasienergy and Lagrangian formalisms are combined to derive response functions and their residues by straightforward differentiation of the quasienergy derivative Lagrangian using the elements of the density matrix in the atomic orbital representation as variational parameters. Response functions and response equations are expressed in the atomic orbital basis, allowing recent advances in the field of linear-scaling methodology to be used. Time-dependent and static perturbations are treated on an equal footing, and atomic basis sets that depend on the applied frequency-dependent perturbations may be used, *e.g.* frequency-dependent London atomic orbitals.

The $2n+1$ rule may be applied, if computationally favorable, but alternative formulations using higher-order perturbed density matrices are also derived. These may be advantageous in order to minimize the number of response equations that needs to be solved, for instance when one of the perturbations has many components, as is the case for the first-order geometrical derivative of the hyperpolarizability.

I. INTRODUCTION

Molecular properties represent the link between observable quantities that can be determined in experimental investigations and quantum chemical calculations. For this reason, the calculation of molecular properties has been an essential target since the development of modern electronic-structure methods was initiated.

The focus in theoretical and experimental chemistry has in the last decade shifted towards larger molecular systems. For the treatment of time-dependent phenomena of large molecules, the method of choice today is time-dependent Kohn–Sham density functional theory (KS-DFT) [1–4] (including hybrid methods and Hartree–Fock) which offers reasonable accuracy at a low computational cost. In order to facilitate computations on increasingly larger systems, it is important that the computational time scales linearly with the size of the system. In conventional KS methods, the determination of the molecular (spin-)orbital (MO) coefficients requires a diagonalization of the KS matrix, a procedure that scales cubically with the size of the system. To obtain linear scaling, it is necessary to abandon the MO description and work solely in terms of the density matrix in the atomic (spin-)orbital (AO) representation [5–8]. By deriving working equations in the AO basis, linear scaling can be achieved when the molecular system becomes sufficiently large and sparse matrix algebra is used.

Molecular properties may be evaluated using the response function approach. Response theory as developed in the eighties [9]—where response functions are subjected to a pole and residue analysis—has been used successfully to calculate a large variety of molecular properties. In the nineties, the quasienergy approach [10, 11] tied response function theory closely to the energy-derivative techniques in time-independent theory. Using the quasienergy approach, response functions may be straightforwardly derived for both variational and non-variational wave functions [11].

In this paper we apply the quasienergy approach to determine response functions and their residues within KS theory using the elements of the AO density matrix (which in the following will be referred to simply as the density matrix) as variational parameters. Response functions are then obtained in the AO basis and linear scaling may therefore be achieved. Standard basis sets and basis sets that depend explicitly on applied frequency-dependent perturbations (perturbation-dependent basis sets, PDBS) are treated on an equal footing.

The presented derivation is a generalization of the developments by Helgaker *et al.* [12, 13], who introduced an unconstrained exponential parameterization of the density matrix in the AO basis and used this parameterization to determine response functions for standard basis sets. The exponential parameterization was also extended to PDBS, but only for a static perturbation [14]. However, for PDBS the exponential parameterization cannot be applied without an additional idempotency constraint on the *reference* density matrix. To simplify the derivations for PDBS and to obtain a more uniform description of static and time-dependent perturbations, we will impose the idempotency constraint of the density matrix explicitly. The response equations that are obtained will be shown to have the same structure as the ones obtained using the exponential parameterization [13], and the response equations may therefore be solved using the linear response solver of Coriani *et al.* [5].

In exact theory, the quasienergy and the density operator (or density matrix) are fundamentally different quantities with respect to operations on the bra and ket vectors. As a consequence, the quasienergy cannot be expressed in terms of the density operator (or density matrix) in the same way as the energy in time-independent theory. However, we demonstrate that the *perturbation strength-derivative* of the quasienergy may be expressed

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in terms of the density matrix and its time derivative, and use this to identify molecular response functions by differentiation of the quasienergy perturbation-strength derivative.

The formalism has been derived with emphasis on an easy extension to higher-order molecular properties and to provide a uniform framework for the calculation of static and frequency-dependent molecular properties. It focuses on defining generic building blocks, making it straightforward to implement molecular properties of arbitrary order.

Most implementations of response functions and energy derivatives utilize the so-called $2n+1$ rule, also known as Wigner's theorem [15, 16], which states that the quasienergy to order $2n+1$ can be determined from perturbed parameters to order n, thereby avoiding the solution of higher-order perturbed parameters. Whereas this is advantageous when the applied perturbations have approximately the same number of components, this is not necessarily the case if one of the applied perturbations has a larger number of components than the other perturbations. Examples may be the evaluation of first-order geometrical derivatives of electromagnetic properties, such as Raman intensities [17], Raman optical activity [18], and pure vibrational contributions to nonlinear optical properties [19]. The latter requires the calculation of the first-order geometrical derivatives of the dipole moment, the polarizability and the first hyperpolarizability. For large molecules, it will for these properties be advantageous to solve for higher-order responses with respect to the electromagnetic perturbations instead of the nuclear displacement perturbations. For this reason, we derive response expressions that comply with the $2n+1$ rule, but also alternative expressions that require the calculation of higher-order perturbed density matrices.

In our derivations, static and frequency-dependent perturbations are treated on an equal footing, as are also standard basis sets and PDBS. Traditionally, derivations of static molecular properties using PDBS (*e.g.* molecular gradients and Hessians and magnetic properties calculated using so-called London atomic orbitals [20–22]) and frequency-dependent properties using standard basis sets have been performed independently of each other. During the last 10-15 years, however, new developments have appeared involving the use of PDBS for the calculation of frequency-dependent response properties [17–19, 23–36], including some works where the basis sets also depend on the applied frequency-dependent perturbation [37]. Linear-scaling methodologies for static PDBS [38, 39] have also been discussed in this context. Our formalism is AO based and matrix oriented and includes the use of frequency-dependent PDBS.

The outline for this paper is as follows. In the next section we summarize the quasienergy method for an exact state. In Section III we consider response theory at the KS level of theory and write our equations in terms of the MO coefficients. This is an intermediate step which allows us to rewrite the main equations in terms of the density matrix in Section IV. In Section IV A the perturbation-strength derivative of the time-averaged quasienergy is expressed in terms of the density matrix and its time derivative. In Sections IV B-IV E we discuss how the density matrix may be determined to arbitrary order. The determination of response functions according to the $n+1$ rule—where response parameters to order n determine molecular properties to order $n+1$—is discussed in Section IV F. The evaluation of higher-order response functions is considered in Section IV G, where we develop expressions that comply with the $2n+1$ rule, but also consider alternative formulations that are intermediate between the $n+1$ and $2n+1$ rules. In Section IV H we show how residues of response functions may easily be identified from the corresponding response function expressions by replacing the density matrix by a "residue density matrix". Finally, we give some concluding remarks in Section V.

II. THE QUASIENERGY METHOD FOR AN EXACT STATE

A. The time evolution of an exact state

We consider a system described by the non-relativistic time-dependent electronic Schrödinger equation (in atomic units)

$$H|\bar{0}\rangle = i\frac{\partial}{\partial t}|\bar{0}\rangle \tag{1}$$

where the total Hamiltonian H is written as a sum of the time-independent zeroth-order electronic Hamiltonian H_0 and a time-dependent operator V^t representing the perturbation

$$H = H_0 + V^t \tag{2}$$

The zeroth-order Hamiltonian is given by

$$H_0 = h + \frac{1}{2}\sum_{i\neq j}\frac{1}{r_{ij}} + h_{nuc} \tag{3}$$

where h is a one-electron operator,

$$h = \sum_j h_j \tag{4}$$

containing the kinetic energy of the electrons and the electron–nucleus interaction,

$$h_j = -\frac{1}{2}\nabla_j^2 - \sum_K \frac{Z_K}{|\mathbf{R}_K - \mathbf{r}_j|} \tag{5}$$

and h_{nuc} contains the contribution from nuclear repulsion,

$$h_{nuc} = \frac{1}{2}\sum_{K\neq L}\frac{Z_K Z_L}{|\mathbf{R}_K - \mathbf{R}_L|} \tag{6}$$

For the calculation of magnetic properties (*e.g.* NMR parameters), h_{nuc} contains additional purely magnetic interactions, such as the Zeeman interaction between the nuclear magnetic dipole moments and the external magnetic field [40].

The operator representing the perturbation is Hermitian and periodic and may be expressed in terms of its Fourier components

$$V^t = \sum_{k=-N}^{N} \exp(-i\omega_k t)V(\omega_k) \tag{7}$$

$$V(\omega_k) = \sum_A \varepsilon_A(\omega_k)A \tag{8}$$

where A is a one-electron operator

$$A = \sum_j a_j \tag{9}$$

and $\varepsilon_A(\omega_k)$ is a complex perturbation strength parameter which controls the field amplitude and phase. We note from the form of Eqs. (7)–(9) that V^t may be written as

$$V^t = \sum_j v_j^t \tag{10}$$

where

$$v_j^t = \sum_A \sum_{k=-N}^{N} \exp(-i\omega_k t)\varepsilon_A(\omega_k)a_j \tag{11}$$

The Hermicity of V^t is ensured by requiring that

$$A^\dagger = A \tag{12}$$
$$\omega_{-k} = -\omega_k \tag{13}$$
$$\varepsilon_A^*(\omega_k) = \varepsilon_A(\omega_{-k}) \tag{14}$$

Since $\varepsilon_A(\omega_k) = \varepsilon_A^R(\omega_k) + i\varepsilon_A^I(\omega_k)$ is linearly independent of $\varepsilon_A^*(\omega_k) = \varepsilon_A^R(\omega_k) - i\varepsilon_A^I(\omega_k)$, we may consider $\varepsilon_A(\omega_k)$ and $\varepsilon_A(\omega_{-k})$ as the linearly independent parameters instead of $\varepsilon_A^R(\omega_k)$ and $\varepsilon_A^I(\omega_k)$. For notational convenience, we may collect the operator (A) and frequency index (k) in a common index a such that

$$\varepsilon_a = \varepsilon_A(\omega_k) = \varepsilon_A^*(\omega_{-k}) = \varepsilon_{-a}^* \tag{15}$$

Using Eq. (11), the one-electron operator v_j^t may be written in the more compact form

$$v_j^t = \sum_a \exp(-i\omega_a t)\varepsilon_a a_j \tag{16}$$

The wave function may be written in a phase-isolated form

$$|\bar{0}\rangle = \exp[-iF(t)]|\tilde{0}\rangle \tag{17}$$

where we expand $|\tilde{0}\rangle$ in orders of the perturbation strengths

$$|\tilde{0}\rangle = |0\rangle + |\tilde{0}^{(1)}(t)\rangle + |\tilde{0}^{(2)}(t)\rangle + \ldots \tag{18}$$

The zeroth-order wave function $|0\rangle$ is an eigenfunction of H_0 with energy E_0

$$H_0|0\rangle = E_0|0\rangle \tag{19}$$

and $|\tilde{0}\rangle$ is chosen to be normalized

$$\langle\tilde{0}|\tilde{0}\rangle = 1 \tag{20}$$

A basic assumption in the quasienergy method is that all frequencies in V^t can be written as an integer times some fundamental frequency ω_0

$$\omega_k = n_k\omega_0; \qquad n_k \in \mathbb{Z} \tag{21}$$

This restricts the frequency components of for instance the first- and second-order wave functions to [11]

$$|\tilde{0}^{(1)}(t)\rangle = \sum_{k_1=-N}^{N} \exp(-i\omega_{k_1}t)|\tilde{0}^{(1)}(\omega_{k_1})\rangle \tag{22}$$

$$|\tilde{0}^{(2)}(t)\rangle = \tfrac{1}{2}\sum_{k_1=-N}^{N}\sum_{k_2=-N}^{N} \exp\big(-i(\omega_{k_1}+\omega_{k_2})t\big)|\tilde{0}^{(2)}(\omega_{k_1},\omega_{k_2})\rangle \tag{23}$$

The wave function $|\tilde{0}\rangle$ is thus periodic in time, with period T

$$|\tilde{0}(t)\rangle = |\tilde{0}(t+T)\rangle \; ; \qquad T = \frac{2\pi}{\omega_0} \tag{24}$$

and hence all quantities describing the system must have period T. We will make frequent use of this fact in later sections.

When a time-dependent perturbation is applied, the system has no well-defined energy. Instead we introduce the quasienergy $Q(t)$ as the time derivative of the phase function in Eq. (17), $\dot{F}(t)$. By inserting Eq. (17) into the time-dependent Schrödinger equation, Eq. (1), and using that H commutes with the phase factor $\exp[-iF(t)]$, the quasienergy may be determined as

$$Q(t) = \dot{F}(t) = \langle \tilde{0}|H - i\tfrac{\partial}{\partial t}|\tilde{0}\rangle \tag{25}$$

Using Eqs. (19) and (20), it is easily seen that $Q(t) \to E_0$ for the unperturbed system. As the time-dependent Schrödinger equation, Eq. (1), is norm conserving

$$\tfrac{\partial}{\partial t}\langle \tilde{0}|\tilde{0}\rangle = \langle \dot{\tilde{0}}|\tilde{0}\rangle + \langle \tilde{0}|\dot{\tilde{0}}\rangle = 0 \tag{26}$$

it follows that $Q(t)$ is a real function of time

$$\begin{aligned} Q(t)^* &= \langle H\tilde{0}|\tilde{0}\rangle + i\langle \dot{\tilde{0}}|\tilde{0}\rangle \\ &= \langle \tilde{0}|H|\tilde{0}\rangle - i\langle \tilde{0}|\dot{\tilde{0}}\rangle \\ &= Q(t) \end{aligned} \tag{27}$$

The periodicity of the wave function, Eq. (24), may be used to remove the explicit time-dependence from the quasienergy by introducing the *time-averaged* quasienergy

$$\{Q(t)\}_T = \frac{1}{T}\int_{-T/2}^{T/2} Q(t)dt = \frac{1}{T}\int_{-T/2}^{T/2} \langle \tilde{0}|H - i\tfrac{\partial}{\partial t}|\tilde{0}\rangle dt \; ; \qquad T = \frac{2\pi}{\omega_0} \tag{28}$$

B. Response functions for an exact state in the quasienergy formulation

Let us now consider an operator A and expand its expectation value in orders of the perturbation

$$\begin{aligned} \langle A\rangle(t) &= \langle \bar{0}|A|\bar{0}\rangle = \langle \tilde{0}|A|\tilde{0}\rangle \\ &= \langle 0|A|0\rangle + \sum_b \exp(-i\omega_b t)\langle\langle A;B\rangle\rangle_{\omega_b}\varepsilon_b \\ &\quad + \tfrac{1}{2}\sum_{b,c} \exp[-i(\omega_b+\omega_c)t]\langle\langle A;B,C\rangle\rangle_{\omega_b,\omega_c}\varepsilon_b\varepsilon_c \\ &\quad + \ldots \end{aligned} \tag{29}$$

where $\langle\langle A;B\rangle\rangle_{\omega_b}$ is the linear response function, $\langle\langle A;B,C\rangle\rangle_{\omega_b,\omega_c}$ is the quadratic response function, and so on.

Following Ref. [11], the time-averaged quasienergy, Eq. (28), fulfills the variational principle

$$\delta\{Q(t)\}_T = 0 \tag{30}$$

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which may be used to determine the wave function parameters. Furthermore, according to the time-averaged Hellmann-Feynmann theorem, response functions may be determined from the perturbation-strength derivative of the time-averaged quasienergy

$$\frac{d\{Q(t)\}_T}{d\varepsilon_a} = \left\{\langle\tilde{0}|A|\tilde{0}\rangle\exp(-i\omega_a t)\right\}_T \tag{31}$$

Inserting Eq. (29) into Eq. (31), we obtain

$$\begin{aligned}\frac{d\{Q(t)\}_T}{d\varepsilon_a} &= \langle 0|A|0\rangle\delta(\omega_a) + \sum_b\langle\langle A;B\rangle\rangle_{\omega_b}\varepsilon_b\delta(\omega_a+\omega_b) \\ &+ \tfrac{1}{2}\sum_{b,c}\langle\langle A;B,C\rangle\rangle_{\omega_b,\omega_c}\varepsilon_b\varepsilon_c\delta(\omega_a+\omega_b+\omega_c) + \ldots\end{aligned} \tag{32}$$

where $\delta(\omega_i) = 1$ only for $\omega_i = 0$ and zero otherwise. From this expansion we identify response functions as perturbation-strength derivatives of the time-averaged quasienergy evaluated at zero perturbation strength

$$\langle\langle A;B\rangle\rangle_{\omega_b} = \frac{d^2\{Q(t)\}_T}{d\varepsilon_a d\varepsilon_b}\bigg|_{\{\varepsilon\}=0} \quad ; \qquad \omega_a = -\omega_b \tag{33}$$

$$\langle\langle A;B,C\rangle\rangle_{\omega_b,\omega_c} = \frac{d^3\{Q(t)\}_T}{d\varepsilon_a d\varepsilon_b d\varepsilon_c}\bigg|_{\{\varepsilon\}=0} \quad ; \qquad \omega_a = -\omega_b - \omega_c \tag{34}$$

We note that since $\{Q(t)\}_T$ is variational, the $2n+1$ rule applies.

C. Quasienergy response theory using a density formulation

In the expression for the quasienergy, Eq. (25), time differentiation occurs only on the ket state. The quasienergy is therefore an asymmetric quantity with respect to operations on the bra and ket states. For an exact state, the density operator $\mathcal{D}$ is [41]

$$\mathcal{D} = |\tilde{0}\rangle\langle\tilde{0}| \tag{35}$$

and consequently its time derivative becomes

$$\dot{\mathcal{D}} = |\dot{\tilde{0}}\rangle\langle\tilde{0}| + |\tilde{0}\rangle\langle\dot{\tilde{0}}| \tag{36}$$

which is clearly a symmetric quantity with respect to operations on the bra and ket states. As opposed to the energy, the (time-averaged) quasienergy may therefore not readily be expressed in terms of the density operator and its time derivative. Thus, the quasienergy method cannot be directly applied in a density operator (or density matrix) formulation of quantum chemistry.

In the remainder of this paper we will determine molecular response functions at the KS level of theory using the quasienergy formalism. This may straightforwardly be done when the expansion coefficients of the MOs in the KS determinant are used as variational parameters (the C parameterization of KS theory) as described in Section III. However, it is advantageous to use the elements of the density matrix as variational parameters since the response functions are then expressed in the AO basis, i.e. the basis where linear scaling may be achieved. As described above, this cannot be done straightforwardly. We therefore

show that the working equations in the C parameterization may be rewritten in a form where the *perturbation-strength derivative* of the time-averaged quasienergy is expressed in terms of the density matrix and its time derivative. Using this approach, molecular response functions may be obtained by differentiation of the quasienergy perturbation-strength derivative in accordance with Eq. (32), and may thus be obtained directly in the AO basis.

III. THE QUASIENERGY FORMALISM IN KOHN-SHAM THEORY USING THE C PARAMETERIZATION

In this section we express the quasienergy at the KS level of theory in terms of MOs and discuss how the MO coefficients $\tilde{C}$ may be determined from the variational principle in Eq. (30).

However, before introducing the C parameterization we summarize our notation convention. A lower-case superscript letter denotes a derivative with respect to some perturbation strength. Superscripts a, b, c denote derivatives with respect to the perturbation strengths $\varepsilon_a, \varepsilon_b, \varepsilon_c$ at $\omega_a, \omega_b, \omega_c$, respectively. Tildes are introduced to denote quantities at general field strengths which in general are time-dependent. For example, for a general perturbation V^t, the overlap matrix (derivative with respect to ε_a) is written as $\tilde{\mathbf{S}}$ ($\tilde{\mathbf{S}}^a$), whereas the notation $\mathbf{S}$ ($\mathbf{S}^a$) is used when the matrices are evaluated at $V^t = 0$. We use the indices I, J, K, L to label occupied MOs, and Greek letters to denote AOs, which may in general depend both on time and on the perturbation strengths.

A. C parameterization

In KS theory, the molecular system containing N electrons is represented by a single time-dependent Slater determinant $|\widetilde{KS}\rangle$

$$|\widetilde{KS}\rangle = (N!)^{-\frac{1}{2}}|\tilde{\phi}_1\tilde{\phi}_2\ldots\tilde{\phi}_N| \tag{37}$$

where the MOs $\tilde{\phi}$ are expanded in a set of AOs $\tilde{\chi}$

$$\tilde{\phi}_I = \sum_\nu \tilde{C}_{\nu I}\tilde{\chi}_\nu \tag{38}$$

In the C parameterization, the MO coefficients $\tilde{C}$ are the variational parameters. The MOs must stay orthonormal at all perturbation strengths

$$\langle \tilde{\phi}_I | \tilde{\phi}_J \rangle = \delta_{IJ} \tag{39}$$

to ensure that $|\widetilde{KS}\rangle$ is normalized. The MO matrix $\tilde{\mathbf{C}}$ contains coefficients for both occupied and virtual MOs. As only the occupied orbitals enter in $|\widetilde{KS}\rangle$, it is convenient to introduce the MO density matrix $\boldsymbol{\rho}$

$$\boldsymbol{\rho} = \begin{pmatrix} \mathbf{1}_N & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix} \tag{40}$$

which is idempotent

$$\boldsymbol{\rho}^2 = \boldsymbol{\rho} \tag{41}$$

and projects out the occupied part of the $\tilde{\mathbf{C}}$ matrix

$$\tilde{\mathbf{C}}\boldsymbol{\rho} = \begin{pmatrix} \tilde{\mathbf{C}}_{occ} & \tilde{\mathbf{C}}_{virt} \end{pmatrix} \begin{pmatrix} \mathbf{1}_N & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix} = \begin{pmatrix} \tilde{\mathbf{C}}_{occ} & \mathbf{0} \end{pmatrix} \tag{42}$$

The electron density $\tilde{\rho}$ is the sum of the absolute squares of the MOs

$$\tilde{\rho} = \sum_I |\tilde{\phi}_I|^2 = \sum_I \sum_{\mu\nu} \tilde{\chi}_\mu^* \tilde{\chi}_\nu \tilde{C}_{\mu I}^* \tilde{C}_{\nu I} = \sum_I \sum_{\mu\nu} \tilde{\Omega}_{\mu\nu} \tilde{C}_{\mu I}^* \tilde{C}_{\nu I} \tag{43}$$

where we have introduced the overlap distribution $\tilde{\Omega}_{\mu\nu}$

$$\tilde{\Omega}_{\mu\nu} = \tilde{\chi}_\mu^* \tilde{\chi}_\nu \tag{44}$$

B.   The quasienergy in Kohn-Sham theory

The KS energy is written as a functional of $\tilde{\rho}$ [42]

$$\tilde{E}[\tilde{\rho}, t] = \tilde{T}_s[\tilde{\rho}] + \tilde{V}_{ne}[\tilde{\rho}] + \tilde{V}^t[\tilde{\rho}, t] + \tilde{J}[\tilde{\rho}] - \gamma \tilde{K}[\tilde{\rho}] + \tilde{E}_{xc}[\tilde{\rho}] + \tilde{h}_{nuc} \tag{45}$$

The first term is the kinetic energy evaluated as an expectation value

$$\tilde{T}_s[\tilde{\rho}] = \langle \widetilde{KS} | - \tfrac{1}{2}\nabla^2 | \widetilde{KS} \rangle = -\tfrac{1}{2}\sum_I \langle \tilde{\phi}_I | \nabla^2 | \tilde{\phi}_I \rangle \tag{46}$$

The second and third terms represent the electron-nucleus attraction and the perturbing operator in Eq. (16), respectively,

$$\tilde{V}_{ne}[\tilde{\rho}] + \tilde{V}^t[\tilde{\rho}, t] = \sum_I \left\langle \tilde{\phi}_I \left| -\sum_K \frac{Z_K}{|\mathbf{R}_K - \mathbf{r}|} + v^t \right| \tilde{\phi}_I \right\rangle \tag{47}$$

The fourth and fifth terms represent the Coulomb interaction of the electron density with itself and the exchange contribution, respectively,

$$\tilde{J}[\tilde{\rho}] = \tfrac{1}{2} \int\int \frac{\tilde{\rho}(\mathbf{r}_1, t)\tilde{\rho}(\mathbf{r}_2, t)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 = \tfrac{1}{2}\sum_{IJ} \tilde{g}_{IIJJ} \tag{48}$$

$$\tilde{K}[\tilde{\rho}] = \tfrac{1}{2}\sum_{IJ} \tilde{g}_{IJJI} \tag{49}$$

where we have introduced the two-electron integral

$$\tilde{g}_{IJKL} = \int\int \tilde{\phi}_I^*(\mathbf{x}_1)\tilde{\phi}_J(\mathbf{x}_1) \frac{1}{r_{12}} \tilde{\phi}_K^*(\mathbf{x}_2)\tilde{\phi}_L(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \tag{50}$$

Here, $\mathbf{x}$ refers to both spatial and spin coordinates. $\tilde{E}_{xc}[\tilde{\rho}]$ is the exchange-correlation functional which includes the remaining part of the energy contribution. It thus contains the effects of electron correlation and corrects the error made in the kinetic energy by evaluating it in terms of a single Slater determinant. The last term $\tilde{h}_{nuc}$ contains purely nuclear contributions.

In pure DFT, the scaling factor for the exchange energy $\gamma = 0$, whereas it is nonzero in hybrid theories. By setting $\gamma = 1$ and removing the exchange-correlation potential altogether, we obtain the Hartree-Fock (HF) energy.

In Eq. (45) we have adopted the widely used adiabatic approximation [2–4] where it is assumed that the exchange-correlation potential depends on time only through the electron density $\tilde{\rho}$. We are in other words assuming that the electron density responds instantaneously to the oscillations of the fields in the external potential in Eq. (16). Within this approximation, only the external perturbing potential $\tilde{V}^t[\tilde{\rho}, t]$ depends explicitly on time.

As $\tilde{E}_{xc}[\tilde{\rho}]$ depends on the MO coefficients $\tilde{C}$ through $\tilde{\rho}$, see Eq. (43), all terms in the KS energy $\tilde{E}[\tilde{\rho}]$ are now expressed in terms of the $\tilde{C}$ coefficients. Inserting Eqs. (46)-(49) into Eq. (45) we may write the KS energy in terms of molecular integrals

$$
\begin{aligned}
\tilde{E}(\tilde{\mathbf{C}}, t) = & -\tfrac{1}{2} \sum_I \langle \tilde{\phi}_I | \nabla^2 | \tilde{\phi}_I \rangle + \sum_I \left\langle \tilde{\phi}_I \left| - \sum_K \frac{Z_K}{|\mathbf{R}_K - \mathbf{r}|} + v^t \right| \tilde{\phi}_I \right\rangle \\
& + \tfrac{1}{2} \sum_{IJ} \tilde{g}_{IIJJ} - \tfrac{1}{2} \gamma \sum_{IJ} \tilde{g}_{IJJI} + \tilde{E}_{xc}[\tilde{\rho}(\tilde{\mathbf{C}})]
\end{aligned}
\tag{51}
$$

From Eq. (25), the quasienergy in KS theory is given by

$$
\tilde{Q}(\tilde{\mathbf{C}}, t) = \tilde{E}(\tilde{\mathbf{C}}, t) - i \sum_I \langle \tilde{\phi}_I | \dot{\tilde{\phi}}_I \rangle
\tag{52}
$$

since the time-differentiation operator is a one-electron operator

$$
-i \langle \widetilde{KS} | \tfrac{\partial}{\partial t} | \widetilde{KS} \rangle = -i \sum_I \langle \tilde{\phi}_I | \dot{\tilde{\phi}}_I \rangle
\tag{53}
$$

C. Variational conditions in the C representation

In this subsection, the variational condition for the time-averaged quasienergy, Eq. (30), will be used to obtain an equation for the $\tilde{C}$ coefficients. The variations of the $\tilde{C}$ coefficients in the time-averaged quasienergy in Eq. (52) are constrained by the orthonormality requirement in Eq. (39). In order to allow for unconstrained variations of the $\tilde{C}$ coefficients, we therefore introduce a set of Lagrange multipliers $\tilde{\lambda}$ for the orthonormality constraint in Eq. (39) and obtain the quasienergy Lagrangian $\tilde{L}(\tilde{\mathbf{C}}, \tilde{\boldsymbol{\lambda}}, t)$

$$
\tilde{L}(\tilde{\mathbf{C}}, \tilde{\boldsymbol{\lambda}}, t) = \tilde{Q}(\tilde{\mathbf{C}}, t) - \sum_{IJ} \tilde{\lambda}_{JI} (\langle \tilde{\phi}_I | \tilde{\phi}_J \rangle - \delta_{IJ})
\tag{54}
$$

where $\tilde{\boldsymbol{\lambda}}$ is Hermitian

$$
\tilde{\boldsymbol{\lambda}} = \tilde{\boldsymbol{\lambda}}^\dagger
\tag{55}
$$

The time-average of the quasienergy Lagrangian is variational, that is

$$
\delta \{ \tilde{L}(\tilde{\mathbf{C}}, \tilde{\boldsymbol{\lambda}}, t) \}_T = 0
\tag{56}
$$

Differentiating $\tilde{L}(\tilde{\mathbf{C}}, \tilde{\boldsymbol{\lambda}}, t)$ with respect to the $\tilde{\lambda}$ parameters gives the equation for the orthonormality condition for the occupied MOs, Eq. (39), which in matrix form may be written as

$$
\boldsymbol{\rho} \tilde{\mathbf{C}}^\dagger \tilde{\mathbf{S}} \tilde{\mathbf{C}} \boldsymbol{\rho} = \boldsymbol{\rho}
\tag{57}
$$

Differentiation of $\tilde{L}(\tilde{\mathbf{C}}, \tilde{\boldsymbol{\lambda}}, t)$ with respect to the complex conjugated $\tilde{C}^*$ parameters yields the time-dependent self-consistent-field (TDSCF) equation for the $\tilde{\mathbf{C}}$ matrix

$$\tilde{\mathbf{F}}\tilde{\mathbf{C}}\boldsymbol{\rho} - i(\tilde{\mathbf{R}}\tilde{\mathbf{C}} + \tilde{\mathbf{S}}\dot{\tilde{\mathbf{C}}})\boldsymbol{\rho} - \tilde{\mathbf{S}}\tilde{\mathbf{C}}\boldsymbol{\rho}\tilde{\boldsymbol{\lambda}}\boldsymbol{\rho} = \mathbf{0} \tag{58}$$

where we have introduced the KS matrix $\tilde{\mathbf{F}}$,

$$\tilde{\mathbf{F}} = \tilde{\mathbf{h}} + \tilde{\mathbf{V}}^t + \tilde{\mathbf{G}}^\gamma(\tilde{\mathbf{C}}\boldsymbol{\rho}\tilde{\mathbf{C}}^\dagger) + \tilde{\mathbf{F}}_{xc} \tag{59}$$

The overlap matrix $\tilde{\mathbf{S}}$, the ket time-differentiated overlap matrix $\tilde{\mathbf{R}}$, and the one-electron matrices $\tilde{\mathbf{h}}$ and $\tilde{\mathbf{V}}^t$ are given by

$$\tilde{S}_{\mu\nu} = \langle \tilde{\chi}_\mu | \tilde{\chi}_\nu \rangle \tag{60}$$

$$\tilde{R}_{\mu\nu} = \langle \tilde{\chi}_\mu | \dot{\tilde{\chi}}_\nu \rangle \tag{61}$$

$$\tilde{h}_{\mu\nu} = \left\langle \tilde{\chi}_\mu \left| -\tfrac{1}{2}\nabla^2 - \sum_K \frac{Z_K}{|\mathbf{R}_K - \mathbf{r}|} \right| \tilde{\chi}_\nu \right\rangle \tag{62}$$

$$\tilde{V}_{\mu\nu}^t = \sum_a \exp(-i\omega_a t)\varepsilon_a \langle \tilde{\chi}_\mu | a | \tilde{\chi}_\nu \rangle \tag{63}$$

whereas the two-electron matrix $\tilde{\mathbf{G}}^\gamma(\mathbf{M})$ with scaled exchange is defined as

$$\tilde{G}_{\mu\nu}^\gamma(\mathbf{M}) = \sum_{\alpha\beta} M_{\beta\alpha}(\tilde{g}_{\mu\nu\alpha\beta} - \gamma\tilde{g}_{\mu\beta\alpha\nu}) \tag{64}$$

To obtain $\tilde{\mathbf{F}}_{xc}$ in Eq. (59), we have used the adiabatic approximation and Eq. (43) to obtain

$$\begin{aligned} \frac{\partial}{\partial \tilde{C}_{\alpha K}^*}\tilde{E}_{xc}[\tilde{\rho}(\mathbf{r}, t)] &= \int \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})}\bigg|_{\rho(\mathbf{r})=\tilde{\rho}(\mathbf{r},t)} \frac{\partial \tilde{\rho}(\mathbf{r}, t)}{\partial \tilde{C}_{\alpha K}^*}d\mathbf{x} \\ &= \sum_\nu \int \tilde{\Omega}_{\alpha\nu}(\mathbf{r}, t)\tilde{v}_{xc}(\mathbf{r}, t)d\mathbf{x}\tilde{C}_{\nu K} \\ &= \sum_\nu (\tilde{F}_{xc})_{\alpha\nu}\tilde{C}_{\nu K} \\ &= (\tilde{\mathbf{F}}_{xc}\tilde{\mathbf{C}}\boldsymbol{\rho})_{\alpha K} \end{aligned} \tag{65}$$

where the exchange-correlation potential $\tilde{v}_{xc}$

$$\tilde{v}_{xc}(\mathbf{r}, t) = \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})}\bigg|_{\rho(\mathbf{r})=\tilde{\rho}(\mathbf{r},t)} \tag{66}$$

and the functional derivative matrix $\tilde{\mathbf{F}}_{xc}$

$$\tilde{F}_{xc,\mu\nu} = \int \tilde{\Omega}_{\mu\nu}\tilde{v}_{xc}d\mathbf{x} \tag{67}$$

have been introduced. The adiabatic approximation was introduced in Eq. (66) by evaluating the functional derivative at $\rho(\mathbf{r}) = \tilde{\rho}(\mathbf{r}, t)$.

When the perturbation is turned off, the coefficients $\tilde{C}$ and the AOs $\tilde{\chi}$ are reduced to the zeroth-order coefficients C and the AOs χ, respectively, and the TDSCF equation, Eq. (58), becomes the standard Roothaan-Hall equation for the occupied part of the C coefficients [43]

$$\mathbf{FC}\boldsymbol{\rho} = \mathbf{SC}\boldsymbol{\rho}\boldsymbol{\lambda}\boldsymbol{\rho} \tag{68}$$

where the zeroth-order KS matrix is

$$\mathbf{F} = \mathbf{h} + \mathbf{G}^{\gamma}(\mathbf{C}\boldsymbol{\rho}\mathbf{C}^{\dagger}) + \mathbf{F}_{xc} \tag{69}$$

and the zeroth-order MO coefficient matrix fulfills the orthonormality condition

$$\boldsymbol{\rho}\mathbf{C}^{\dagger}\mathbf{S}\mathbf{C}\boldsymbol{\rho} = \boldsymbol{\rho} \tag{70}$$

Having now obtained an expression for the time-averaged quasienergy Lagrangian, Eq. (54), suitable for obtaining response functions by differentiation with respect to applied perturbation strengths, we will in the next section make a change of the variational parameters from the MO coefficient matrix $\tilde{\mathbf{C}}$ to the density matrix $\tilde{\mathbf{D}}$. We will demonstrate that this transformation allows us to obtain working equations for the response functions expressed entirely in the AO basis.

IV. THE QUASIENERGY FORMALISM IN KOHN-SHAM THEORY USING THE D PARAMETERIZATION

The density matrix is defined by [43]

$$\tilde{\mathbf{D}} = \tilde{\mathbf{C}}\boldsymbol{\rho}\tilde{\mathbf{C}}^{\dagger} \tag{71}$$

The use of $\boldsymbol{\rho}$ in Eq. (71) ensures that only the occupied part of the $\tilde{\mathbf{C}}$ matrix contributes to $\tilde{\mathbf{D}}$. As discussed in Section II C, the time-averaged quasienergy cannot be expressed directly in terms of $\tilde{\mathbf{D}}$ and its time derivative $\dot{\tilde{\mathbf{D}}}$

$$\dot{\tilde{\mathbf{D}}} = \dot{\tilde{\mathbf{C}}}\boldsymbol{\rho}\tilde{\mathbf{C}}^{\dagger} + \tilde{\mathbf{C}}\boldsymbol{\rho}\dot{\tilde{\mathbf{C}}}^{\dagger} \tag{72}$$

since $\dot{\tilde{\mathbf{D}}}$ is symmetric with respect to time differentiation of the $\tilde{C}$ and $\tilde{C}^{*}$ coefficients, whereas only the $\tilde{C}$ coefficients are differentiated with respect to time in the quasienergy expression, see Eq. (52). However, we will here show that the *perturbation-strength derivative* of the time-averaged quasienergy Lagrangian in the C representation

$$\{\tilde{L}^{a}(\tilde{\mathbf{D}}, t)\}_{T} = \frac{d\{\tilde{L}(\tilde{\mathbf{C}}, \tilde{\boldsymbol{\lambda}}, t)\}_{T}}{d\varepsilon_{a}} \tag{73}$$

and the variational condition

$$\delta\{\tilde{L}(\tilde{\mathbf{D}}, t)\}_{T} = 0 \tag{74}$$

may be expressed in terms of the density matrix. Note that Eqs. (73) and (74) are valid for any perturbation strengths and are *not* evaluated at zero field strengths. We may thus identify response functions directly in the D representation by differentiating Eq. (73) with respect to the perturbation strengths since $\{\tilde{L}^{a}(\tilde{\mathbf{D}}, t)\}_{T}$ is just the left-hand side of Eq. (32), from which response functions may be determined, as done for instance in Eqs. (33)-(34).

A. The quasienergy derivative in the D representation

As $\{\tilde{L}(\tilde{\mathbf{C}}, \tilde{\boldsymbol{\lambda}}, t)\}_{T}$ in Eq. (56) is variational with respect to the $\tilde{C}$ and $\tilde{\lambda}$ parameters

$$\frac{\partial}{\partial\tilde{\mathbf{C}}}\{L(\tilde{\mathbf{C}}, \tilde{\boldsymbol{\lambda}}, t)\}_{T} = \frac{\partial}{\partial\tilde{\boldsymbol{\lambda}}}\{L(\tilde{\mathbf{C}}, \tilde{\boldsymbol{\lambda}}, t)\}_{T} = \mathbf{0} \tag{75}$$

the *total* perturbation-strength derivative of $\{\tilde{L}(\tilde{\mathbf{C}}, \tilde{\boldsymbol{\lambda}}, t)\}_T$ may be obtained as a *partial* derivative (the time-averaged Hellmann-Feynmann theorem)

$$\{\tilde{L}^a(\tilde{\mathbf{C}}, \tilde{\boldsymbol{\lambda}}, t)\}_T = \frac{d\{L(\tilde{\mathbf{C}}, \tilde{\boldsymbol{\lambda}}, t)\}_T}{d\varepsilon_a} = \frac{\partial\{L(\tilde{\mathbf{C}}, \tilde{\boldsymbol{\lambda}}, t)\}_T}{\partial\varepsilon_a}$$

$$= \frac{\partial}{\partial\varepsilon_a}\left\{\tilde{E}(\tilde{\mathbf{C}}, t) - i\sum_I\langle\tilde{\phi}_I|\dot{\tilde{\phi}}_I\rangle - \sum_{IJ}\tilde{\lambda}_{JI}(\langle\tilde{\phi}_I|\tilde{\phi}_J\rangle - \delta_{IJ})\right\}_T \quad (76)$$

Thus, differentiated MO coefficients $\tilde{C}^a$ and multipliers $\tilde{\boldsymbol{\lambda}}^a$ do not contribute to $\{\tilde{L}^a(\tilde{\mathbf{C}}, \tilde{\boldsymbol{\lambda}}, t)\}_T$. We can now express each term in Eq. (76) in terms of the density matrix. Consider first the KS energy in Eq. (51). The one-electron parts of this equation may be written as

$$\tilde{T}_s[\tilde{\rho}] + \tilde{V}_{ne}[\tilde{\rho}] + \tilde{V}^t[\tilde{\rho}, t] \stackrel{\text{Tr}}{=} (\tilde{\mathbf{h}} + \tilde{\mathbf{V}}^t)\tilde{\mathbf{D}} \quad (77)$$

where we have used Eqs. (46), (47), (62), and (63) to arrive at the final expression. The symbol " $\stackrel{\text{Tr}}{=}$ " denotes that we will take the trace of the involved matrix products on both sides of the equality.

The two-electron terms in Eqs. (48)-(49) may in a similar manner be determined as

$$\tilde{J}[\tilde{\rho}] - \gamma\tilde{K}[\tilde{\rho}] \stackrel{\text{Tr}}{=} \tfrac{1}{2}\tilde{\mathbf{G}}^\gamma(\tilde{\mathbf{D}})\tilde{\mathbf{D}} \quad (78)$$

using the definition of the $\tilde{\mathbf{G}}^\gamma(\tilde{\mathbf{D}})$ matrix in Eq. (64). By inserting Eq. (71) into Eq. (43), we see that the electron density may be expressed in terms of the density matrix as

$$\tilde{\rho} = \sum_{\mu\nu}\tilde{\Omega}_{\mu\nu}\tilde{D}_{\nu\mu} \stackrel{\text{Tr}}{=} \tilde{\boldsymbol{\Omega}}\tilde{\mathbf{D}} \quad (79)$$

It is thus clear that the exchange-correlation functional $\tilde{E}_{xc}[\tilde{\rho}]$ depends on $\tilde{\mathbf{D}}$ through $\tilde{\rho}$. We may now express the KS energy in Eq. (51) in terms of $\tilde{\mathbf{D}}$

$$\tilde{E}(\tilde{\mathbf{D}}, t) \stackrel{\text{Tr}}{=} (\tilde{\mathbf{h}} + \tilde{\mathbf{V}}^t)\tilde{\mathbf{D}} + \tfrac{1}{2}\tilde{\mathbf{G}}^\gamma(\tilde{\mathbf{D}})\tilde{\mathbf{D}} + \tilde{E}_{xc}[\tilde{\rho}(\tilde{\mathbf{D}})] + \tilde{h}_{nuc} \quad (80)$$

The partial derivative of the KS energy with respect to ε_a becomes

$$\tilde{E}^{0,a}(\tilde{\mathbf{D}}, t) = \frac{\partial}{\partial\varepsilon_a}\tilde{E}(\tilde{\mathbf{D}}, t) \stackrel{\text{Tr}}{=} \left(\tilde{\mathbf{h}}^a + \tilde{\mathbf{V}}^{t,a} + \tfrac{1}{2}\tilde{\mathbf{G}}^{\gamma,a}(\tilde{\mathbf{D}}) + \tilde{\mathbf{F}}_{xc}^{\Omega^a}\right)\tilde{\mathbf{D}} + \tilde{h}_{nuc}^a \quad (81)$$

where we have introduced the superscript notation "$0, a$" to denote a *partial* derivative with respect to ε_a (and zeroth order with respect to $\tilde{\mathbf{D}}$, as it will be explained in Section IV F). In order to evaluate the exchange-correlation contribution within the adiabatic approximation we have used Eqs. (66), (67), and (79) to obtain

$$\frac{\partial}{\partial\varepsilon_a}\tilde{E}_{xc}[\tilde{\rho}(\tilde{\mathbf{D}})] = \int\left.\frac{\delta E_{xc}}{\delta\rho(\mathbf{r})}\right|_{\rho(\mathbf{r})=\tilde{\rho}(\mathbf{r},t)}\frac{\partial\tilde{\rho}(\mathbf{r}, t)}{\partial\varepsilon_a}d\mathbf{x}$$

$$= \sum_{\mu\nu}\int\tilde{\Omega}_{\mu\nu}^a(\mathbf{r}, t)\tilde{v}_{xc}(\mathbf{r}, t)d\mathbf{x}\tilde{D}_{\nu\mu} \stackrel{\text{Tr}}{=} \tilde{\mathbf{F}}_{xc}^{\Omega_a}\tilde{\mathbf{D}} \quad (82)$$

where we have introduced the functional derivative matrix $\tilde{\mathbf{F}}_{xc}^{\Omega^a}$, defined in terms of the perturbed overlap distributions Ω^a

$$(\tilde{F}_{xc}^{\Omega^a})_{\mu\nu} = \int\tilde{\Omega}_{\mu\nu}^a(\mathbf{r}, t)\tilde{v}_{xc}(\mathbf{r}, t)d\mathbf{x} \quad (83)$$

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Let us now consider the second and third contributions of Eq. (76) – that is, the time derivative term

$$-i\sum_I \langle \tilde{\phi}_I | \dot{\tilde{\phi}}_I \rangle \;=\; -i\sum_{I,\mu\nu} \left(\tilde{C}^*_{\mu I} \tilde{C}_{\nu I} \langle \tilde{\chi}_\mu | \dot{\tilde{\chi}}_\nu \rangle + \tilde{C}^*_{\mu I} \dot{\tilde{C}}_{\nu I} \langle \tilde{\chi}_\mu | \tilde{\chi}_\nu \rangle \right)$$
$$\overset{\mathrm{Tr}}{=} -i\left(\boldsymbol{\rho}\tilde{\mathbf{C}}^\dagger \tilde{\mathbf{R}}\tilde{\mathbf{C}}\boldsymbol{\rho} + \boldsymbol{\rho}\tilde{\mathbf{C}}^\dagger \tilde{\mathbf{S}}\dot{\tilde{\mathbf{C}}}\boldsymbol{\rho} \right) \tag{84}$$

and the multiplier term

$$-\sum_{IJ} \tilde{\lambda}_{JI}(\langle \tilde{\phi}_I | \tilde{\phi}_J \rangle - \delta_{IJ}) \;\overset{\mathrm{Tr}}{=}\; -\left(\tilde{\mathbf{C}}^\dagger \tilde{\mathbf{S}}\tilde{\mathbf{C}}\boldsymbol{\rho}\tilde{\boldsymbol{\lambda}}\boldsymbol{\rho} - \boldsymbol{\rho}\tilde{\boldsymbol{\lambda}}\boldsymbol{\rho} \right) \tag{85}$$

It is convenient to rewrite Eq. (84) in a symmetric form in the C representation before introducing the density matrix. In order to do this, we differentiate Eq. (57) with respect to time

$$\boldsymbol{\rho}\dot{\tilde{\mathbf{C}}}^\dagger \tilde{\mathbf{S}}\tilde{\mathbf{C}}\boldsymbol{\rho} + \boldsymbol{\rho}\tilde{\mathbf{C}}^\dagger(\tilde{\mathbf{R}} + \tilde{\mathbf{R}}^\dagger)\tilde{\mathbf{C}}\boldsymbol{\rho} + \boldsymbol{\rho}\tilde{\mathbf{C}}^\dagger \tilde{\mathbf{S}}\dot{\tilde{\mathbf{C}}}\boldsymbol{\rho} = \mathbf{0} \tag{86}$$

with

$$\dot{\tilde{\mathbf{S}}} = \tilde{\mathbf{R}} + \tilde{\mathbf{R}}^\dagger \tag{87}$$

and write Eq. (84) as

$$-i\sum_I \langle \tilde{\phi}_I | \dot{\tilde{\phi}}_I \rangle \;\overset{\mathrm{Tr}}{=}\; -\tfrac{i}{2}\left(2\boldsymbol{\rho}\tilde{\mathbf{C}}^\dagger \tilde{\mathbf{R}}\tilde{\mathbf{C}}\boldsymbol{\rho} + \boldsymbol{\rho}\tilde{\mathbf{C}}^\dagger \tilde{\mathbf{S}}\dot{\tilde{\mathbf{C}}}\boldsymbol{\rho} + \boldsymbol{\rho}\tilde{\mathbf{C}}^\dagger \tilde{\mathbf{S}}\dot{\tilde{\mathbf{C}}}\boldsymbol{\rho} \right)$$

$$\overset{\mathrm{Tr}}{=} -\tfrac{i}{2}\left(2\boldsymbol{\rho}\tilde{\mathbf{C}}^\dagger \tilde{\mathbf{R}}\tilde{\mathbf{C}}\boldsymbol{\rho} + \boldsymbol{\rho}\tilde{\mathbf{C}}^\dagger \tilde{\mathbf{S}}\dot{\tilde{\mathbf{C}}}\boldsymbol{\rho} - \boldsymbol{\rho}\dot{\tilde{\mathbf{C}}}^\dagger \tilde{\mathbf{S}}\tilde{\mathbf{C}} - \boldsymbol{\rho}\tilde{\mathbf{C}}^\dagger(\tilde{\mathbf{R}} + \tilde{\mathbf{R}}^\dagger)\tilde{\mathbf{C}}\boldsymbol{\rho} \right)$$

$$\overset{\mathrm{Tr}}{=} -\tfrac{i}{2}\left(\boldsymbol{\rho}\tilde{\mathbf{C}}^\dagger \tilde{\mathbf{T}}\tilde{\mathbf{C}}\boldsymbol{\rho} + \boldsymbol{\rho}\tilde{\mathbf{C}}^\dagger \tilde{\mathbf{S}}\dot{\tilde{\mathbf{C}}}\boldsymbol{\rho} - \boldsymbol{\rho}\dot{\tilde{\mathbf{C}}}^\dagger \tilde{\mathbf{S}}\tilde{\mathbf{C}}\boldsymbol{\rho} \right) \tag{88}$$

where the anti-Hermitian matrix $\tilde{\mathbf{T}}$

$$\tilde{\mathbf{T}} = \tilde{\mathbf{R}} - \tilde{\mathbf{R}}^\dagger \tag{89}$$

has been introduced. Due to the fact that $-i\langle \widetilde{KS} | \frac{\partial}{\partial t} | \widetilde{KS} \rangle = -i\sum_I \langle \tilde{\phi}_I | \dot{\tilde{\phi}}_I \rangle$ is real, in accordance with the properties of exact theory, see Eq. (27), the right-hand side of Eq. (88) is Hermitian.

After these manipulations, we can evaluate the perturbation-strength derivative of the time derivative and multiplier terms of Eq. (76)

$$\frac{\partial}{\partial \varepsilon_a}\left(-i\sum_I \langle \tilde{\phi}_I | \dot{\tilde{\phi}}_I \rangle - \sum_{IJ} \tilde{\lambda}_{JI}(\langle \tilde{\phi}_I | \tilde{\phi}_J \rangle - \delta_{IJ}) \right)$$

$$\overset{\mathrm{Tr}}{=} \frac{\partial}{\partial \varepsilon_a}\left(-\tfrac{i}{2}\left(\boldsymbol{\rho}\tilde{\mathbf{C}}^\dagger \tilde{\mathbf{T}}\tilde{\mathbf{C}}\boldsymbol{\rho} + \boldsymbol{\rho}\tilde{\mathbf{C}}^\dagger \tilde{\mathbf{S}}\dot{\tilde{\mathbf{C}}}\boldsymbol{\rho} - \boldsymbol{\rho}\dot{\tilde{\mathbf{C}}}^\dagger \tilde{\mathbf{S}}\tilde{\mathbf{C}}\boldsymbol{\rho} \right) - \left(\tilde{\mathbf{C}}^\dagger \tilde{\mathbf{S}}\tilde{\mathbf{C}}\boldsymbol{\rho}\tilde{\boldsymbol{\lambda}}\boldsymbol{\rho} - \boldsymbol{\rho}\tilde{\boldsymbol{\lambda}}\boldsymbol{\rho} \right) \right)$$

$$\overset{\mathrm{Tr}}{=} -\tfrac{i}{2}\tilde{\mathbf{T}}^a \tilde{\mathbf{D}} - \tilde{\mathbf{S}}^a \tilde{\mathbf{W}} \tag{90}$$

where we have introduced the Hermitian matrix $\tilde{\mathbf{W}}$

$$\tilde{\mathbf{W}} = \tfrac{i}{2}\dot{\tilde{\mathbf{C}}}\boldsymbol{\rho}\tilde{\mathbf{C}}^\dagger - \tfrac{i}{2}\tilde{\mathbf{C}}\boldsymbol{\rho}\dot{\tilde{\mathbf{C}}}^\dagger + \tilde{\mathbf{C}}\boldsymbol{\rho}\tilde{\boldsymbol{\lambda}}\boldsymbol{\rho}\tilde{\mathbf{C}}^\dagger$$
$$= \tfrac{1}{2}\left(i\dot{\tilde{\mathbf{C}}}\boldsymbol{\rho}\tilde{\mathbf{C}}^\dagger + \tilde{\mathbf{C}}\boldsymbol{\rho}\tilde{\boldsymbol{\lambda}}\boldsymbol{\rho}\tilde{\mathbf{C}}^\dagger \right) + \tfrac{1}{2}\left(i\dot{\tilde{\mathbf{C}}}\boldsymbol{\rho}\tilde{\mathbf{C}}^\dagger + \tilde{\mathbf{C}}\boldsymbol{\rho}\tilde{\boldsymbol{\lambda}}\boldsymbol{\rho}\tilde{\mathbf{C}}^\dagger \right)^\dagger \tag{91}$$

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To obtain Eq. (90) we have used the definition of the density matrix, Eq. (71), and the idempotency relation for the $\boldsymbol{\rho}$ matrix in Eq. (41).

We now have to rewrite the second term in Eq. (90) in terms of the density matrix. Using Eqs. (57), (58), and (72), we can express the terms in the first parenthesis of Eq. (91) as

$$
\begin{aligned}
i\dot{\tilde{\mathbf{C}}}\boldsymbol{\rho}\tilde{\mathbf{C}}^{\dagger} + \tilde{\mathbf{C}}\boldsymbol{\rho}\tilde{\boldsymbol{\lambda}}\boldsymbol{\rho}\tilde{\mathbf{C}}^{\dagger} &= i\dot{\tilde{\mathbf{C}}}\boldsymbol{\rho}\tilde{\mathbf{C}}^{\dagger} + \tilde{\mathbf{C}}\boldsymbol{\rho}\tilde{\mathbf{C}}^{\dagger}(\tilde{\mathbf{S}}\tilde{\mathbf{C}}\boldsymbol{\rho}\tilde{\boldsymbol{\lambda}}\boldsymbol{\rho})\tilde{\mathbf{C}}^{\dagger} \\
&= i\dot{\tilde{\mathbf{C}}}\boldsymbol{\rho}\tilde{\mathbf{C}}^{\dagger} + \tilde{\mathbf{C}}\boldsymbol{\rho}\tilde{\mathbf{C}}^{\dagger}\big[(\tilde{\mathbf{F}} - i\tilde{\mathbf{R}})\tilde{\mathbf{C}}\boldsymbol{\rho} - i\tilde{\mathbf{S}}\dot{\tilde{\mathbf{C}}}\boldsymbol{\rho}\big]\tilde{\mathbf{C}}^{\dagger} \\
&= \tilde{\mathbf{D}}(\tilde{\mathbf{F}} - i\tilde{\mathbf{R}})\tilde{\mathbf{D}} + i(1 - \tilde{\mathbf{C}}\boldsymbol{\rho}\tilde{\mathbf{C}}^{\dagger}\tilde{\mathbf{S}})\dot{\tilde{\mathbf{C}}}\boldsymbol{\rho}\tilde{\mathbf{C}}^{\dagger} \\
&= \tilde{\mathbf{D}}(\tilde{\mathbf{F}} - i\tilde{\mathbf{R}})\tilde{\mathbf{D}} + i(1 - \tilde{\mathbf{C}}\boldsymbol{\rho}\tilde{\mathbf{C}}^{\dagger}\tilde{\mathbf{S}})(\dot{\tilde{\mathbf{D}}} - \tilde{\mathbf{C}}\boldsymbol{\rho}\dot{\tilde{\mathbf{C}}}^{\dagger}) \\
&= \tilde{\mathbf{D}}(\tilde{\mathbf{F}} - i\tilde{\mathbf{R}})\tilde{\mathbf{D}} + i\dot{\tilde{\mathbf{D}}} - i\tilde{\mathbf{D}}\tilde{\mathbf{S}}\dot{\tilde{\mathbf{D}}} + i\big[\tilde{\mathbf{C}}(\boldsymbol{\rho}\tilde{\mathbf{C}}^{\dagger}\tilde{\mathbf{S}}\tilde{\mathbf{C}}\boldsymbol{\rho})\dot{\tilde{\mathbf{C}}}^{\dagger} - \tilde{\mathbf{C}}\boldsymbol{\rho}\dot{\tilde{\mathbf{C}}}^{\dagger}\big] \\
&= \tilde{\mathbf{D}}(\tilde{\mathbf{F}} - i\tilde{\mathbf{R}})\tilde{\mathbf{D}} + i\dot{\tilde{\mathbf{D}}} - i\tilde{\mathbf{D}}\tilde{\mathbf{S}}\dot{\tilde{\mathbf{D}}}
\end{aligned}
\tag{92}
$$

The $\tilde{\mathbf{W}}$ matrix may then be expressed in terms of $\tilde{\mathbf{D}}$

$$
\begin{aligned}
\tilde{\mathbf{W}} &= \tfrac{1}{2}\big(\tilde{\mathbf{D}}(\tilde{\mathbf{F}} - i\tilde{\mathbf{R}})\tilde{\mathbf{D}} + i\dot{\tilde{\mathbf{D}}} - i\tilde{\mathbf{D}}\tilde{\mathbf{S}}\dot{\tilde{\mathbf{D}}}\big) + \tfrac{1}{2}\big(\tilde{\mathbf{D}}(\tilde{\mathbf{F}} - i\tilde{\mathbf{R}})\tilde{\mathbf{D}} + i\dot{\tilde{\mathbf{D}}} - i\tilde{\mathbf{D}}\tilde{\mathbf{S}}\dot{\tilde{\mathbf{D}}}\big)^{\dagger} \\
&= \tilde{\mathbf{D}}\big(\tilde{\mathbf{F}} - \tfrac{i}{2}\tilde{\mathbf{T}}\big)\tilde{\mathbf{D}} + \tfrac{i}{2}\big(\dot{\tilde{\mathbf{D}}}\tilde{\mathbf{S}}\tilde{\mathbf{D}} - \tilde{\mathbf{D}}\tilde{\mathbf{S}}\dot{\tilde{\mathbf{D}}}\big)
\end{aligned}
\tag{93}
$$

Introducing a generalized KS matrix $\tilde{\boldsymbol{\mathcal{F}}}$

$$
\tilde{\boldsymbol{\mathcal{F}}} = \tilde{\mathbf{F}} - \tfrac{i}{2}\tilde{\mathbf{T}} = \tilde{\mathbf{h}} + \tilde{\mathbf{G}}^{\gamma}(\tilde{\mathbf{D}}) + \tilde{\mathbf{V}}^{t} + \tilde{\mathbf{F}}_{xc} - \tfrac{i}{2}\tilde{\mathbf{T}}
\tag{94}
$$

where we have inserted Eq. (59), we may write $\tilde{\mathbf{W}}$ as

$$
\tilde{\mathbf{W}} = \tilde{\mathbf{D}}\tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}} + \tfrac{i}{2}\big(\dot{\tilde{\mathbf{D}}}\tilde{\mathbf{S}}\tilde{\mathbf{D}} - \tilde{\mathbf{D}}\tilde{\mathbf{S}}\dot{\tilde{\mathbf{D}}}\big)
\tag{95}
$$

By inserting Eqs. (81) and (90) into Eq. (76), the perturbation-strength derivative of the time-averaged quasienergy Lagrangian matrix in the C representation can be expressed in terms of the density matrix as

$$
\begin{aligned}
\{\tilde{L}^{a}(\tilde{\mathbf{D}},t)\}_{T} &= \frac{\partial}{\partial\varepsilon_{a}}\bigg\{\tilde{E}(\tilde{\mathbf{D}},t) - i\sum_{I}\langle\tilde{\phi}_{I}|\dot{\tilde{\phi}}_{I}\rangle - \sum_{IJ}\tilde{\lambda}_{JI}(\langle\tilde{\phi}_{I}|\tilde{\phi}_{J}\rangle - \delta_{IJ})\bigg\}_{T} \\
&\overset{\{\mathrm{Tr}\}_{T}}{=} \big(\tilde{\mathbf{h}}^{a} + \tilde{\mathbf{V}}^{t,a} + \tfrac{1}{2}\tilde{\mathbf{G}}^{\gamma,a}(\tilde{\mathbf{D}}) + \tilde{\mathbf{F}}_{xc}^{\Omega a} - \tfrac{i}{2}\tilde{\mathbf{T}}^{a}\big)\tilde{\mathbf{D}} - \tilde{\mathbf{S}}^{a}\tilde{\mathbf{W}} + \tilde{h}_{nuc}^{a}
\end{aligned}
\tag{96}
$$

where $\overset{\{\mathrm{Tr}\}_{T}}{=}$ is a short-hand notation for tracing and time-averaging. $\{\tilde{L}^{a}(\tilde{\mathbf{D}},t)\}_{T}$ is not a Lagrangian function and will be referred to as *the quasienergy derivative in the D parameterization*. In order to obtain a compact expression for Eq. (96), we introduce the generalized KS energy $\tilde{\mathcal{E}}$ in analogy with Eq. (94)

$$
\begin{aligned}
\tilde{\mathcal{E}} &\overset{\{\mathrm{Tr}\}_{T}}{=} \tilde{E}(\tilde{\mathbf{D}},t) - \tfrac{i}{2}\tilde{\mathbf{T}}\tilde{\mathbf{D}} \\
&\overset{\{\mathrm{Tr}\}_{T}}{=} \big(\tilde{\mathbf{h}} + \tilde{\mathbf{V}}^{t} + \tfrac{1}{2}\tilde{\mathbf{G}}^{\gamma}(\tilde{\mathbf{D}}) - \tfrac{i}{2}\tilde{\mathbf{T}}\big)\tilde{\mathbf{D}} + \tilde{E}_{xc}[\tilde{\rho}(\tilde{\mathbf{D}})] + \tilde{h}_{nuc}
\end{aligned}
\tag{97}
$$

and write the time-averaged quasienergy derivative in the D parameterization as

$$
\tilde{L}^{a}(\tilde{\mathbf{D}},t) \overset{\{\mathrm{Tr}\}_{T}}{=} \tilde{\mathcal{E}}^{0,a} - \tilde{\mathbf{S}}^{a}\tilde{\mathbf{W}}
\tag{98}
$$

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We note the close relationship between Eq. (98) and the expression derived by Pulay for the molecular gradient [44]. The main difference lies in the generalization of the energy function $\tilde{\mathcal{E}}^{0,a}$ and the $\tilde{\mathbf{W}}$ matrix which is a generalization of the energy-weighted density matrix.

Response functions can now be obtained in the D representation by straightforward differentiation of $\{\tilde{L}^a(\tilde{\mathbf{D}}, t)\}_T$ with respect to the perturbation strengths, as follows from Eqs. (33)-(34)

$$\langle\langle A; B\rangle\rangle_{\omega_b} = \frac{d\{\tilde{L}^a(\tilde{\mathbf{D}}, t)\}_T}{d\varepsilon_b}\bigg|_{\{\varepsilon\}=0} = L^{ab} \ ; \qquad \omega_a = -\omega_b \tag{99}$$

$$\langle\langle A; B, C\rangle\rangle_{\omega_b,\omega_c} = \frac{d^2\{\tilde{L}^a(\tilde{\mathbf{D}}, t)\}_T}{d\varepsilon_b d\varepsilon_c}\bigg|_{\{\varepsilon\}=0} = L^{abc} \ ; \qquad \omega_a = -\omega_b - \omega_c \tag{100}$$

We note that for perturbation-*in*dependent basis sets, $\tilde{\mathbf{S}} = \mathbf{S}$, and Eq. (98) reduces to the simple expression

$$\tilde{L}^a(\tilde{\mathbf{D}}, t) \overset{\{\mathrm{Tr}\}_T}{=} \tilde{\mathbf{V}}^{t,a}\tilde{\mathbf{D}} + \tilde{h}_{nuc}^a \tag{101}$$

B. Time-dependent SCF equation for the density matrix

In order to introduce the $\tilde{\mathbf{D}}$ parameters into the variational conditions in Eqs. (57) and (58), we multiply Eq. (58) by $\tilde{\mathbf{C}}^\dagger\tilde{\mathbf{S}}$ from the right and take the adjoint of the resulting equation

$$(\tilde{\mathbf{F}} - i\tilde{\mathbf{R}})\tilde{\mathbf{D}}\tilde{\mathbf{S}} - i\tilde{\mathbf{S}}\dot{\tilde{\mathbf{C}}}\boldsymbol{\rho}\tilde{\mathbf{C}}^\dagger\tilde{\mathbf{S}} = \tilde{\mathbf{S}}\tilde{\mathbf{C}}\boldsymbol{\rho}\tilde{\boldsymbol{\lambda}}\boldsymbol{\rho}\tilde{\mathbf{C}}^\dagger\tilde{\mathbf{S}} \tag{102}$$

$$\tilde{\mathbf{S}}\tilde{\mathbf{D}}(\tilde{\mathbf{F}} + i\tilde{\mathbf{R}}^\dagger) + i\tilde{\mathbf{S}}\tilde{\mathbf{C}}\boldsymbol{\rho}\dot{\tilde{\mathbf{C}}}^\dagger\tilde{\mathbf{S}} = \tilde{\mathbf{S}}\tilde{\mathbf{C}}\boldsymbol{\rho}\tilde{\boldsymbol{\lambda}}\boldsymbol{\rho}\tilde{\mathbf{C}}^\dagger\tilde{\mathbf{S}} \tag{103}$$

Subtracting Eq. (103) from Eq. (102) and inserting Eq. (72) yields

$$(\tilde{\mathbf{F}} - i\tilde{\mathbf{R}})\tilde{\mathbf{D}}\tilde{\mathbf{S}} - \tilde{\mathbf{S}}\tilde{\mathbf{D}}(\tilde{\mathbf{F}} + i\tilde{\mathbf{R}}^\dagger) - i\tilde{\mathbf{S}}\dot{\tilde{\mathbf{D}}}\tilde{\mathbf{S}} = \mathbf{0} \tag{104}$$

By expressing $\tilde{\mathbf{R}}$ in terms of its Hermitian ($\dot{\tilde{\mathbf{S}}}$) and anti-Hermitian ($\tilde{\mathbf{T}}$) components

$$\tilde{\mathbf{R}} = \tfrac{1}{2}\big(\dot{\tilde{\mathbf{S}}} + \tilde{\mathbf{T}}\big) \tag{105}$$

and inserting Eq. (94), we may write Eq. (104) as

$$\big[\tilde{\mathcal{F}} - \tfrac{i}{2}\tilde{\mathbf{S}}\tfrac{d}{dt}\big]\tilde{\mathbf{D}}\tilde{\mathbf{S}} - \big[\tilde{\mathbf{S}}\tilde{\mathbf{D}}\tilde{\mathcal{F}} + \tfrac{i}{2}\big(\tfrac{d}{dt}\tilde{\mathbf{S}}\tilde{\mathbf{D}}\big)\tilde{\mathbf{S}}\big] = \mathbf{0} \tag{106}$$

Eq. (106) is the TDSCF equation for the density matrix. For time-independent basis sets where $\tilde{\mathbf{R}} = \mathbf{0}$, Eq. (106) was derived by Larsen *et al.* [13].

The $\tilde{D}$ parameters are constrained by the idempotency relation for the density matrix which is obtained by multiplying Eq. (57) by $\tilde{\mathbf{C}}$ from the left and $\tilde{\mathbf{C}}^\dagger$ from the right

$$\tilde{\mathbf{D}}\tilde{\mathbf{S}}\tilde{\mathbf{D}} = \tilde{\mathbf{D}} \tag{107}$$

Eqs. (106) and (107) determine the time evolution of the KS state and a valid density matrix must fulfill both equations. In the absence of the perturbation, Eq. (106) reduces to the zeroth-order KS variational conditions

$$\mathbf{FDS} = \mathbf{SDF} \tag{108}$$

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where $\mathbf{D}$ is the optimized density matrix for the unperturbed system, which satisfies the zeroth-order idempotency relation,

$$\mathbf{DSD} = \mathbf{D} \tag{109}$$

Response equations are obtained by differentiation of the TDSCF equation, Eq. (106), with respect to the perturbation strengths. In order to simplify formulas for response equations, it is convenient to introduce the operators $[\ldots]^{\oplus}$ and $[\ldots]^{\ominus}$ as twice the Hermitian and anti-Hermitian components of a matrix $\mathbf{M}$

$$\left[\mathbf{M}\right]^{\oplus} = \mathbf{M} + \mathbf{M}^{\dagger} \tag{110}$$

$$\left[\mathbf{M}\right]^{\ominus} = \mathbf{M} - \mathbf{M}^{\dagger} \tag{111}$$

where the adjungation operation is considered to act *before* any field strength differentiation, for instance

$$[\tilde{\boldsymbol{\mathcal{F}}}^{b}\tilde{\mathbf{D}}\tilde{\mathbf{S}}]^{\ominus} = \tilde{\boldsymbol{\mathcal{F}}}^{b}\tilde{\mathbf{D}}\tilde{\mathbf{S}} - \tilde{\mathbf{S}}\tilde{\mathbf{D}}\tilde{\boldsymbol{\mathcal{F}}}^{b} \tag{112}$$

even though $\tilde{\boldsymbol{\mathcal{F}}}^{b}$ for a complex perturbation strength ε_b is in general not Hermitian, see the discussion in Section IV C. This slightly complex definition allows us to differentiate inside the commutator brackets

$$\frac{d}{d\varepsilon_b}\left[\mathbf{MN}\ldots\right]^{\ominus} = \left[\frac{d}{d\varepsilon_b}(\mathbf{MN}\ldots)\right]^{\ominus} \tag{113}$$

Using the definition in Eq. (111), the TDSCF equation in Eq. (106) may be written compactly as

$$\left[\left(\tilde{\boldsymbol{\mathcal{F}}} - \tfrac{i}{2}\tilde{\mathbf{S}}\tfrac{d}{dt}\right)\tilde{\mathbf{D}}\tilde{\mathbf{S}}\right]^{\ominus} = \mathbf{0}, \tag{114}$$

We are now in a position to solve the TDSCF equation, Eq. (114), order by order, by introducing a perturbation expansion of the density matrix.

C. Perturbation expansion of the density matrix

In accordance with the wave function expansion in exact theory, Eq. (18), we expand the density matrix in orders of the perturbation strengths

$$\tilde{\mathbf{D}} = \mathbf{D} + \tilde{\mathbf{D}}^{(1)} + \tilde{\mathbf{D}}^{(2)} + \ldots \tag{115}$$

where $\mathbf{D}$ is the optimized zeroth-order density matrix. From Eqs. (22) and (23) it follows that the first- and second-order density matrices only contain sums of the frequencies included in V^t, see Eq. (16)

$$\tilde{\mathbf{D}}^{(1)} = \sum_{b} \exp(-i\omega_b t)\varepsilon_b \mathbf{D}_{\omega}^{b} \tag{116}$$

$$\tilde{\mathbf{D}}^{(2)} = \tfrac{1}{2}\sum_{bc} \exp\big(-i(\omega_b + \omega_b)t\big)\varepsilon_b\varepsilon_c \mathbf{D}_{\omega}^{bc} \tag{117}$$

where the subscript ω is used to denote a derivative in the frequency domain, *e.g.* $\mathbf{D}_{\omega}^{b}$, whereas the notation $\mathbf{D}^{b}$ refers to a derivative in the time domain

$$\mathbf{D}^{b} = \exp(-i\omega_b t)\mathbf{D}_{\omega}^{b} \tag{118}$$

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The n'th order density matrix $\tilde{\mathbf{D}}^{(n)}$ may in a similar manner be written as

$$
\begin{aligned}
\tilde{\mathbf{D}}^{(n)} &= \frac{1}{n!} \sum_{b_1,b_2,\ldots,b_n} \exp\big(-i(\omega_{b_1} + \omega_{b_2} + \ldots + \omega_{b_n})t\big)\varepsilon_{b_1}\varepsilon_{b_2}\ldots\varepsilon_{b_n}\mathbf{D}_\omega^{b_1 b_2 \ldots b_n} \\
&= \frac{1}{n!} \sum_{b_1,b_2,\ldots,b_n} \exp(-i\omega_{b_N}t)\varepsilon_{b_1}\varepsilon_{b_2}\ldots\varepsilon_{b_n}\mathbf{D}_\omega^{b_N}
\end{aligned}
\tag{119}
$$

where we have introduced the short-hand notations

$$
\omega_{b_N} = \sum_{i=1}^{n}\omega_{b_i} \tag{120}
$$

$$
\mathbf{D}_\omega^{b_N} = \mathbf{D}_\omega^{b_1 b_2 \ldots b_n} \tag{121}
$$

As in Eq. (118), the time and frequency domains are related by the simple expression

$$
\mathbf{D}^{b_N} = \exp(-i\omega_{b_N}t)\mathbf{D}_\omega^{b_N} \tag{122}
$$

Note that even though $\tilde{\mathbf{D}}$ is itself Hermitian, its perturbation-strength derivatives, Eqs. (118) and (122), are *not* Hermitian due to the exponential phase factor which enters because complex perturbation strength parameters are used. However, as $\tilde{\mathbf{D}}$ is Hermitian to any order, the ω_b and ω_{-b} components are related by

$$
\mathbf{D}_\omega^{b_N\dagger} = \mathbf{D}_\omega^{-b_N} \tag{123}
$$

Differentiation of Eq. (119) with respect to time followed by differentiation with respect to the n perturbation strengths and evaluation at zero perturbation yields a simple expression for the time derivative $\dot{\mathbf{D}}^{b_1\ldots b_n}$

$$
\dot{\mathbf{D}}^{b_1\ldots b_n} = \frac{d}{d\varepsilon_{b_1}\ldots\varepsilon_{b_n}}\left(\frac{d\tilde{\mathbf{D}}}{dt}\right)\bigg|_{\{\varepsilon\}=0} = -i\omega_{b_N}\exp(-i\omega_{b_N}t)\mathbf{D}_\omega^{b_N} = -i\omega_{b_N}\mathbf{D}^{b_N} \tag{124}
$$

In this subsection we have expanded the density matrix in orders of the perturbation strengths. However, any matrix or scalar quantity that is used to characterize the system, *e.g.* $\tilde{v}_{xc}$, $\tilde{\mathbf{S}}$ or any of the matrices in the generalized KS matrix $\tilde{\mathcal{F}}$, see Eq. (94), may be expanded in the same way as the density matrix.

We now proceed to evaluate the density matrix derivatives using the idempotency condition, Eq. (107), and the TDSCF equation for the density matrix, Eq. (114), to different orders.

D. Partitioning of the density matrix

By differentiating the idempotency relation in Eq. (107) with respect to ε_b and evaluating at zero perturbation strengths, we obtain

$$
\mathbf{D}_\omega^b\mathbf{S}\mathbf{D} + \mathbf{D}\mathbf{S}\mathbf{D}_\omega^b - \mathbf{D}_\omega^b = \mathbf{K}_\omega^{(0)} \tag{125}
$$

$$
\mathbf{K}_\omega^{(0)} = -(\mathbf{D}\mathbf{S}\mathbf{D})_{\omega,0}^b = -\mathbf{D}\mathbf{S}_\omega^b\mathbf{D} \tag{126}
$$

where we have used Eq. (118) and a similar expression for the overlap matrix derivative $\mathbf{S}^b$ to remove the $\exp(-i\omega_b t)$ factor common to all terms. In Eq. (125) we have collected

the first-order density matrix derivatives on the left-hand side of the equation, whereas the right-hand side only contains the zeroth-order density matrix $\mathbf{D}$. The notation $(\mathbf{DSD})_{\omega,m}^{bcd\ldots}$ generally denotes the terms in $(\mathbf{DSD})_{\omega}^{bcd\ldots}$ which contain density matrices up to order m.

Differentiating Eq. (107) n times with respect to the perturbation strengths $\varepsilon_{b_1}, \varepsilon_{b_2}, \ldots, \varepsilon_{b_n}$ gives an equation with a structure similar to that of Eq. (125)

$$\mathbf{D}_{\omega}^{b_N}\mathbf{SD} + \mathbf{DSD}_{\omega}^{b_N} - \mathbf{D}_{\omega}^{b_N} = \mathbf{K}_{\omega}^{(n-1)} \tag{127}$$

where

$$\mathbf{K}_{\omega}^{(n-1)} = -(\mathbf{DSD})_{\omega,n-1}^{b_N} \tag{128}$$

Introducing the $\mathbf{P}$ and $\mathbf{Q}$ projectors [43]

$$\mathbf{P} = \mathbf{DS} \tag{129}$$
$$\mathbf{Q} = \mathbf{1} - \mathbf{DS} = \mathbf{1} - \mathbf{P} \tag{130}$$

which project onto the occupied and virtual spaces, respectively, and which satisfy the relations

$$\mathbf{PP} = \mathbf{P} \tag{131}$$
$$\mathbf{QQ} = \mathbf{Q} \tag{132}$$
$$\mathbf{PQ} = \mathbf{0} \tag{133}$$

we may write Eq. (127) as

$$\mathbf{D}_{\omega}^{b_N}\mathbf{P}^{\dagger} - \mathbf{QD}_{\omega}^{b_N} = \mathbf{K}_{\omega}^{(n-1)} \tag{134}$$

To obtain Eqs. (131)–(133), we have used the idempotency relation for the optimized zeroth-order density matrix $\mathbf{D}$, Eq. (109).

In order to solve the differential equation in Eq. (134), we partition $\mathbf{D}_{\omega}^{b_N}$ as

$$\mathbf{D}_{\omega}^{b_N} = \mathbf{D}_{P}^{b_N} + \mathbf{D}_{H}^{b_N} \tag{135}$$

where $\mathbf{D}_{P}^{b_N}$ is a *particular* solution to Eq. (134)

$$\mathbf{D}_{P}^{b_N}\mathbf{P}^{\dagger} - \mathbf{QD}_{P}^{b_N} = \mathbf{K}_{\omega}^{(n-1)} \tag{136}$$

whereas $\mathbf{D}_{H}^{b_N}$ solves the *homogeneous* equation

$$\mathbf{D}_{H}^{b_N}\mathbf{P}^{\dagger} - \mathbf{QD}_{H}^{b_N} = \mathbf{0} \tag{137}$$

By applying the $\mathbf{P}$ and $\mathbf{Q}$ projectors to Eq. (136) and using Eqs. (131)–(133), we may separate the different components of $\mathbf{D}_{P}^{b_N}$

$$\mathbf{PD}_{P}^{b_N}\mathbf{P}^{\dagger} = \mathbf{PK}_{\omega}^{(n-1)}\mathbf{P}^{\dagger} \tag{138}$$
$$\mathbf{QD}_{P}^{b_N}\mathbf{Q}^{\dagger} = -\mathbf{QK}_{\omega}^{(n-1)}\mathbf{Q}^{\dagger} \tag{139}$$
$$\mathbf{0} = \mathbf{PK}_{\omega}^{(n-1)}\mathbf{Q}^{\dagger} \tag{140}$$
$$\mathbf{0} = \mathbf{QK}_{\omega}^{(n-1)}\mathbf{P}^{\dagger} \tag{141}$$

$\mathbf{D}_{P}^{b_N}$ only contains occupied–occupied and virtual–virtual components and may be evaluated from lower-order density matrices

$$\mathbf{D}_{P}^{b_N} = \mathbf{PD}_{P}^{b_N}\mathbf{P}^{\dagger} + \mathbf{QD}_{P}^{b_N}\mathbf{Q}^{\dagger} = \mathbf{PK}_{\omega}^{(n-1)}\mathbf{P}^{\dagger} - \mathbf{QK}_{\omega}^{(n-1)}\mathbf{Q}^{\dagger} \tag{142}$$

For $\mathbf{D}_H^{b_N}$, projection of the homogeneous equation Eq. (137) yields

$$\mathbf{P}\mathbf{D}_H^{b_N}\mathbf{P}^\dagger = \mathbf{0} \tag{143}$$

$$\mathbf{Q}\mathbf{D}_H^{b_N}\mathbf{Q}^\dagger = \mathbf{0} \tag{144}$$

whereas the $\mathbf{P}\mathbf{D}_H^{b_N}\mathbf{Q}^\dagger$ and $\mathbf{Q}\mathbf{D}_H^{b_N}\mathbf{P}^\dagger$ components are undetermined by Eq. (137). We may thus write $\mathbf{D}_H^{b_N}$ as

$$\mathbf{D}_H^{b_N} = \mathbf{P}\mathbf{D}_H^{b_N}\mathbf{Q}^\dagger + \mathbf{Q}\mathbf{D}_H^{b_N}\mathbf{P}^\dagger \tag{145}$$

Eqs. (137) and (145) are equivalent and satisfied by the following ansatz for $\mathbf{D}_H^{b_N}$

$$\mathbf{D}_H^{b_N} = \mathbf{P}\mathbf{X}^{b_N} - \mathbf{X}^{b_N}\mathbf{P}^\dagger = [\mathbf{D}, \mathbf{X}^{b_N}]_S \tag{146}$$

where we have introduced the S commutator

$$[\mathbf{A}, \mathbf{B}]_S = \mathbf{A}\mathbf{S}\mathbf{B} - \mathbf{B}\mathbf{S}\mathbf{A} \tag{147}$$

and the n'th order response parameters X^{b_N} which may be determined from the n'th order TDSCF equation, where lower-order density matrices and $\mathbf{D}_P^{b_N}$ are introduced, as discussed in the next subsection. Inserting $\mathbf{P} + \mathbf{Q} = \mathbf{1}$ in Eq. (146) we obtain

$$\begin{aligned}
\mathbf{D}_H^{b_N} &= \mathbf{P}\mathbf{X}^{b_N} - \mathbf{X}^{b_N}\mathbf{P}^\dagger \\
&= \mathbf{P}\big(\mathbf{P}\mathbf{X}^{b_N}\mathbf{P}^\dagger + \mathbf{Q}\mathbf{X}^{b_N}\mathbf{Q}^\dagger + \mathbf{P}\mathbf{X}^{b_N}\mathbf{Q}^\dagger + \mathbf{Q}\mathbf{X}^{b_N}\mathbf{P}^\dagger\big) \\
&\quad - \big(\mathbf{P}\mathbf{X}^{b_N}\mathbf{P}^\dagger + \mathbf{Q}\mathbf{X}^{b_N}\mathbf{Q}^\dagger + \mathbf{P}\mathbf{X}^{b_N}\mathbf{Q}^\dagger + \mathbf{Q}\mathbf{X}^{b_N}\mathbf{P}^\dagger\big)\mathbf{P}^\dagger \\
&= \mathbf{P}\mathbf{X}^{b_N}\mathbf{Q}^\dagger - \mathbf{Q}\mathbf{X}^{b_N}\mathbf{P}^\dagger
\end{aligned} \tag{148}$$

and we see that the $\mathbf{P}\mathbf{X}^{b_N}\mathbf{P}^\dagger$ and $\mathbf{Q}\mathbf{X}^{b_N}\mathbf{Q}^\dagger$ components of $\mathbf{X}^{b_N}$ are redundant. We may therefore require $\mathbf{X}^{b_N}$ to satisfy the projection relation

$$\mathbf{X}^{b_N} = \mathbf{P}\mathbf{X}^{b_N}\mathbf{Q}^\dagger + \mathbf{Q}\mathbf{X}^{b_N}\mathbf{P}^\dagger \tag{149}$$

thereby eliminating the redundant occupied-occupied and virtual-virtual components of the $\mathbf{X}^{b_N}$ matrix.

Eq. (146) represents the first term of a Baker-Campbell-Hausdorff expansion of the density matrix in an exponential parameterization (see Ref. [13]) and the projection relation for the $\mathbf{X}^{b_N}$ matrix in Eq. (149) is identical to the one used in Refs. [5, 13] to ensure a non-redundant parameterization of the density matrix.

In the next subsection we address the determination of the X^{b_N} response parameters from the n'th order TDSCF equation, Eq. (106). We will show that response parameters may be determined to arbitrary order in an iterative fashion from a set of linear response equations which all have the same form, and consequently may all be solved by the same linear equation solver.

E. Response equations for the X parameters

1. First-order response parameters $\mathbf{X}^b$

To determine the first-order response parameters $\mathbf{X}^b$, we differentiate the TDSCF equation for the density matrix, Eq. (114), with respect to the perturbation strength ε_b to obtain

$$\mathbf{0} = \left[\begin{array}{l} \big(\tilde{\boldsymbol{\mathcal{F}}}^b - \frac{i}{2}\tilde{\mathbf{S}}^b\frac{d}{dt}\big)(\tilde{\mathbf{D}}\tilde{\mathbf{S}}) \\ +\big(\tilde{\boldsymbol{\mathcal{F}}} - \frac{i}{2}\tilde{\mathbf{S}}\frac{d}{dt}\big)(\tilde{\mathbf{D}}\tilde{\mathbf{S}})^b \end{array}\right]^\ominus \tag{150}$$

Evaluation at zero perturbation strengths yields

$$\begin{aligned}
\mathbf{0} = {}& [\boldsymbol{\mathcal{F}}^b \mathbf{DS} + \mathbf{FD}^b \mathbf{S}]^\ominus - \omega_b \mathbf{SD}^b \mathbf{S} \\
& + [\mathbf{FDS}^b]^\ominus - \tfrac{1}{2}\omega_b [\mathbf{SDS}^b]^\oplus
\end{aligned} \tag{151}$$

where we have used Eq. (124) and collected the terms containing the density matrix derivative in the upper line of Eq. (151). Note that the second term in the lower line of Eq. (151) is written in terms of $[\ldots]^\oplus$ instead of $[\ldots]^\ominus$ since the $-i$ factor from Eq. (124) multiplies the $-\tfrac{i}{2}$ factor in Eq. (150) and thus affects the adjungation operations in Eqs. (110) and (111).

From Eq. (135) the differentiated density matrix in the frequency domain $\mathbf{D}^b_\omega$ is given by

$$\mathbf{D}^b_\omega = \mathbf{D}^b_P + \mathbf{D}^b_H \tag{152}$$

where it from Eq. (142) follows that

$$\mathbf{D}^b_P = \mathbf{P}\mathbf{K}^{(0)}_\omega \mathbf{P}^\dagger - \mathbf{Q}\mathbf{K}^{(0)}_\omega \mathbf{Q}^\dagger \tag{153}$$

with $\mathbf{K}^{(0)}_\omega$ given by Eq. (126). $\mathbf{D}^b_H$ is parameterized in terms of the first-order response matrix $\mathbf{X}^b$, Eq. (146)

$$\mathbf{D}^b_H = [\mathbf{D}, \mathbf{X}^b]_S \tag{154}$$

where $\mathbf{X}^b$ fulfills the projection relation in Eq. (149)

$$\mathbf{X}^b = \mathbf{P}\mathbf{X}^b \mathbf{Q}^\dagger + \mathbf{Q}\mathbf{X}^b \mathbf{P}^\dagger \tag{155}$$

From Eq. (94), the generalized differentiated KS matrix $\boldsymbol{\mathcal{F}}^b$ takes the form

$$\boldsymbol{\mathcal{F}}^b = \exp(-i\omega_b t)\boldsymbol{\mathcal{F}}^b_\omega \tag{156}$$
$$\boldsymbol{\mathcal{F}}^b_\omega = \mathbf{h}^b_\omega + \mathbf{G}^{\gamma,b}_\omega(\mathbf{D}) + \mathbf{G}^\gamma(\mathbf{D}^b_\omega) + \mathbf{B} + \mathbf{F}^b_{xc,\omega} - \tfrac{i}{2}\mathbf{T}^b_\omega \tag{157}$$

where we have renamed $\mathbf{V}^{t,b}_\omega$ to be consistent with the literature [9]

$$\mathbf{B} = \mathbf{V}^{t,b}_\omega \tag{158}$$

In Appendix A 1 b, it is shown that the perturbation-strength derivative of the functional derivative matrix may be written in the form, see Eq. (A25)

$$\mathbf{F}^b_{xc,\omega} = \mathbf{G}^{xc}\!\left(\mathbf{D}^b_H\right) + \breve{\mathbf{F}}^b_{xc,\omega} \tag{159}$$

where $\breve{\mathbf{F}}^b_{xc,\omega}$ in Eq. (A26) does not depend on the X^b parameters. For a general matrix $\mathbf{A}$, the notation $\breve{\mathbf{A}}^{b_N}$ denotes the total n'th order derivative $\mathbf{A}^{b_N}$, except for the terms containing n'th order response parameters X^{b_N}. Thus, the X^b parameters only enter through $\mathbf{G}^{xc}\!\left(\mathbf{D}^b_H\right)$, see Eq. (A24),

$$G^{xc}_{\mu\nu}(\mathbf{D}^b_H) = \sum_{\alpha\beta} (D^b_H)_{\beta\alpha} \int \Omega_{\mu\nu}(\mathbf{r})\left(\int \Omega_{\alpha\beta}(\mathbf{r}_1)\frac{\delta v_{xc}}{\delta\rho(\mathbf{r}_1)}d\mathbf{x}_1 \right)d\mathbf{x} \tag{160}$$

In order to isolate the X^b parameters, it is convenient to express the total generalized KS matrix derivative $\boldsymbol{\mathcal{F}}^b_\omega$ in Eq. (157) as

$$\boldsymbol{\mathcal{F}}^b_\omega = \mathbf{G}^{KS}\!\left(\mathbf{D}^b_H\right) + \breve{\boldsymbol{\mathcal{F}}}^b_\omega \tag{161}$$

where

$$\breve{\mathcal{F}}_\omega^b = \mathbf{h}_\omega^b + \mathbf{G}_\omega^{\gamma,b}(\mathbf{D}) + \mathbf{G}^\gamma(\mathbf{D}_P^b) + \mathbf{B} + \breve{\mathbf{F}}_{xc,\omega}^b - \tfrac{i}{2}\mathbf{T}_\omega^b \tag{162}$$

and the two-electron KS matrix $\mathbf{G}^{KS}$ is a sum of the $\mathbf{X}^b$-dependent terms

$$\mathbf{G}^{KS}(\mathbf{D}_H^b) = \mathbf{G}^\gamma(\mathbf{D}_H^b) + \mathbf{G}^{xc}(\mathbf{D}_H^b) \tag{163}$$

Using Eqs. (118), (124), (154), and (161), we may reorganize Eq. (151) such that all terms containing $\mathbf{X}^b$ only appear on the left-hand side of the equation

$$\mathbf{G}^{KS}([\mathbf{X}^b,\mathbf{D}]_S)\mathbf{DS} - \mathbf{SDG}^{KS}([\mathbf{X}^b,\mathbf{D}]_S)$$
$$+\mathbf{F}[\mathbf{X}^b,\mathbf{D}]_S\mathbf{S} - \mathbf{S}[\mathbf{X}^b,\mathbf{D}]_S\mathbf{F} - \omega_b\mathbf{S}[\mathbf{X}^b,\mathbf{D}]_S\mathbf{S} = \mathbf{M}_{RHS}^b \tag{164}$$

whereas the right-hand side $\mathbf{M}_{RHS}^b$

$$\mathbf{M}_{RHS}^b = \left[\breve{\mathcal{F}}_\omega^b\mathbf{DS} + \mathbf{FD}_P^b\mathbf{S} + \mathbf{FDS}_\omega^b\right]^\ominus$$
$$- \tfrac{1}{2}\omega_b\left[\mathbf{SD}_P^b\mathbf{S} + \mathbf{SDS}_\omega^b\right]^\oplus \tag{165}$$

only contains the density matrix to zeroth order. In Eq. (164) we have removed the $\exp(-i\omega_b t)$ factor common to all terms and inserted $\mathbf{D}_H^b$ from Eq. (154).

Eq. (164) constitutes a set of linear equations often referred to as the linear response equations [9, 13, 45]. In order to solve Eq. (164) in an efficient manner, an understanding of the underlying structure of the equations is needed. In Refs. [13, 45], generalized Hessian $\mathbf{E}^{[2]}$ and metric $\mathbf{S}^{[2]}$ matrices were introduced, and their transformations on $\mathbf{X}^b$ were found to be

$$\mathbf{E}^{[2]}\mathbf{X}^b = \mathbf{G}([\mathbf{X}^b,\mathbf{D}]_S)\mathbf{DS} - \mathbf{SDG}([\mathbf{X}^b,\mathbf{D}]_S) + \mathbf{F}[\mathbf{X}^b,\mathbf{D}]_S\mathbf{S} - \mathbf{S}[\mathbf{X}^b,\mathbf{D}]_S\mathbf{F} \tag{166}$$
$$\mathbf{S}^{[2]}\mathbf{X}^b = \mathbf{S}[\mathbf{X}^b,\mathbf{D}]_S\mathbf{S} \tag{167}$$

We may therefore write the linear response equation Eq. (164), in terms of $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$ as

$$(\mathbf{E}^{[2]} - \omega_b\mathbf{S}^{[2]})\mathbf{X}^b = \mathbf{M}_{RHS}^b \tag{168}$$

where both $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$ are Hermitian matrices and $\mathbf{E}^{[2]}$ is positive definite. Eq. (168) with $\mathbf{X}^b$ subject to the projection relation in Eq. (155) may be solved efficiently using the linearly scaling, density matrix-based response solver of Coriani *et al.* [5]. In this response solver, the pairing properties of $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$

$$(\mathbf{E}^{[2]}\mathbf{X}^b)^\dagger = \mathbf{E}^{[2]}\mathbf{X}^{b\dagger} \tag{169}$$
$$(\mathbf{S}^{[2]}\mathbf{X}^b)^\dagger = -\mathbf{S}^{[2]}\mathbf{X}^{b\dagger} \tag{170}$$

are used to add trial vectors in pairs to ensure that the response equations in the reduced space have the same structure as Eq. (168). We refer to Ref. [5] for more details.

2. Second-order response parameters $\mathbf{X}^{bc}$

To obtain an equation for the second-order $\mathbf{X}^{bc}$ parameters, we differentiate Eq. (114) with respect to ε_b and ε_c

$$\mathbf{0} = \begin{bmatrix} \left(\tilde{\mathcal{F}}^{bc} - \tfrac{i}{2}\tilde{\mathbf{S}}^{bc}\tfrac{d}{dt}\right)(\tilde{\mathbf{D}}\tilde{\mathbf{S}}) \\ +\left(\tilde{\mathcal{F}}^{b} - \tfrac{i}{2}\tilde{\mathbf{S}}^{b}\tfrac{d}{dt}\right)(\tilde{\mathbf{D}}\tilde{\mathbf{S}})^c \\ +\left(\tilde{\mathcal{F}}^{c} - \tfrac{i}{2}\tilde{\mathbf{S}}^{c}\tfrac{d}{dt}\right)(\tilde{\mathbf{D}}\tilde{\mathbf{S}})^b \\ +\left(\tilde{\mathcal{F}} - \tfrac{i}{2}\tilde{\mathbf{S}}\tfrac{d}{dt}\right)(\tilde{\mathbf{D}}\tilde{\mathbf{S}})^{bc} \end{bmatrix}^\ominus \tag{171}$$

and evaluate Eq. (171) at zero perturbation strengths using Eq. (124) to obtain

$$
\begin{aligned}
\mathbf{0} = {} & \left[\boldsymbol{\mathcal{F}}^{bc}\mathbf{DS} + \mathbf{FD}^{bc}\mathbf{S} \right]^{\ominus} - (\omega_b + \omega_c)\mathbf{SD}^{bc}\mathbf{S} \\
& + \left[\boldsymbol{\mathcal{F}}^{b}(\mathbf{DS})^{c} + \boldsymbol{\mathcal{F}}^{c}(\mathbf{DS})^{b} + \mathbf{F}(\mathbf{D}^{b}\mathbf{S}^{c} + \mathbf{D}^{c}\mathbf{S}^{b} + \mathbf{DS}^{bc}) \right]^{\ominus} \\
& - \tfrac{1}{2} \left[\begin{matrix} \omega_c \mathbf{S}^{b}(\mathbf{D}^{c}\mathbf{S} + \mathbf{DS}^{c}) + \omega_b \mathbf{S}^{c}(\mathbf{D}^{b}\mathbf{S} + \mathbf{DS}^{b}) \\ + (\omega_b + \omega_c)\mathbf{S}(\mathbf{D}^{b}\mathbf{S}^{c} + \mathbf{D}^{c}\mathbf{S}^{b} + \mathbf{DS}^{bc}) \end{matrix} \right]^{\oplus}
\end{aligned}
\tag{172}
$$

The second-order density matrix derivative is contained in the first and last lines of Eq. (171). We have collected the terms from these two lines containing the second-order density matrix derivative in the upper line of Eq. (172).

The total second-order perturbation-strength derivative of the density matrix in the frequency domain is, according to Eq. (135)

$$
\mathbf{D}^{bc}_{\omega} = \mathbf{D}^{bc}_{H} + \mathbf{D}^{bc}_{P}
\tag{173}
$$

$\mathbf{D}^{bc}_{P}$ only contains first-order derivatives of the density matrix and is given by, see Eq. (142)

$$
\mathbf{D}^{bc}_{P} = \mathbf{PK}^{(1)}_{\omega}\mathbf{P}^{\dagger} - \mathbf{QK}^{(1)}_{\omega}\mathbf{Q}^{\dagger}
\tag{174}
$$

where $\mathbf{K}^{(1)}_{\omega}$ is found from Eq. (128) with $n = 2$

$$
\mathbf{K}^{(1)}_{\omega} = -(\mathbf{DSD})^{bc}_{\omega,1} = -(\mathbf{DS})^{b}_{\omega}\mathbf{D}^{c}_{\omega} - (\mathbf{DS})^{c}_{\omega}\mathbf{D}^{b}_{\omega} - (\mathbf{D}^{b}_{\omega}\mathbf{S}^{c}_{\omega} + \mathbf{D}^{c}_{\omega}\mathbf{S}^{b}_{\omega} + \mathbf{DS}^{bc}_{\omega})\mathbf{D}
\tag{175}
$$

with

$$
(\mathbf{DS})^{b}_{\omega} = \mathbf{D}^{b}_{\omega}\mathbf{S} + \mathbf{DS}^{b}_{\omega}
\tag{176}
$$

In Eqs. (174) and (175), we see that $\mathbf{D}^{bc}_{P}$ only contains first-order derivatives of the total density matrix.

$\mathbf{D}^{bc}_{H}$, see Eq. (146), contains the second-order response parameters

$$
\mathbf{D}^{bc}_{H} = [\mathbf{D}, \mathbf{X}^{bc}]_{S}
\tag{177}
$$

with $\mathbf{X}^{bc}$ subject to the projection relation in Eq. (149)

$$
\mathbf{X}^{bc} = \mathbf{PX}^{bc}\mathbf{Q}^{\dagger} + \mathbf{QX}^{bc}\mathbf{P}^{\dagger}
\tag{178}
$$

We now proceed to isolate $\mathbf{D}^{bc}_{H}$ in $\boldsymbol{\mathcal{F}}^{bc}_{\omega}$. Differentiating Eq. (94) twice yields

$$
\boldsymbol{\mathcal{F}}^{bc}_{\omega} = \mathbf{h}^{bc}_{\omega} + \left(\mathbf{G}^{\gamma}(\mathbf{D}) \right)^{bc}_{\omega} + \mathbf{V}^{t,bc}_{\omega} + \mathbf{F}^{bc}_{xc,\omega} - \tfrac{i}{2}\mathbf{T}^{bc}_{\omega}
\tag{179}
$$

$\mathbf{D}^{bc}_{H}$ enters in the $\left(\mathbf{G}^{\gamma}(\mathbf{D}) \right)^{bc}_{\omega}$ and $\mathbf{F}^{bc}_{xc,\omega}$ terms. By expanding $\left(\mathbf{G}^{\gamma}(\mathbf{D}) \right)^{bc}_{\omega}$, we may isolate the one term containing $\mathbf{D}^{bc}_{H}$

$$
\left(\mathbf{G}^{\gamma}(\mathbf{D}) \right)^{bc}_{\omega} = \mathbf{G}^{\gamma}(\mathbf{D}^{bc}_{H}) + \breve{\mathbf{G}}^{\gamma,bc}_{\omega}
\tag{180}
$$

where $\breve{\mathbf{G}}^{\gamma,bc}_{\omega}$ only contains response parameters to first order

$$
\breve{\mathbf{G}}^{\gamma,bc} = \mathbf{G}^{\gamma,bc}_{\omega}(\mathbf{D}) + \mathbf{G}^{\gamma,b}_{\omega}(\mathbf{D}^{c}) + \mathbf{G}^{\gamma,c}_{\omega}(\mathbf{D}^{b}) + \mathbf{G}^{\gamma}(\mathbf{D}^{bc}_{P})
\tag{181}
$$

As shown in Appendix A 1 c, Eq. (A31), we may write $\mathbf{F}^{bc}_{xc,\omega}$ as

$$
\mathbf{F}^{bc}_{xc,\omega} = \mathbf{G}^{xc}(\mathbf{D}^{bc}_{H}) + \breve{\mathbf{F}}^{bc}_{xc,\omega}
\tag{182}
$$

where $\breve{\mathbf{F}}_{xc,\omega}^{bc}$ contains all terms which are of zeroth and first order in the response parameters. Thus, we may write the second-order KS matrix derivative in a form analogous to Eq. (161)

$$\boldsymbol{\mathcal{F}}_{\omega}^{bc} = \mathbf{G}^{KS}(\mathbf{D}_H^{bc}) + \breve{\boldsymbol{\mathcal{F}}}_{\omega}^{bc} \tag{183}$$

where

$$\breve{\boldsymbol{\mathcal{F}}}_{\omega}^{bc} = \mathbf{h}_{\omega}^{bc} + \breve{\mathbf{G}}_{\omega}^{\gamma,bc} + \mathbf{V}_{\omega}^{t,bc} + \breve{\mathbf{F}}_{xc,\omega}^{bc} - \tfrac{i}{2}\mathbf{T}_{\omega}^{bc} \tag{184}$$

and $\mathbf{G}^{KS}(\mathbf{D}_H^{bc})$ is given as in Eq. (163)

$$\mathbf{G}^{KS}(\mathbf{D}_H^{bc}) = \mathbf{G}^{\gamma}(\mathbf{D}_H^{bc}) + \mathbf{G}^{xc}(\mathbf{D}_H^{bc}) \tag{185}$$

The second-order response equation, Eq. (172), in the frequency domain may now be written as

$$\mathbf{G}^{KS}([\mathbf{X}^{bc},\mathbf{D}]_S)\mathbf{DS} - \mathbf{SDG}^{KS}([\mathbf{X}^{bc},\mathbf{D}]_S) +$$
$$\mathbf{F}[\mathbf{X}^{bc},\mathbf{D}]_S\mathbf{S} - \mathbf{S}[\mathbf{X}^{bc},\mathbf{D}]_S\mathbf{F} - (\omega_b + \omega_c)\mathbf{S}[\mathbf{X}^{bc},\mathbf{D}]_S\mathbf{S} = \mathbf{M}_{RHS}^{bc} \tag{186}$$

where

$$\begin{aligned}
\mathbf{M}_{RHS}^{bc} &= \begin{bmatrix} \breve{\boldsymbol{\mathcal{F}}}_{\omega}^{bc}\mathbf{DS} + \mathbf{FD}_P^{bc}\mathbf{S} + \boldsymbol{\mathcal{F}}_{\omega}^b(\mathbf{DS})_{\omega}^c + \boldsymbol{\mathcal{F}}_{\omega}^c(\mathbf{DS})_{\omega}^b \\ +\mathbf{F}(\mathbf{D}_{\omega}^b\mathbf{S}_{\omega}^c + \mathbf{D}_{\omega}^c\mathbf{S}_{\omega}^b + \mathbf{DS}_{\omega}^{bc}) \end{bmatrix}^{\ominus} \\
&\quad - \tfrac{1}{2}\begin{bmatrix} \omega_c\mathbf{S}_{\omega}^b(\mathbf{DS})_{\omega}^c + \omega_b\mathbf{S}_{\omega}^c(\mathbf{DS})_{\omega}^b \\ +(\omega_b + \omega_c)\big(\mathbf{D}_P^{bc} + \mathbf{S}(\mathbf{D}_{\omega}^b\mathbf{S}_{\omega}^c + \mathbf{D}_{\omega}^c\mathbf{S}_{\omega}^b + \mathbf{DS}_{\omega}^{bc})\big) \end{bmatrix}^{\oplus}
\end{aligned} \tag{187}$$

$\mathbf{M}_{RHS}^{bc}$ only contains response parameters to first order. Note that the computational effort is eased by the fact that the matrices needed to evaluate $\mathbf{D}_P^{bc}$ in Eq. (174) via the $\mathbf{K}_{\omega}^{(1)}$ matrix in Eq. (175), e.g. $(\mathbf{DS})_{\omega}^b$, are present in $\mathbf{M}_{RHS}^{bc}$. Similar simplifications arise for higher-order response equations.

We may write Eq. (186) in terms of the $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$ matrices in Eqs. (166) and (167)

$$\big(\mathbf{E}^{[2]} - (\omega_b + \omega_c)\mathbf{S}^{[2]}\big)\mathbf{X}^{bc} = \mathbf{M}_{RHS}^{bc} \tag{188}$$

The structure of Eq. (188) is analogous to the first-order response equation, Eq. (168), and may be solved using the same linear response solver [5]. Thus, to determine $\mathbf{X}^{bc}$ we need to solve the first-order equations for $\mathbf{X}^b$ and $\mathbf{X}^c$, Eq. (168), and the second-order equation for $\mathbf{X}^{bc}$, Eq. (188), with $\mathbf{X}^b$ and $\mathbf{X}^c$ substituted into $\mathbf{M}_{RHS}^{bc}$ in terms of $\mathbf{D}_{\omega}^b$ and $\mathbf{D}_{\omega}^c$, respectively.

3. Higher-order response parameters $\mathbf{X}^{b_N}$

The derivation of the equations that determine the higher-order response parameters $\mathbf{X}^{b_N}$ is analogous to the discussion of the second-order response parameters in the previous subsection. Differentiating the TDSCF equation with respect to the perturbation strengths $\varepsilon_{b_1}, \varepsilon_{b_2}, \ldots, \varepsilon_{b_n}$ yields an equation of the form

$$\mathbf{0} = \begin{bmatrix} \big(\tilde{\boldsymbol{\mathcal{F}}}^{b_N} - \tfrac{i}{2}\tilde{\mathbf{S}}^{b_N}\tfrac{d}{dt}\big)(\tilde{\mathbf{D}}\tilde{\mathbf{S}}) \\ +\ldots \\ +\big(\tilde{\boldsymbol{\mathcal{F}}} - \tfrac{i}{2}\tilde{\mathbf{S}}\tfrac{d}{dt}\big)(\tilde{\mathbf{D}}\tilde{\mathbf{S}})^{b_N} \end{bmatrix}^{\ominus} \tag{189}$$

where the middle terms contain mixed derivatives of the $\left(\tilde{\mathcal{F}} - \frac{i}{2}\tilde{\mathbf{S}}\frac{d}{dt}\right)$ and $\tilde{\mathbf{D}}\tilde{\mathbf{S}}$ terms. By evaluating Eq. (189) at zero perturbation strength, we may isolate the terms containing $\mathbf{D}^{b_N}$

$$0 = \left[(\mathcal{F}^{b_N}\mathbf{DS} + \mathbf{FD}^{b_N}\mathbf{S} - \omega_{b_N}\mathbf{SD}^{b_N}\mathbf{S}) \atop + \dots \right]^{\ominus} \tag{190}$$

The n'th order density matrix derivative in the frequency domain takes the form

$$\mathbf{D}_{\omega}^{b_N} = \mathbf{D}_P^{b_N} + \mathbf{D}_H^{b_N} \tag{191}$$

where $\mathbf{D}_P^{b_N}$ only contains $\mathbf{X}$ parameters up to order $n-1$, see Eq. (142), and $\mathbf{D}_H^{b_N}$ is given by Eq. (146)

$$\mathbf{D}_H^{b_N} = [\mathbf{D}, \mathbf{X}^{b_N}]_S \tag{192}$$

with $\mathbf{X}^{b_N}$ subject to the projection relation in Eq. (149). From the discussion in the previous section and iterative arguments, it follows that we may write the n'th order KS matrix derivative as

$$\mathcal{F}_{\omega}^{b_N} = \mathbf{G}^{KS}(\mathbf{D}_H^{b_N}) + \breve{\mathcal{F}}_{\omega}^{b_N} \tag{193}$$

where $\breve{\mathcal{F}}_{\omega}^{b_N}$ only contains response parameters to order $n-1$. Thus, we may write Eq. (190) as

$$\mathbf{G}^{KS}([\mathbf{X}^{b_N}, \mathbf{D}]_S)\mathbf{DS} - \mathbf{SDG}^{KS}([\mathbf{X}^{b_N}, \mathbf{D}]_S) +$$
$$\mathbf{F}[\mathbf{X}^{b_N}, \mathbf{D}]_S\mathbf{S} - \mathbf{S}[\mathbf{X}^{b_N}, \mathbf{D}]_S\mathbf{F} - \omega_{b_N}\mathbf{S}[\mathbf{X}^b, \mathbf{D}]_S\mathbf{S} = \mathbf{M}_{RHS}^{b_N} \tag{194}$$

or, in terms of the $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$ matrices in Eqs. (166) and (167) as

$$\left(\mathbf{E}^{[2]} - \omega_{b_N}\mathbf{S}^{[2]}\right)\mathbf{X}^{b_N} = \mathbf{M}_{RHS}^{b_N} \tag{195}$$

where $\mathbf{M}_{RHS}^{b_N}$ contains response parameters up to order $n-1$. The structure of Eq. (195) is analogous to the first- and second-order response equations, Eqs. (168) and (188), and may consequently be solved using the same linear solver [5].

The procedure for determining the n'th order response parameters can thus be summarized as follows:

(1) The $\mathbf{X}^{b_1}, \mathbf{X}^{b_2}, \dots, \mathbf{X}^{b_n}$ parameters are determined from the first-order response equation, Eq. (168).

(2) These first-order parameters are then substituted into Eq. (187) in order to solve Eq. (188) for the $\mathbf{X}^{b_1 b_2}, \mathbf{X}^{b_1 b_3}, \dots, \mathbf{X}^{b_{n-1} b_n}$ parameters.

(3) This iterative procedure is continued until all relevant $\mathbf{X}$ parameters below order n have been determined.

(4) By substituting lower-order response parameters into $\mathbf{M}_{RHS}^{b_N}$, Eq. (195) may be solved for the $\mathbf{X}^{b_N}$ matrix.

We emphasize that all response equations have the same form and therefore may be solved using the same linear solver [5]. We have thus set up a scheme for determining response parameters to arbitrary order by solving a set of response equations which are all of the same form. We note the symmetry of the response matrices,

$$\mathbf{X}^{bc} = \mathbf{X}^{cb} \tag{196}$$
$$\mathbf{X}^{bcd} = \mathbf{X}^{bdc} = \mathbf{X}^{cbd} = \mathbf{X}^{cdb} = \mathbf{X}^{dbc} = \mathbf{X}^{dcb} \tag{197}$$

and similarly for higher orders, which follows from the fact that the n'th order response equation is obtained by n'th order differentiation of the TDSCF equation, Eq. (114). This reduces the number of response equations that need to be solved in order to identify $\mathbf{X}^{b_N}$.

F.   Response functions using the $n+1$ rule

The quasienergy derivative L^a, Eq. (98), and its term-by-term higher derivatives evaluated at zero perturbations strengths are given by

$$L^a \overset{\{\mathrm{Tr}\}_T}{=} \mathcal{E}^{0,a} - \mathbf{S}^a\mathbf{W} \tag{198}$$

$$L^{ab} \overset{\{\mathrm{Tr}\}_T}{=} \mathcal{E}^{0,ab} + \boldsymbol{\mathcal{E}}^{1,a}\mathbf{D}^b - \mathbf{S}^{ab}\mathbf{W} - \mathbf{S}^a\mathbf{W}^b \tag{199}$$

$$\begin{aligned} L^{abc} \overset{\{\mathrm{Tr}\}_T}{=} \ & \mathcal{E}^{0,abc} + \boldsymbol{\mathcal{E}}^{1,ac}\mathbf{D}^b + \boldsymbol{\mathcal{E}}^{1,ab}\mathbf{D}^c + \boldsymbol{\mathcal{E}}^{2,a}(\mathbf{D}^b)\mathbf{D}^c \\ & + \ \boldsymbol{\mathcal{E}}^{1,a}\mathbf{D}^{bc} - \mathbf{S}^{abc}\mathbf{W} - \mathbf{S}^{ab}\mathbf{W}^c - \mathbf{S}^{ac}\mathbf{W}^b - \mathbf{S}^a\mathbf{W}^{bc} \end{aligned} \tag{200}$$

where we have introduced density matrix and perturbation-strength derivatives of the generalized KS energy, Eq. (97), as

$$\tilde{\mathcal{E}}^{0,ab} = \frac{\partial\tilde{\mathcal{E}}}{\partial\varepsilon_a\partial\varepsilon_b} \tag{201}$$

$$\boldsymbol{\tilde{\mathcal{E}}}^{1,a} = \frac{\partial\tilde{\mathcal{E}}}{\partial\varepsilon_a\partial\tilde{\mathbf{D}}^T} \tag{202}$$

In this notation, the first index in the superscript refers to density matrix differentiation whereas the second index denotes partial perturbation strength differentiation. We recall that the presence of a tilde (*e.g.* $\boldsymbol{\tilde{\mathcal{E}}}^{1,a}$) indicates that general perturbation strengths are used, whereas the absence of a tilde ($\boldsymbol{\mathcal{E}}^{1,a}$) represents evaluation at zero field strength. Also note that, from Eqs. (94) and (97)

$$\boldsymbol{\tilde{\mathcal{F}}} = \boldsymbol{\tilde{\mathcal{E}}}^1 = \frac{\partial\tilde{\mathcal{E}}}{\partial\tilde{\mathbf{D}}^T} \tag{203}$$

$$\frac{\partial\boldsymbol{\tilde{\mathcal{F}}}}{\partial\tilde{\boldsymbol{D}}^T} = \boldsymbol{\tilde{\mathcal{E}}}^2 = \frac{\partial\tilde{\mathcal{E}}}{\partial\tilde{\mathbf{D}}^T\partial\tilde{\mathbf{D}}^T} \tag{204}$$

We have here introduced the contracted $\boldsymbol{\tilde{\mathcal{E}}}^2(\mathbf{M})$ matrix

$$\tilde{\mathcal{E}}^2_{\mu\nu}(\mathbf{M}) = \sum_{\alpha\beta} M_{\beta\alpha}\tilde{\mathcal{E}}^2_{\mu\nu\alpha\beta} \tag{205}$$

Eqs. (198)-(200) express the evaluation of molecular properties in terms of the $n+1$ rule where perturbed density matrices to order n are required for evaluating molecular properties to order $n+1$. For instance, for evaluating L^{abc} we will need the first- and second-order density matrix derivatives, $\mathbf{D}^b$, $\mathbf{D}^c$, and $\mathbf{D}^{bc}$. No density matrix derivatives with respect to ε_a are present in Eqs. (198)–(200), as these terms were eliminated by applying the time-averaged Hellmann–Feynmann theorem in the derivation of Eq. (98) in Sec. IV A.

L^{ab} in Eq. (199) equals the linear response function $\langle\langle A; B\rangle\rangle_{\omega_b}$ in Eq. (99) when the frequency condition

$$\omega_a = -\omega_b \tag{206}$$

is satisfied. In this case the time-averaging in Eq. (199) becomes unnecessary as the exponential phase factors present in each term, $\exp(-i\omega_a t)\exp(-i\omega_b t)$, cancel. We then obtain the linear response function in the frequency domain as

$$\langle\langle A; B\rangle\rangle_{\omega_b} \overset{\mathrm{Tr}}{=} \mathcal{E}^{0,ab}_\omega + \boldsymbol{\mathcal{E}}^{1,a}_\omega\mathbf{D}^b_\omega - \mathbf{S}^{ab}_\omega\mathbf{W} - \mathbf{S}^a_\omega\mathbf{W}^b_\omega \tag{207}$$

$\mathcal{E}_\omega^{0,ab}$ is identified by taking the partial derivatives of Eq. (97) with respect to ε_a and ε_b

$$\mathcal{E}_\omega^{0,ab} \stackrel{\mathrm{Tr}}{=} \left(\mathbf{h}_\omega^{ab} + \mathbf{V}_\omega^{t,ab} + \tfrac{1}{2}\mathbf{G}_\omega^{\gamma,ab}(\mathbf{D}) - \tfrac{i}{2}\mathbf{T}_\omega^{ab}\right)\mathbf{D} + E_{xc,\omega}^{0,ab} + h_{nuc,\omega}^{ab} \tag{208}$$

The exchange-correlation contribution $E_{xc,\omega}^{0,ab}$ is discussed in Appendix A 2, see Eq. (A39).

The density matrix derivative of $\mathcal{E}^{0,a}$ may also be identified from Eq. (97),

$$\mathcal{E}_\omega^{1,a}\mathbf{D}_\omega^b \stackrel{\mathrm{Tr}}{=} \left.\frac{\partial\tilde{\mathcal{E}}}{\partial\varepsilon_a\partial\tilde{\mathbf{D}}^T}\right|_{\{\varepsilon\}=0}\mathbf{D}^b \stackrel{\mathrm{Tr}}{=} \left(\mathbf{h}_\omega^a + \mathbf{A} + \mathbf{G}_\omega^{\gamma,a}(\mathbf{D}) + \mathbf{F}_{xc,\omega}^{\Omega a} + \mathbf{E}_{xc,\omega}^{2,a}(\mathbf{D}) - \tfrac{i}{2}\mathbf{T}_\omega^a\right)\mathbf{D}_\omega^b \tag{209}$$

where the relation

$$\mathrm{Tr}\mathbf{G}^\gamma(\mathbf{N})\mathbf{M} = \mathrm{Tr}\mathbf{G}^\gamma(\mathbf{M})\mathbf{N} \tag{210}$$

which follows from Eq. (64), has been used and, as in Eq. (158), we have renamed

$$\mathbf{A} = \mathbf{V}_\omega^{t,a} \tag{211}$$

The exchange-correlation contributions to Eq. (209), $\mathbf{F}_{xc,\omega}^{\Omega a}$ and $\mathbf{E}_{xc,\omega}^{2,a}(\mathbf{D})$, are treated in Appendix A 2, see Eq. (A35).

From Eq. (95) we identify $\mathbf{W}$ and $\mathbf{W}_\omega^b$ as

$$\mathbf{W} = \mathbf{DFD} \tag{212}$$
$$\mathbf{W}_\omega^b = [\mathbf{D}_\omega^b\mathbf{FD}]^\oplus + \mathbf{D}\boldsymbol{\mathcal{F}}_\omega^b\mathbf{D} + \tfrac{1}{2}\omega_b[\mathbf{D}_\omega^b\mathbf{SD}]^\ominus \tag{213}$$

where we have used Eq. (124) and where $\boldsymbol{\mathcal{F}}_\omega^b$ is given by Eq. (157). For a perturbation-independent basis set, the linear response function simplifies to

$$\langle\langle A; B\rangle\rangle_{\omega_b} \stackrel{\mathrm{Tr}}{=} \mathbf{A}\mathbf{D}_H^b + h_{nuc,\omega}^{ab} \tag{214}$$

The quadratic response function $\langle\langle A; B, C\rangle\rangle_{\omega_b,\omega_c}$ is given by Eq. (200) for

$$\omega_a = -\omega_b - \omega_c \tag{215}$$

However, in order to minimize the number of response equations to be solved in order to determine the quadratic and higher-order response functions, it may be preferable to rewrite the derivatives of the quasienergy in forms that comply with the $2n+1$ rule, or in alternative forms that are intermediate between the $n+1$ and the $2n+1$ expressions. This is the focus of the next subsection.

G.   Response functions using the $2n+1$ and $2n+2$ rules and alternative rules

According to the $2n+1$-rule (Wigner's theorem) it is possible from a variationally determined quasienergy to evaluate molecular properties to order $2n+1$ from perturbed wave function parameters up to order n. Thus, if the quasienergy could be expressed in terms of the density matrix, the $2n+1$ rule could straightforwardly be applied and molecular properties to order $2n+1$ could be determined from density matrix derivatives to order n. However, as the quasienergy cannot be expressed in terms of the density matrix, but only the first derivative of the quasienergy Eq. (98), the $2n+1$ rule cannot be directly be applied. In the following we describe the modifications that are needed in a density matrix formulation to allow for the evaluation of molecular properties in accordance with the $2n+1$ rule.

In the $n+1$ formulation of response functions given in the previous subsection, molecular properties were determined from derivatives of the time-averaged quasienergy gradient $\{\tilde{L}^a\}_T$, Eq. (98), where the density matrix derivatives were determined from the TDSCF equation, Eq. (114), subject to the idempotency constraint given in Eq. (107). We may thus construct a variational Lagrangian function $\tilde{\mathcal{L}}^a$ by adding products of Lagrange multipliers with each equation satisfied by $\tilde{\mathbf{D}}$

$$\tilde{\mathcal{L}}^a = \tilde{\mathcal{L}}^a(\tilde{\mathbf{D}}, \tilde{\boldsymbol{\zeta}}_a, \tilde{\boldsymbol{\lambda}}_a) \stackrel{\{\mathrm{Tr}\}_T}{=} \tilde{L}^a(\tilde{\mathbf{D}}) - \tilde{\boldsymbol{\lambda}}_a\big[\tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}}\tilde{\mathbf{S}} - \tfrac{i}{2}\tilde{\mathbf{S}}(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}})\big]^{\ominus} - \tilde{\boldsymbol{\zeta}}_a(\tilde{\mathbf{D}}\tilde{\mathbf{S}}\tilde{\mathbf{D}} - \tilde{\mathbf{D}}) \tag{216}$$

where $\tilde{\boldsymbol{\lambda}}_a$ multiplies the TDSCF equation, Eq. (114), while $\tilde{\boldsymbol{\zeta}}_a$ multiplies the idempotency constraint, Eq. (107). Note that the Lagrangian multipliers $\tilde{\boldsymbol{\lambda}}_a$ and $\tilde{\boldsymbol{\zeta}}_a$ carry a *subscript* merely to denote their relation to $\tilde{\mathcal{L}}^a$ and are not derivatives. We also note that $\tilde{\mathcal{L}}^a$ carries a time-averaging, which is omitted for reasons of brevity.

The quasienergy derivative Lagrangian $\tilde{\mathcal{L}}^a$ is fully variational with respect to $\tilde{\mathbf{D}}$, $\tilde{\boldsymbol{\lambda}}_a$, and $\tilde{\boldsymbol{\zeta}}_a$. By construction, $\tilde{\mathcal{L}}^a$ therefore satisfies the $2n+1$ rule for the density matrix derivatives and the $2n+2$ rule for the multipliers [15, 16]. We emphasize that the $2n+1$ rule applies to the *density matrix derivatives* $\mathbf{D}^b$, $\mathbf{D}^{bc}$ etc., and *not* to the response matrices $\mathbf{X}^b$, $\mathbf{X}^{bc}$ etc., discussed in Section IV E.

Differentiation of Eq. (216) with respect to $\tilde{\boldsymbol{\lambda}}_a$ and $\tilde{\boldsymbol{\zeta}}_a$ trivially yields the TDSCF equation and the idempotency constraint

$$\big[\tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}}\tilde{\mathbf{S}} - \tfrac{i}{2}\tilde{\mathbf{S}}(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}})\big]^{\ominus} = \mathbf{0} \tag{217}$$

$$\tilde{\mathbf{D}}\tilde{\mathbf{S}}\tilde{\mathbf{D}} - \tilde{\mathbf{D}} = \mathbf{0} \tag{218}$$

For variations in $\tilde{\mathbf{D}}$

$$\frac{\partial}{\partial\tilde{\mathbf{D}}}\tilde{\mathcal{L}}^a = \mathbf{0} \tag{219}$$

we show in Appendix B that by making the following ansatz for $\tilde{\boldsymbol{\lambda}}_a$

$$\tilde{\boldsymbol{\lambda}}_a = \tilde{\mathbf{D}}^a\tilde{\mathbf{S}}\tilde{\mathbf{D}} - \tilde{\mathbf{D}}\tilde{\mathbf{S}}\tilde{\mathbf{D}}^a = [\tilde{\mathbf{D}}^a\tilde{\mathbf{S}}\tilde{\mathbf{D}}]^{\ominus} \tag{220}$$

where $\tilde{\mathbf{D}}^a$ satisfies the differentiated TDSCF and idempotency equations

$$\big[\tilde{\boldsymbol{\mathcal{F}}}^a\tilde{\mathbf{D}}\tilde{\mathbf{S}} + \tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}}^a\tilde{\mathbf{S}} - \tfrac{i}{2}\tilde{\mathbf{S}}(\tilde{\mathbf{D}}^a\dot{\tilde{\mathbf{S}}}) + \tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}}\tilde{\mathbf{S}}^a - \tfrac{i}{2}\tilde{\mathbf{S}}^a(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}) - \tfrac{i}{2}\tilde{\mathbf{S}}(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}^a)\big]^{\ominus} = \mathbf{0} \tag{221}$$

$$\tilde{\mathbf{D}}^a\tilde{\mathbf{S}}\tilde{\mathbf{D}} + \tilde{\mathbf{D}}\tilde{\mathbf{S}}^a\tilde{\mathbf{D}} + \tilde{\mathbf{D}}\tilde{\mathbf{S}}\tilde{\mathbf{D}}^a - \tilde{\mathbf{D}}^a = \mathbf{0} \tag{222}$$

we may rewrite Eq. (219) as

$$\mathbf{0} = \big[\big[\tilde{\boldsymbol{\mathcal{F}}}^a\tilde{\mathbf{D}}\tilde{\mathbf{S}} + \tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}}^a\tilde{\mathbf{S}} - \tfrac{i}{2}\tilde{\mathbf{S}}(\tilde{\mathbf{D}}^a\dot{\tilde{\mathbf{S}}}) + \tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}}\tilde{\mathbf{S}}^a - \tfrac{i}{2}\tilde{\mathbf{S}}^a(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}) - \tfrac{i}{2}\tilde{\mathbf{S}}(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}^a)\big]^{\ominus}\tilde{\mathbf{D}}\tilde{\mathbf{S}}\big]^{\oplus}$$
$$+ \big[\big(\big[\tilde{\boldsymbol{\mathcal{F}}}^a(\tilde{\mathbf{D}}\tilde{\mathbf{S}}-\tfrac{1}{2}) - (\tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}} - \tfrac{i}{2}\dot{\tilde{\mathbf{S}}}\tilde{\mathbf{D}} - i\tilde{\mathbf{S}}\dot{\tilde{\mathbf{D}}})\tilde{\mathbf{S}}^a\big]^{\oplus} - \tilde{\boldsymbol{\zeta}}_a\big)(\tilde{\mathbf{D}}\tilde{\mathbf{S}}-\tfrac{1}{2})\big]^{\oplus} \tag{223}$$

Using Eq. (221), it is seen that the upper line in Eq. (223) is zero, and $\tilde{\boldsymbol{\zeta}}_a$ may therefore be determined as

$$\tilde{\boldsymbol{\zeta}}_a = \big[\tilde{\boldsymbol{\mathcal{F}}}^a(\tilde{\mathbf{D}}\tilde{\mathbf{S}}-\tfrac{1}{2}) - (\tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}} - \tfrac{i}{2}\dot{\tilde{\mathbf{S}}}\tilde{\mathbf{D}} - i\tilde{\mathbf{S}}\dot{\tilde{\mathbf{D}}})\tilde{\mathbf{S}}^a\big]^{\oplus} \tag{224}$$

As $\tilde{\mathcal{L}}^a$ in Eq. (216) satisfies the $2n+1$ and $2n+2$ rules we may simply omit all terms that do not comply with the $2n+1$ rule for the perturbed density matrices and the $2n+2$ rule for

the multipliers in Eqs. (220) and (224) when evaluating the response functions,

$$\langle\langle A; B\rangle\rangle_{\omega_b} = \mathcal{L}^{ab} \; ; \qquad \omega_a = -\omega_b \tag{225}$$

$$\langle\langle A; B, C\rangle\rangle_{\omega_b,\omega_c} = \mathcal{L}^{abc} \; ; \qquad \omega_a = -\omega_b - \omega_c \tag{226}$$

$$\langle\langle A; B, C, D\rangle\rangle_{\omega_b,\omega_c,\omega_d} = \mathcal{L}^{abcd} \; ; \qquad \omega_a = -\omega_b - \omega_c - \omega_d \tag{227}$$

The $2n$+1 and $2n$+2 rules may be used for reducing the number of equations to be solved [46]. If, for instance, the perturbation strengths are vectorial entities (electric and magnetic fields), the determination of the quadratic response functions using the n+1 rule in Eq. (200) requires the solution of twelve response equations—3+3 equations for the $\mathbf{D}^b$ and $\mathbf{D}^c$ matrices and 3^2–3 equations (we subtract by three due to symmetry of the response matrices, see Eq. (196)) for the $\mathbf{D}^{bc}$ matrix. In contrast, by applying the $2n$+1 and $2n$+2 rules in Eq. (226), we only need to solve nine response equations—3 equations for $\mathbf{D}^a$ (to determine $\tilde{\boldsymbol{\lambda}}_a$ and $\tilde{\boldsymbol{\zeta}}_a$), and 3+3 equations to determine $\mathbf{D}^b$ and $\mathbf{D}^c$. For higher-order response functions, the use of the $2n$+1 and $2n$+2 rules is even more advantageous.

We recall, however, that if one of the applied perturbations has a significantly higher number of components than the other perturbations, as is for instance the case when considering geometrical distortions of the nuclei, nuclear magnetic moments, or electric-field gradients at the nuclei in large molecules, the n+1 rule will be the method of choice in order to avoid solving the $3N_{nuclei}$ response equations to determine $\mathbf{D}^a$ for these perturbations.

As discussed in Sec. IV A, we cannot express the quasienergy in terms of the density matrix, but only its perturbation-strength derivative. However, the above described $2n$+1 rule is in agreement with the one obtained for $\tilde{E}(\tilde{\mathbf{D}})$ in time-independent theory [16].

In the following subsection we consider property formulas that comply with the $2n$+1 and $2n$+2 rules, but also with the n+1 rule, and formulas that are intermediate between the n+1 and $2n$+1 formulas.

2. Property formulas

Formulas for higher-order properties can be obtained by differentiating $\tilde{\mathcal{L}}^a$ with respect to perturbation strengths, while keeping as many perturbed arguments $\tilde{\mathbf{D}}$, $\tilde{\boldsymbol{\lambda}}_a$, and $\tilde{\boldsymbol{\zeta}}_a$ as required by the $2n$+1 and $2n$+2 rules. Differentiating twice, evaluating at zero field strength, and keeping first-order perturbed arguments and zeroth-order multipliers ($\boldsymbol{\lambda}_a$ and $\boldsymbol{\zeta}_a$), we get a formula for a third-order property (the quadratic response function) which reads

$$\begin{aligned}
\mathcal{L}^{abc} \stackrel{\{\mathrm{Tr}\}_T}{=} & \; \boldsymbol{\mathcal{E}}^{0,abc} + \boldsymbol{\mathcal{E}}^{1,ac}\mathbf{D}^b + \boldsymbol{\mathcal{E}}^{1,ab}\mathbf{D}^c + \boldsymbol{\mathcal{E}}^{2,a}(\mathbf{D}^b)\mathbf{D}^c \\
& - \; \mathbf{S}^{abc}\mathbf{W} - \mathbf{S}^{ac}\mathbf{W}^b - \mathbf{S}^{ab}\mathbf{W}^c - \mathbf{S}^a\mathbf{W}_1^{bc} \\
& - \; \boldsymbol{\lambda}_a\mathbf{Y}_1^{bc} - \boldsymbol{\zeta}_a\mathbf{Z}_1^{bc}
\end{aligned} \tag{228}$$

where we have introduced the "TDSCF equation matrix"

$$\tilde{\mathbf{Y}} = [(\tilde{\mathbf{F}} - \tfrac{i}{2}\tilde{\mathbf{S}}\tfrac{d}{dt})\tilde{\mathbf{D}}\tilde{\mathbf{S}}]^{\ominus} \tag{229}$$

and "idempotency constraint matrix"

$$\tilde{\mathbf{Z}} = \tilde{\mathbf{D}}\tilde{\mathbf{S}}\tilde{\mathbf{D}} - \tilde{\mathbf{D}} \tag{230}$$

The first-order perturbed multipliers are not needed because of the $2n$+2 rule for the Lagrange multipliers. The "1" subscript on the matrices $\mathbf{W}_1^{bc}$, $\mathbf{Y}_1^{bc}$, and $\mathbf{Z}_1^{bc}$ in Eq. (228) indicates that

they only contain contributions with up to first-order perturbed density matrices, and we thus miss the terms with $\mathbf{D}^{bc}$ since they are not needed due to the $2n+1$ rule

$$
\begin{aligned}
\mathbf{W}_1^{bc} &= \left[\mathbf{D}^b\boldsymbol{\mathcal{F}}^c\mathbf{D} + \mathbf{D}^b\mathbf{F}\mathbf{D}^c + \mathbf{D}^c\boldsymbol{\mathcal{F}}^b\mathbf{D}\right]^\oplus + \mathbf{D}\boldsymbol{\mathcal{F}}_1^{bc}\mathbf{D} \\
&+ \tfrac{1}{2}\left[\omega_b(\mathbf{D}^b\mathbf{S}^c\mathbf{D} + \mathbf{D}^b\mathbf{S}\mathbf{D}^c) + \omega_c(\mathbf{D}^c\mathbf{S}^b\mathbf{D} + \mathbf{D}^c\mathbf{S}\mathbf{D}^b)\right]^\ominus
\end{aligned}
\tag{231}
$$

$$
\begin{aligned}
\mathbf{Y}_1^{bc} &= \left[\begin{array}{c}\boldsymbol{\mathcal{F}}_1^{bc}\mathbf{D}\mathbf{S} + \boldsymbol{\mathcal{F}}^b(\mathbf{D}^c\mathbf{S} + \mathbf{D}\mathbf{S}^c) + \boldsymbol{\mathcal{F}}^c(\mathbf{D}^b\mathbf{S} + \mathbf{D}\mathbf{S}^b) \\ +\mathbf{F}(\mathbf{D}^b\mathbf{S}^c + \mathbf{D}^c\mathbf{S}^b + \mathbf{D}\mathbf{S}^{bc})\end{array}\right]^\ominus \\
&- \tfrac{1}{2}\left[\begin{array}{c}\omega_b\mathbf{S}^c(\mathbf{D}^b\mathbf{S} + \mathbf{D}\mathbf{S}^b) + \omega_c\mathbf{S}^b(\mathbf{D}^c\mathbf{S} + \mathbf{D}\mathbf{S}^c) \\ +(\omega_b+\omega_c)\mathbf{S}(\mathbf{D}^b\mathbf{S}^c + \mathbf{D}^c\mathbf{S}^b + \mathbf{D}\mathbf{S}^{bc})\end{array}\right]^\oplus
\end{aligned}
\tag{232}
$$

$$
\mathbf{Z}_1^{bc} = \left[\mathbf{D}^b\mathbf{S}^c\mathbf{D} + \mathbf{D}^b\mathbf{S}\mathbf{D}^c + \mathbf{D}^c\mathbf{S}^b\mathbf{D}\right]^\oplus + \mathbf{D}\mathbf{S}^{bc}\mathbf{D}
\tag{233}
$$

where we have used Eqs. (95) and (124) to obtain Eq. (231). We have in the above equations introduced a second-order KS matrix derivative, $\boldsymbol{\mathcal{F}}_1^{bc}$, containing only up to first-order density matrices

$$
\boldsymbol{\mathcal{F}}_1^{bc} = \boldsymbol{\mathcal{E}}^{1,bc} + \boldsymbol{\mathcal{E}}^{2,c}(\mathbf{D}^b) + \boldsymbol{\mathcal{E}}^{2,b}(\mathbf{D}^c) + \boldsymbol{\mathcal{E}}^3(\mathbf{D}^b, \mathbf{D}^c)
\tag{234}
$$

We will denote the formula given by Eq. (228) by $\mathcal{L}_{1,1}^{abc}$, since it involves first-order density matrices with respect to ε_a (the first index) as $\mathbf{D}^a$ appears in $\boldsymbol{\lambda}_a$ and $\boldsymbol{\zeta}_a$, see Eqs. (220) and (224), and first-order with respect to $\varepsilon_b, \varepsilon_c$ differentiation (the second index) as $\mathbf{D}^b$ and $\mathbf{D}^c$ but *not* $\mathbf{D}^{bc}$ enter

$$
\begin{aligned}
\mathcal{L}_{1,1}^{abc} \overset{\{\text{Tr}\}_T}{=} \ & (\boldsymbol{\mathcal{E}}^{0,a})_1^{bc} - \mathbf{S}^{abc}\mathbf{W} - \mathbf{S}^{ac}\mathbf{W}^b - \mathbf{S}^{ab}\mathbf{W}^c \\
&- \mathbf{S}^a\mathbf{W}_1^{bc} - \boldsymbol{\lambda}_a\mathbf{Y}_1^{bc} - \boldsymbol{\zeta}_a\mathbf{Z}_1^{bc}
\end{aligned}
\tag{235}
$$

where

$$
(\boldsymbol{\mathcal{E}}^{0,a})_1^{bc} = \boldsymbol{\mathcal{E}}^{0,abc} + \boldsymbol{\mathcal{E}}^{1,ac}\mathbf{D}^b + \boldsymbol{\mathcal{E}}^{1,ab}\mathbf{D}^c + \boldsymbol{\mathcal{E}}^{2,a}(\mathbf{D}^b)\mathbf{D}^c
\tag{236}
$$

$\mathcal{L}_{0,2}^{abc}$ denotes the quasienergy derivative Lagrangian which is obtained by differentiating Eq. (216) twice, but *keeping* the second-order arguments. Thus, $\mathcal{L}_{0,2}^{abc}$ is in accordance with the $n+1$ rule and may analogously be derived by differentiating $\tilde{L}^a$ in Eq. (98) twice

$$
\mathcal{L}_{0,2}^{abc} = L^{abc} \overset{\{\text{Tr}\}_T}{=} (\boldsymbol{\mathcal{E}}^{0,a})^{bc} - \mathbf{S}^{abc}\mathbf{W} - \mathbf{S}^{ac}\mathbf{W}^b - \mathbf{S}^{ab}\mathbf{W}^c - \mathbf{S}^a\mathbf{W}^{bc}
\tag{237}
$$

Similarly, we always have for the higher-order derivatives that

$$
\mathcal{L}_{0,n}^{ab_1...b_{n-1}} = \{L^{ab_1...b_{n-1}}\}_T
\tag{238}
$$

A formula for $\mathcal{L}_{2,1}^{abcd}$ (the cubic response function) is obtained by differentiating $\tilde{\mathcal{L}}^a$ in Eq. (216) three times, and keeping up to first-order density matrices and first-order multipliers in accordance with the $2n+1$ and $2n+2$ rules

$$
\begin{aligned}
\mathcal{L}_{2,1}^{abcd} \overset{\{\text{Tr}\}_T}{=} \ & (\boldsymbol{\mathcal{E}}^{0,a})_1^{bcd} - \mathbf{S}^{abcd}\mathbf{W} - \mathbf{S}^{acd}\mathbf{W}^b - \mathbf{S}^{abd}\mathbf{W}^c - \mathbf{S}^{abc}\mathbf{W}^d \\
&- \mathbf{S}^{ad}\mathbf{W}_1^{bc} - \mathbf{S}^{ac}\mathbf{W}_1^{bd} - \mathbf{S}^{ab}\mathbf{W}_1^{cd} - \mathbf{S}^a\mathbf{W}_1^{bcd} \\
&- \boldsymbol{\lambda}_a^d\mathbf{Y}_1^{bc} - \boldsymbol{\lambda}_a^c\mathbf{Y}_1^{bd} - \boldsymbol{\lambda}_a^b\mathbf{Y}_1^{cd} - \boldsymbol{\lambda}_a\mathbf{Y}_1^{bcd} \\
&- \boldsymbol{\zeta}_a^d\mathbf{Z}_1^{bc} - \boldsymbol{\zeta}_a^c\mathbf{Z}_1^{bd} - \boldsymbol{\zeta}_1^b\mathbf{Z}_1^{cd} - \boldsymbol{\zeta}_a\mathbf{Z}_1^{bcd}
\end{aligned}
\tag{239}
$$

The notation $\mathcal{L}_{2,1}^{abcd}$ arises because second-order density matrices involving "a" ($\mathbf{D}^{ab}$, $\mathbf{D}^{ac}$, and $\mathbf{D}^{ad}$) appear in the first-order multipliers, whereas only first-order density matrices involving "bcd" occurs in $\mathcal{L}_{2,1}^{abcd}$.

We may also obtain an expression which is somewhat intermediate between the $n+1$ and $2n+1$ expressions [47]. That is, by keeping second-order "bcd" density matrices, we may eliminate first-order multipliers and express the cubic response function as $\mathcal{L}_{1,2}^{abcd}$ (first-order in "a", second-order in "bcd")

$$\mathcal{L}_{1,2}^{abcd} \overset{\{\text{Tr}\}_T}{=} (\mathcal{E}^{0,a})_2^{bcd} - \mathbf{S}^{abcd}\mathbf{W} - \mathbf{S}^{acd}\mathbf{W}^b - \mathbf{S}^{abd}\mathbf{W}^c - \mathbf{S}^{abc}\mathbf{W}^d$$
$$- \mathbf{S}^{ad}\mathbf{W}^{bc} - \mathbf{S}^{ac}\mathbf{W}^{bd} - \mathbf{S}^{ab}\mathbf{W}^{cd}$$
$$- \mathbf{S}^a\mathbf{W}_2^{bcd} - \boldsymbol{\lambda}_a\mathbf{Y}_2^{bcd} - \boldsymbol{\zeta}_a\mathbf{Z}_2^{bcd} \tag{240}$$

Finally, we may apply the $n+1$ rule by differentiating Eq. (98) and keeping third-order density matrices $\mathbf{D}^{bcd}$ and obtain

$$\mathcal{L}_{0,3}^{abcd} \overset{\{\text{Tr}\}_T}{=} (\mathcal{E}^{0,a})^{bcd} - \mathbf{S}^{abcd}\mathbf{W} - \mathbf{S}^{acd}\mathbf{W}^b - \mathbf{S}^{abd}\mathbf{W}^c - \mathbf{S}^{abc}\mathbf{W}^d$$
$$- \mathbf{S}^{ad}\mathbf{W}^{bc} - \mathbf{S}^{ac}\mathbf{W}^{bd} - \mathbf{S}^{ab}\mathbf{W}^{cd} - \mathbf{S}^a\mathbf{W}^{bcd} \tag{241}$$

Analogously, there are three formulas for fifth order properties,

$$\mathcal{L}_{2,2}^{abcde} = \mathcal{L}_{1,3}^{abcde} = \mathcal{L}_{0,4}^{abcde} \tag{242}$$

four formulas for sixth order properties,

$$\mathcal{L}_{3,2}^{abcdef} = \mathcal{L}_{2,3}^{abcdef} = \mathcal{L}_{1,4}^{abcdef} = \mathcal{L}_{0,5}^{abcdef} \tag{243}$$

and four formulas for seventh order properties,

$$\mathcal{L}_{3,3}^{abcdefg} = \mathcal{L}_{2,4}^{abcdefg} = \mathcal{L}_{1,5}^{abcdefg} = \mathcal{L}_{0,6}^{abcdefg} \tag{244}$$

and so on.

To summarize: The $k+n+1$'th order property formula $\mathcal{L}_{k,n}^{ab_1...b_{n+k}}$ contains density matrices up to n'th order involving "$b_1,\ldots,b_{n+k}$" and up to k'th order involving "a"—that is, perturbed multipliers up to order $k-1$. The optimal choice of k,n, which minimizes the number of equations to solve, depends on how many *components* each of the perturbations has.

With all perturbations having approximately the same number of components, the lowest-order formulas (the $2n+1$ and $2n+2$ rules) $\mathcal{L}_{n,n}^{ab_1...b_{n+k}}$ ($k+n+1$ odd) and $\mathcal{L}_{n,n-1}^{ab_1...b_{n+k}}$ ($k+n+1$ even) are preferred.

In case the number of components in the perturbations differ significantly the formulas should be chosen which minimize the total number of equations that have to be solved. For example, the optimal dipole gradient formula is $\mathcal{L}_{0,1}^{gf}$, with the geometry perturbation (g) first. In this way no geometric equations are involved, only the 3 electric field equations (f). Similarly, the optimal hyperpolarizability gradient formula is $\mathcal{L}_{0,3}^{gfff}$, and involves no geometric equations. The optimal polarizability Hessian formula is $\mathcal{L}_{1,2}^{ggff}$, which involves geometric- and mixed geometric-field equations, but no second-order geometric equations. For the "dipole cubic force field" the optimal formula is $\mathcal{L}_{2,1}^{fggg}$, and involves geometric and geometry-field equations, but no higher-order geometric equations.

The property formulas introduced in this subsection are generally asymmetric with respect to "a". In the next subsection we show how these equations may be written in simplified and (almost) symmetric forms, which are to be preferred from a computational point of view. However, as we shall see, it is not possible to express derivatives of $\tilde{\mathcal{L}}^a$ in totally symmetric forms with respect to $\varepsilon_a, \varepsilon_b, \varepsilon_c, \ldots$ differentiations. This is due to the fact that "a" is fundamentally different from "$b, c, \ldots$" because the quasienergy derivative and not the quasienergy itself is our fundamental quantity for the determination of response functions.

3. Simplified property formulas

The *total* first-order derivative with respect to ε_b of $\tilde{\mathcal{L}}^a$ in Eq. (216), evaluated at *general* perturbation strengths, equals the *partial* derivative since $\tilde{\mathcal{L}}^a$ is variational with respect to its arguments in agreement with the time-averaged Hellmann-Feynmann theorem

$$\frac{\partial}{\partial \tilde{\mathbf{D}}}\tilde{\mathcal{L}}^a = \frac{\partial}{\partial \tilde{\boldsymbol{\lambda}}_a}\tilde{\mathcal{L}}^a = \frac{\partial}{\partial \tilde{\boldsymbol{\zeta}}_a}\tilde{\mathcal{L}}^a = \mathbf{0} \tag{245}$$

We may therefore write $\tilde{\mathcal{L}}^{ab}$ as $\tilde{\mathcal{L}}^{ab}_{1,0}$

$$
\begin{aligned}
\tilde{\mathcal{L}}^{ab} \;&=\; \frac{d\tilde{\mathcal{L}}^a}{d\varepsilon_b} = \frac{\partial \tilde{\mathcal{L}}^a}{\partial \varepsilon_b} = \tilde{\mathcal{L}}^{ab}_{1,0} \\
&\overset{\{\mathrm{Tr}\}_T}{=} (\tilde{\boldsymbol{\mathcal{E}}}^{0,a})^b_0 - \tilde{\mathbf{S}}^{ab}\tilde{\mathbf{W}} - \tilde{\mathbf{S}}^a \tilde{\mathbf{W}}^b_0 - \tilde{\boldsymbol{\lambda}}_a \tilde{\mathbf{Y}}^b_0 - \tilde{\boldsymbol{\zeta}}_a \tilde{\mathbf{Z}}^b_0 \\
&\overset{\{\mathrm{Tr}\}_T}{=} \tilde{\boldsymbol{\mathcal{E}}}^{0,ab} - \tilde{\mathbf{S}}^{ab}\tilde{\mathbf{W}} \\
&\quad - \tilde{\mathbf{S}}^a \big(\tilde{\mathbf{D}}\tilde{\boldsymbol{\mathcal{E}}}^{1,b}\tilde{\mathbf{D}} + \tfrac{i}{2}\dot{\tilde{\mathbf{D}}}\tilde{\mathbf{S}}^b\tilde{\mathbf{D}} - \tfrac{i}{2}\tilde{\mathbf{D}}\tilde{\mathbf{S}}^b\dot{\tilde{\mathbf{D}}}\big) \\
&\quad - \tilde{\boldsymbol{\lambda}}_a \big[(\tilde{\boldsymbol{\mathcal{E}}}^{1,b} - \tfrac{i}{2}\tilde{\mathbf{S}}^b\tfrac{d}{dt})\tilde{\mathbf{D}}\tilde{\mathbf{S}} + (\tilde{\boldsymbol{\mathcal{F}}} - \tfrac{i}{2}\tilde{\mathbf{S}}\tfrac{d}{dt})\tilde{\mathbf{D}}\tilde{\mathbf{S}}^b\big]^\ominus \\
&\quad - \tilde{\boldsymbol{\zeta}}_a (\tilde{\mathbf{D}}\tilde{\mathbf{S}}^b\tilde{\mathbf{D}})
\end{aligned} \tag{246}
$$

where we have used Eqs. (95), (203), (229), and (230). We emphasize that this relation is valid for all perturbation strengths. Alternatively, we may identify $\tilde{\mathcal{L}}^{ab}$ by replacing a by b in Eq. (216), followed by *total* differentiation with respect to ε_a. In this case the $\tilde{\boldsymbol{\lambda}}_b$ and $\tilde{\boldsymbol{\zeta}}_b$ multiplier terms vanish because they multiply the TDSCF equation, Eq. (217), and the idempotency relation, Eq. (218), respectively, which are both zero. Thus, we may write $\tilde{\mathcal{L}}^{ab}$ as

$$
\begin{aligned}
\tilde{\mathcal{L}}^{ab} \;&=\; \tilde{\mathcal{L}}^{ba} = \frac{d\tilde{\mathcal{L}}^b}{d\varepsilon_a} = \tilde{\mathcal{L}}^{ba}_{0,1} \\
&\overset{\{\mathrm{Tr}\}_T}{=} \tilde{\boldsymbol{\mathcal{E}}}^{0,ba} + \tilde{\boldsymbol{\mathcal{E}}}^{1,b}\tilde{\mathbf{D}}^a - \tilde{\mathbf{S}}^{ba}\tilde{\mathbf{W}} - \tilde{\mathbf{S}}^b\tilde{\mathbf{W}}^a \\
&\overset{\{\mathrm{Tr}\}_T}{=} \tilde{\boldsymbol{\mathcal{E}}}^{0,ab} + \tilde{\boldsymbol{\mathcal{E}}}^{1,b}\tilde{\mathbf{D}}^a - \tilde{\mathbf{S}}^{ab}\tilde{\mathbf{W}} - \tilde{\mathbf{S}}^b\tilde{\mathbf{W}}^a
\end{aligned} \tag{247}
$$

Eqs. (246) and (247) must be equal. Noting that the first two terms in Eq. (246) also appear in Eq. (247), it follows that the terms which differ in the two equations must be equal, that is

$$
\begin{aligned}
\tilde{\boldsymbol{\mathcal{E}}}^{1,b}\tilde{\mathbf{D}}^a - \tilde{\mathbf{S}}^b\tilde{\mathbf{W}}^a \;\overset{\{\mathrm{Tr}\}_T}{=}\; & -\tilde{\mathbf{S}}^a \big(\tilde{\mathbf{D}}\tilde{\boldsymbol{\mathcal{E}}}^{1,b}\tilde{\mathbf{D}} + \tfrac{i}{2}\dot{\tilde{\mathbf{D}}}\tilde{\mathbf{S}}^b\tilde{\mathbf{D}} - \tfrac{i}{2}\tilde{\mathbf{D}}\tilde{\mathbf{S}}^b\dot{\tilde{\mathbf{D}}}\big) \\
& - \tilde{\boldsymbol{\lambda}}_a \big[(\tilde{\boldsymbol{\mathcal{E}}}^{1,b} - \tfrac{i}{2}\tilde{\mathbf{S}}^b\tfrac{d}{dt})\tilde{\mathbf{D}}\tilde{\mathbf{S}} + (\tilde{\boldsymbol{\mathcal{F}}} - \tfrac{i}{2}\tilde{\mathbf{S}}\tfrac{d}{dt})\tilde{\mathbf{D}}\tilde{\mathbf{S}}^b\big]^\ominus \\
& - \tilde{\boldsymbol{\zeta}}_a(\tilde{\mathbf{D}}\tilde{\mathbf{S}}^b\tilde{\mathbf{D}})
\end{aligned} \tag{248}
$$

As $\tilde{\boldsymbol{\mathcal{E}}}^{1,b}$ and $\tilde{\mathbf{S}}^b$ represent independent integral matrices, and Eq. (248) contains no mixed terms, we may separate the $\tilde{\boldsymbol{\mathcal{E}}}^{1,b}$ and $\tilde{\mathbf{S}}^b$ terms and write Eq. (248) as two equations

$$\tilde{\boldsymbol{\mathcal{E}}}^{1,b}\tilde{\mathbf{D}}^a \;\overset{\{\mathrm{Tr}\}_T}{=}\; -\tilde{\mathbf{S}}^a \big(\tilde{\mathbf{D}}\tilde{\boldsymbol{\mathcal{E}}}^{1,b}\tilde{\mathbf{D}} - \tilde{\boldsymbol{\lambda}}_a \big[\tilde{\boldsymbol{\mathcal{E}}}^{1,b}\tilde{\mathbf{D}}\tilde{\mathbf{S}}\big]^\ominus \tag{249}$$

$$
\begin{aligned}
-\tilde{\mathbf{S}}^b\tilde{\mathbf{W}}^a \;\overset{\{\mathrm{Tr}\}_T}{=}\; & -\tilde{\mathbf{S}}^a \big(\tfrac{i}{2}\dot{\tilde{\mathbf{D}}}\tilde{\mathbf{S}}^b\tilde{\mathbf{D}} - \tfrac{i}{2}\tilde{\mathbf{D}}\tilde{\mathbf{S}}^b\dot{\tilde{\mathbf{D}}}\big) - \tilde{\boldsymbol{\zeta}}_a(\tilde{\mathbf{D}}\tilde{\mathbf{S}}^b\tilde{\mathbf{D}}) \\
& - \tilde{\boldsymbol{\lambda}}_a\big[-\tfrac{i}{2}\tilde{\mathbf{S}}^b(\tilde{\mathbf{D}}\tilde{\mathbf{S}})\dot{} + (\tilde{\boldsymbol{\mathcal{F}}} - \tfrac{i}{2}\tilde{\mathbf{S}}\tfrac{d}{dt})\tilde{\mathbf{D}}\tilde{\mathbf{S}}^b\big]^\ominus
\end{aligned} \tag{250}
$$

However, as $\tilde{\boldsymbol{\mathcal{E}}}^{1,b}$ and $\tilde{\mathbf{S}}^b$ does not depend on the particular perturbation but only on the perturbation dependence of the basis functions, Eqs. (249)–(250) must hold also for *arbitrary* matrices $\mathbf{M}$ and $\mathbf{N}$

$$\mathbf{M}\tilde{\mathbf{D}}^a \overset{\{\mathrm{Tr}\}_T}{=} -\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}\mathbf{M}\tilde{\mathbf{D}} - \tilde{\boldsymbol{\lambda}}_a\big[\mathbf{M}\tilde{\mathbf{D}}\tilde{\mathbf{S}}\big]^{\ominus} \tag{251}$$

$$-\mathbf{N}\tilde{\mathbf{W}}^a \overset{\{\mathrm{Tr}\}_T}{=} -\tilde{\mathbf{S}}^a\big(\tfrac{i}{2}\dot{\tilde{\mathbf{D}}}\mathbf{N}\tilde{\mathbf{D}} - \tfrac{i}{2}\tilde{\mathbf{D}}\mathbf{N}\dot{\tilde{\mathbf{D}}}\big) - \tilde{\boldsymbol{\zeta}}_a\tilde{\mathbf{D}}\mathbf{N}\tilde{\mathbf{D}}$$
$$- \tilde{\boldsymbol{\lambda}}_a\big[-\tfrac{i}{2}\mathbf{N}(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}) + (\tilde{\boldsymbol{\mathcal{F}}} - \tfrac{i}{2}\tilde{\mathbf{S}}\tfrac{d}{dt})\tilde{\mathbf{D}}\mathbf{N}\big]^{\ominus} \tag{252}$$

We can now rewrite Eq. (235) in a more symmetric form. We first expand the last three terms

$$\begin{aligned}
\mathcal{L}_{1,1}^{abc} \overset{\{\mathrm{Tr}\}_T}{=}& \ (\mathcal{E}^{0,a})_1^{bc} - \mathbf{S}^{abc}\mathbf{W} - \mathbf{S}^{ac}\mathbf{W}^b - \mathbf{S}^{ab}\mathbf{W}^c - \mathbf{S}^a\mathbf{W}_1^{bc} - \boldsymbol{\lambda}_a\mathbf{Y}_1^{bc} - \boldsymbol{\zeta}_a\mathbf{Z}_1^{bc} \\
=& \ (\mathcal{E}^{0,a})_1^{bc} - \mathbf{S}^{abc}\mathbf{W} - \mathbf{S}^{ac}\mathbf{W}^b - \mathbf{S}^{ab}\mathbf{W}^c \\
-& \ \mathbf{S}^a\big(\mathbf{D}\boldsymbol{\mathcal{F}}_1^{bc}\mathbf{D} + \mathbf{W}_{1'}^{bc}\big) \\
-& \ \boldsymbol{\lambda}_a\big(\big[\boldsymbol{\mathcal{F}}_1^{bc}\mathbf{D}\mathbf{S} + \mathbf{F}\mathbf{D}\mathbf{S}^{bc}\big]^{\ominus} - \tfrac{1}{2}(\omega_b + \omega_c)\big[\mathbf{S}\mathbf{D}\mathbf{S}^{bc}\big]^{\oplus} + \mathbf{Y}_{1'}^{bc}\big) \\
-& \ \boldsymbol{\zeta}_a\big(\mathbf{D}\mathbf{S}^{bc}\mathbf{D} + \mathbf{Z}_{1'}^{bc}\big)
\end{aligned} \tag{253}$$

where $\mathbf{W}_{1'}^{bc}$, $\mathbf{Y}_{1'}^{bc}$ and $\mathbf{Z}_{1'}^{bc}$ contain the (complete) lower-order terms but no second-order derivatives, *e.g.* the idempotency matrix $\mathbf{Z}_{1'}^{bc}$ can be written as

$$\mathbf{Z}_{1'}^{bc} = [\mathbf{D}^b\mathbf{S}^c\mathbf{D} + \mathbf{D}^b\mathbf{S}\mathbf{D}^c + \mathbf{D}^c\mathbf{S}^b\mathbf{D}]^{\oplus} \tag{254}$$

We can then apply Eqs. (251) and (252) evaluated at zero perturbation strength with $\mathbf{M} = \boldsymbol{\mathcal{F}}_1^{bc}$ and $\mathbf{N} = \mathbf{S}^{bc}$ to Eq. (253), which then simplifies to

$$\begin{aligned}
\mathcal{L}_{1,1}^{abc} \overset{\{\mathrm{Tr}\}_T}{=}& \ (\mathcal{E}^{0,a})_1^{bc} - \mathbf{S}^{abc}\mathbf{W} - \mathbf{S}^{ac}\mathbf{W}^b - \mathbf{S}^{ab}\mathbf{W}^c \\
+& \ \boldsymbol{\mathcal{F}}_1^{bc}\mathbf{D}^a - \mathbf{S}^{bc}\mathbf{W}^a - \mathbf{S}^a\mathbf{W}_{1'}^{bc} - \boldsymbol{\lambda}_a\mathbf{Y}_{1'}^{bc} - \boldsymbol{\zeta}_a\mathbf{Z}_{1'}^{bc}
\end{aligned} \tag{255}$$

This expression can be made even more compact by noting that

$$(\mathcal{E}^{0,a})_1^{bc} + \boldsymbol{\mathcal{F}}_1^{bc}\mathbf{D}^a \overset{\{\mathrm{Tr}\}_T}{=} (\mathcal{E}^{0,a})_1^{bc} + (\mathcal{E}^1)_1^{bc}\mathbf{D}^a \overset{\{\mathrm{Tr}\}_T}{=} \mathcal{E}_{1,1}^{abc} \tag{256}$$

Introducing the notation $-(\mathbf{SW})_{(1,1)_W}^{abc}$, which indicates that only up to first-order terms in $\mathbf{W}$ should be included

$$-(\mathbf{SW})_{(1,1)_W}^{abc} = -\mathbf{S}^{abc}\mathbf{W} - \mathbf{S}^{ac}\mathbf{W}^b - \mathbf{S}^{ab}\mathbf{W}^c - \mathbf{S}^{bc}\mathbf{W}^a \tag{257}$$

Eq. (255) may be written as

$$\mathcal{L}_{1,1}^{abc} \overset{\{\mathrm{Tr}\}_T}{=} \mathcal{E}_{1,1}^{abc} - (\mathbf{SW})_{(1,1)_W}^{abc} - \mathbf{S}^a\mathbf{W}_{1'}^{bc} - \boldsymbol{\lambda}_a\mathbf{Y}_{1'}^{bc} - \boldsymbol{\zeta}_a\mathbf{Z}_{1'}^{bc} \tag{258}$$

A similar treatment of Eq. (239), applying also the ε_b derivative of Eqs. (251)–(252), results in the simplified fourth-order property formula

$$\begin{aligned}
\mathcal{L}_{2,1}^{abcd} \overset{\{\mathrm{Tr}\}_T}{=}& \ \mathcal{E}_{2,1}^{abcd} - (\mathbf{SW})_{(2,1)_W}^{abcd} \\
-& \ \mathbf{S}^{ad}\mathbf{W}_{1'}^{bc} - \mathbf{S}^{ac}\mathbf{W}_{1'}^{bd} - \mathbf{S}^{ab}\mathbf{W}_{1'}^{cd} - \mathbf{S}^a\mathbf{W}_{1'}^{bcd} \\
-& \ \boldsymbol{\lambda}_a^d\mathbf{Y}_{1'}^{bc} - \boldsymbol{\lambda}_a^c\mathbf{Y}_{1'}^{bd} - \boldsymbol{\lambda}_a^b\mathbf{Y}_{1'}^{cd} - \boldsymbol{\lambda}_a\mathbf{Y}_{1'}^{bcd} \\
-& \ \boldsymbol{\zeta}_a^d\mathbf{Z}_{1'}^{bc} - \boldsymbol{\zeta}_a^c\mathbf{Z}_{1'}^{bd} - \boldsymbol{\zeta}_a^b\mathbf{Z}_{1'}^{cd} - \boldsymbol{\zeta}_a\mathbf{Z}_{1'}^{bcd}
\end{aligned} \tag{259}$$

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while applying first-order relations to the equivalent formula in Eq. (240) results in

$$\mathcal{L}_{1,2}^{abcd} \overset{\{\mathrm{Tr}\}_T}{=} \mathcal{E}_{1,2}^{abcd} - (\mathbf{SW})_{(1,2)_W}^{abcd} - \mathbf{S}^a \mathbf{W}_{2'}^{bcd} - \boldsymbol{\lambda}_a \mathbf{Y}_{2'}^{bcd} - \boldsymbol{\zeta}_a \mathbf{Z}_{2'}^{bcd} \tag{260}$$

Analogously, the fifth-order formulas are given by

$$\begin{aligned}
\mathcal{L}_{2,2}^{abcde} \overset{\{\mathrm{Tr}\}_T}{=} \quad & \mathcal{E}_{2,2}^{abcde} - (\mathbf{SW})_{(2,2)_W}^{abcde} \\
& - \quad \mathbf{S}^{ae} \mathbf{W}_{2'}^{bcd} - \mathbf{S}^{ad} \mathbf{W}_{2'}^{bce} - \mathbf{S}^{ac} \mathbf{W}_{2'}^{bde} - \mathbf{S}^{ab} \mathbf{W}_{2'}^{cde} \\
& - \quad \boldsymbol{\lambda}_a^e \mathbf{Y}_{2'}^{bcd} - \boldsymbol{\lambda}_a^d \mathbf{Y}_{2'}^{bce} - \boldsymbol{\lambda}_a^c \mathbf{Y}_{2'}^{bde} - \boldsymbol{\lambda}_a^b \mathbf{Y}_{2'}^{cde} - \boldsymbol{\lambda}_a \mathbf{Y}_{2'}^{bcde} \\
& - \quad \boldsymbol{\zeta}_a^e \mathbf{Z}_{2'}^{bcd} - \boldsymbol{\zeta}_a^d \mathbf{Z}_{2'}^{bce} - \boldsymbol{\zeta}_a^c \mathbf{Z}_{2'}^{bde} - \boldsymbol{\zeta}_a^b \mathbf{Z}_{2'}^{cde} - \boldsymbol{\zeta}_a \mathbf{Z}_{2'}^{bcde}
\end{aligned} \tag{261}$$

$$\mathcal{L}_{1,3}^{abcde} \overset{\{\mathrm{Tr}\}_T}{=} \mathcal{E}_{1,3}^{abcde} - (\mathbf{SW})_{(1,3)_W}^{abcde} - \mathbf{S}^a \mathbf{W}_{3'}^{bcde} - \boldsymbol{\lambda}_a \mathbf{Y}_{3'}^{bcde} - \boldsymbol{\zeta}_a \mathbf{Z}_{3'}^{bcde} \tag{262}$$

and higher-order formulas follow the same pattern. The advantage of these formulas over those presented in section IV G 2 lies in the symmetry that is obtained in the perturbations "$a, b, c, \ldots$" which may be used to introduce effective intermediates [for example $\mathcal{E}_{1,1}^{abc}$ in Eq. (258)] and which leads to a slight reduction in the number of matrix multiplications.

H. Residues of response functions

1. Residues of response functions in exact theory

In exact theory, response functions have poles at frequencies ω_q corresponding to excitation energies from the ground state $|0\rangle$ to an excited state $|q\rangle$ [9],

$$\omega_q = E_q - E_0 \tag{263}$$

From the residues of response functions, transition matrix elements may be identified, *e.g.* the residue of the linear response function,

$$\lim_{\omega_b \to \omega_q} (\omega_b - \omega_q) \langle\langle A; B \rangle\rangle_{\omega_b} = \langle 0|A|q\rangle\langle q|B|0\rangle \tag{264}$$

yields transition moments between $|0\rangle$ and $|q\rangle$. If A and B are electric dipole operators, the residues of the linear response function determine the dipole transition strength between $|0\rangle$ and $|q\rangle$.

For the quadratic response function $\langle\langle A; B, C\rangle\rangle_{-\omega_b, \omega_c}$, the residue at $\omega_c = \omega_q$ is given by [9]

$$\begin{aligned}
\lim_{\omega_c \to \omega_q} (\omega_c - \omega_q) \langle\langle A; B, C\rangle\rangle_{-\omega_b, \omega_c} = \; & - \sum_{k \neq 0} \left(\frac{\langle 0|A|k\rangle\langle k|B - \langle 0|B|0\rangle|q\rangle}{\omega_k - (\omega_q - \omega_b)} \right. \\
& \left. + \frac{\langle 0|B|k\rangle\langle k|A - \langle 0|A|0\rangle|q\rangle}{\omega_k - \omega_b} \right) \langle q|C|0\rangle
\end{aligned} \tag{265}$$

When A, B, and C are electric dipole operators, the residue in Eq. (265) determines the two-photon absorption transition matrix element between state $|0\rangle$ and state $|q\rangle$. The double residue

$$\lim_{\omega_b \to -\omega_r} (\omega_b + \omega_r) [\lim_{\omega_c \to \omega_q} (\omega_c - \omega_q) \langle\langle A; B, C\rangle\rangle_{\omega_b, \omega_c}] = -\langle 0|B|r\rangle\langle r|A - \langle 0|A|0\rangle|q\rangle\langle q|C|0\rangle \tag{266}$$

determines matrix elements between the excited states $|q\rangle$ and $|r\rangle$. In this way molecular properties for excited states may be evaluated even though we do not have a specific representation of these states.

A general response function $\langle\langle A; B, C, \ldots, M\rangle\rangle_{\omega_b, \omega_c, \ldots, \omega_m}$ have poles when an excitation energy ω_q equals one of the frequencies $\omega_b, \omega_c, \ldots, \omega_m$ or any sum of these frequencies. Double residues are obtained when two frequencies (or sums of frequencies) equals two excitation energies, *e.g.* as in Eq. (266) where $\omega_c \to \omega_q$ and $\omega_b \to -\omega_r$. Similar identifications are possible for triple and higher-order residues.

2. Residues of response functions in Kohn-Sham response theory

Let us consider a string of perturbations $ab \ldots k \ldots m$ where k is an arbitrary index, and investigate the general response function $\langle\langle A; B, C, \ldots, K, \ldots, M\rangle\rangle_{\omega_b, \omega_c, \ldots, \omega_k, \ldots, \omega_m}$ and its residue $\lim_{\omega_{b_K} \to \omega_q}(\omega_{b_K} - \omega_q)\langle\langle A; B, C, \ldots, K, \ldots, M\rangle\rangle_{\omega_b, \omega_c, \ldots, \omega_k, \ldots, \omega_m}$, where

$$\omega_{b_K} = \omega_b + \omega_c + \ldots + \omega_k \tag{267}$$

and ω_q is an excitation energy. For sake of brevity, we will in the following denote $\langle\langle A; B, C, \ldots, K, \ldots, M\rangle\rangle_{\omega_b, \omega_c, \ldots, \omega_k, \ldots, \omega_m}$ by the simplified notation $\langle\langle A; B \ldots M\rangle\rangle_{\omega_b \ldots \omega_m}$.

In Kohn-Sham theory, we express response functions in terms of perturbed density matrices as described in Sections IV F and IV G. The poles of the response functions enter through the density matrices, in particular through the solution vectors to the response equations, Eq. (195), entering the homogeneous part of the density matrix as in Eq. (146). For example, for $\langle\langle A; B \ldots M\rangle\rangle_{\omega_b \ldots \omega_m}$ we only get contributions to $\lim_{\omega_{b_K} \to \omega_q}(\omega_{b_K} - \omega_q)\langle\langle A; B \ldots M\rangle\rangle_{\omega_b \ldots \omega_m}$ through the density matrix

$$\mathbf{D}_\omega^{b_K} = \mathbf{D}_P^{b_K} + \mathbf{D}_H^{b_K} \tag{268}$$

where from Eq. (146)

$$\mathbf{D}_H^{b_K} = [\mathbf{D}, \mathbf{X}^{b_K}]_S \tag{269}$$

and $\mathbf{X}^{b_K}$ is a solution vector to the response equation, Eq. (195),

$$\mathbf{X}^{b_K} = \left(\mathbf{E}^{[2]} - \omega_{b_K}\mathbf{S}^{[2]}\right)^{-1}\mathbf{M}_{RHS}^{b_K} \tag{270}$$

The poles of $\langle\langle A; B \ldots M\rangle\rangle_{\omega_b \ldots \omega_m}$ at ω_{b_K} enter through the inverse matrix $(\mathbf{E}^{[2]} - \omega_{b_K}\mathbf{S}^{[2]})^{-1}$, and it is therefore necessary to consider the structure of $(\mathbf{E}^{[2]} - \omega_{b_K}\mathbf{S}^{[2]})^{-1}$ in more detail. Let us first briefly comment on our notation. $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$ both contain four atomic orbital indices [13, 45], whereas $\mathbf{X}^{b_N}$ and $\mathbf{M}_{RHS}^{b_K}$ contain two atomic orbital indices. It may sometimes be convenient to introduce a supermatrix notation in which the atomic indices $\mu\nu$ are collected into one common index m. We will use a Roman boldface type to describe the conventional matrix-vector notation, whereas Italic boldface type will be used for the supermatrix notation, *e.g.* $\mathbf{E}^{[2]}$ and $\mathbf{X}^{b_K}$ are four- and two-index matrices whereas $\boldsymbol{E}^{[2]}$ and $\boldsymbol{X}^{b_K}$ represent a two-index matrix and a column vector, respectively.

To identify the poles of $\boldsymbol{X}^{b_K}$, we introduce the spectral representation of $(\boldsymbol{E}^{[2]} - \omega_{b_K}\boldsymbol{S}^{[2]})^{-1}$ [45]

$$(\boldsymbol{E}^{[2]} - \omega_{b_K}\boldsymbol{S}^{[2]})^{-1} = \sum_j [\omega_j - \text{sgn}(j)\omega_{b_K}]^{-1}\boldsymbol{X}_j\boldsymbol{X}_j^\dagger \tag{271}$$

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where ω_j is an excitation energy, and $\boldsymbol{X}_j$ is an eigenvector obtained from the generalized eigenvalue problem,

$$(\boldsymbol{E}^{[2]} - \omega_j \boldsymbol{S}^{[2]})\boldsymbol{X}_j = \boldsymbol{0} \tag{272}$$

Eq. (272) may be solved using the linear response solver of Ref. [5]. In Eq. (271), the sum includes both positive and negative j indices, where $\mathrm{sgn}(j)$ is one for positive indices and minus one for negative indices. The eigenvectors for ω_j and $\omega_{-j} = -\omega_j$, $\boldsymbol{X}_j$ and $\boldsymbol{X}_{-j}$, are paired, such that $\boldsymbol{X}_j$ may be determined from the elements of $\boldsymbol{X}_{-j}$ or vice versa. We refer to Ref. [45] for more details.

Inserting Eq. (271) into Eq. (270), we obtain

$$\begin{aligned}
\boldsymbol{X}^{b_K} &= (\boldsymbol{E}^{[2]} - \omega_{b_K}\boldsymbol{S}^{[2]})^{-1}\boldsymbol{M}_{RHS}^{b_K} \\
&= \sum_j [\omega_j - \mathrm{sgn}(j)\omega_{b_K}]^{-1}\boldsymbol{X}_j\boldsymbol{X}_j^\dagger\boldsymbol{M}_{RHS}^{b_K}
\end{aligned} \tag{273}$$

From Eq. (273) it is clearly seen that only the terms in $\langle\langle A; B \ldots M \rangle\rangle_{\omega_b\ldots\omega_m}$ which contain the $\boldsymbol{X}^{b_K}$ response vector (or, equivalently $\mathbf{D}_\omega^{b_K}$) will contribute to $\lim_{\omega_{b_K}\to\omega_q}(\omega_{b_K} - \omega_q)\langle\langle A; B \ldots M \rangle\rangle_{\omega_b\ldots\omega_m}$, as the other response vectors are written in the same form as Eq. (273) but with a frequency that differs from ω_{b_K}. Their residues for $\omega_{b_K} \to \omega_q$ are therefore zero.

The residue of $\boldsymbol{X}^{b_K}$ for $\omega_{b_K} \to \omega_q$, which we denote as $\mathbf{X}^{b_K\to q}$, is given by

$$\boldsymbol{X}^{b_K\to q} = \lim_{\omega_{b_K}\to\omega_q} (\omega_{b_K} - \omega_q)\boldsymbol{X}^{b_K} = -\boldsymbol{X}_q\boldsymbol{X}_q^\dagger\boldsymbol{M}_{RHS}^{b_K\to q} \tag{274}$$

where q is a positive index and $\boldsymbol{X}_q$ is determined from Eq. (272). In the transformed right-hand side $\boldsymbol{M}_{RHS}^{b_K\to q}$, we have made the replacement $\omega_{b_K} \to \omega_q$ whenever ω_{b_K} occurs. In matrix form, $\mathbf{X}^{b_K\to q}$ may be written as

$$\mathbf{X}^{b_K\to q} = -\mathbf{X}_q\mathrm{Tr}(\mathbf{X}_q^*\mathbf{M}_{RHS}^{b_K\to q}) \tag{275}$$

Taking the residue of $\mathbf{D}_\omega^{b_K}$ for $\omega_{b_K} \to \omega_q$, which we denote the "residue density matrix" $\mathbf{D}_\omega^{b_K\to q}$, gives

$$\mathbf{D}_\omega^{b_K\to q} = \lim_{\omega_{b_K}\to\omega_q} (\omega_{b_K} - \omega_q)\mathbf{D}_\omega^{b_K} = [\mathbf{D}, \mathbf{X}^{b_K\to q}]_S \tag{276}$$

where we have used Eq. (268)-(269) and the fact that the particular part $\mathbf{D}_P^{b_K}$ does not contribute to the residue as it does not contain $\mathbf{X}^{b_K}$. When evaluating $\lim_{\omega_{b_K}\to\omega_q}(\omega_{b_K} - \omega_q)\langle\langle A; B \ldots M \rangle\rangle_{\omega_b\ldots\omega_m}$ we thus need to replace $\mathbf{D}_\omega^{b_K}$ by $\mathbf{D}_\omega^{b_K\to q}$.

All terms containing $\mathbf{D}_\omega^{b_K}$ contribute to $\lim_{\omega_{b_K}\to\omega_q}(\omega_{b_K} - \omega_q)\langle\langle A; B \ldots M \rangle\rangle_{\omega_b\ldots\omega_m}$ and terms that do not contain $\mathbf{D}_\omega^{b_K}$ may be removed. $\mathbf{D}_\omega^{b_K}$ itself enters in $\langle\langle A; B \ldots M \rangle\rangle_{\omega_b\ldots\omega_m}$, and it also enters through the particular parts of all density matrices of order $k+1$ and above. In these particular density matrices, only the terms that contain $\mathbf{D}_\omega^{b_K}$ explicitly will survive. In the surviving terms we have to make the replacement $\mathbf{D}_\omega^{b_K} \to \mathbf{D}_\omega^{b_K\to q}$ to get the desired residue.

Consider for example the quadratic response function in Eq. (237). In the corresponding residue, $\lim_{\omega_b\to\omega_q}(\omega_b - \omega_q)\langle\langle A; B, C \rangle\rangle_{\omega_b,\omega_c}$, $\mathbf{D}_\omega^b$ enters in the second-order density matrix $\mathbf{D}_\omega^{bc}$ via the particular component $\mathbf{D}_P^{bc}$, see Eqs. (173)-(175), and in terms containing $\mathbf{D}_\omega^b$ itself. In the terms containing $\mathbf{D}_\omega^{bc}$, it is only the terms in $\mathbf{D}_P^{bc}$ containing $\mathbf{D}_\omega^b$ explicitly that survive. The remaining terms are removed when evaluating $\lim_{\omega_b\to\omega_q}(\omega_b - \omega_q)\langle\langle A; B \ldots M \rangle\rangle_{\omega_b}$. To get the final residue expression we make the replacement $\mathbf{D}_\omega^b \to \mathbf{D}_\omega^{b\to q}$ in the surviving terms.

In conclusion, the procedure for obtaining $\lim_{\omega_{b_K}\to\omega_q}(\omega_{b_K}-\omega_q)\langle\langle A;B\dots M\rangle\rangle_{\omega_b\dots\omega_m}$ from the expression for $\langle\langle A;B\dots M\rangle\rangle_{\omega_b\dots\omega_m}$ may be summarized as follows:

(1) All terms in the response function not containing $\mathbf{D}_\omega^{b_K}$ are removed.

(2) The perturbed density matrix $\mathbf{D}_\omega^{b_K}$ is replaced by $\mathbf{D}_\omega^{b_K\to q}$, Eq. (276), and ω_{b_K} is replaced by ω_q:

$$\mathbf{D}_\omega^{b_K} \;\to\; \mathbf{D}_\omega^{b_K\to q} = [\mathbf{D},\mathbf{X}^{b_K\to q}]_S \tag{277}$$

$$\omega_{b_K} \;\to\; \omega_q \tag{278}$$

Double residues are obtained by applying the above procedure twice to two different response matrices/frequencies. For instance, the double residue in Eq. (266) is obtained by eliminating all terms not containing $\mathbf{D}_\omega^c$ and making the replacements

$$\mathbf{D}_\omega^c \;\to\; \mathbf{D}_\omega^{c\to q} = [\mathbf{D},\mathbf{X}^{c\to q}]_S \tag{279}$$

$$\omega_c \;\to\; \omega_q \tag{280}$$

and then eliminating all terms not involving $\mathbf{D}_\omega^b$, followed by the replacements

$$\mathbf{D}_\omega^b \;\to\; \mathbf{D}_\omega^{b\to -r} = [\mathbf{D},\mathbf{X}^{b\to -r}]_S \tag{281}$$

$$\omega_b \;\to\; -\omega_r \tag{282}$$

Triple and higher-order residues may be obtained in a similar fashion by applying the procedure three or more times.

To exemplify the above procedure we now consider the residue for the linear response function $\lim_{\omega_b\to\omega_q}(\omega_b-\omega_q)\langle\langle A;B,\rangle\rangle_{\omega_b}$. We take as our starting point the linear response function in Eq. (207) and remove all terms not containing $\mathbf{D}_\omega^b$ ($\mathcal{E}_\omega^{0,ab}$ and $-\mathbf{S}_\omega^{ab}\mathbf{W}$) to obtain

$$\mathrm{Tr}\left(\mathcal{E}_\omega^{1,a}\mathbf{D}_\omega^b - \mathbf{S}_\omega^a\big([\mathbf{D}_\omega^b\mathbf{FD}]^\oplus + \mathbf{DG}^{KS}(\mathbf{D}_H^b)\mathbf{D} + \tfrac{1}{2}\omega_b[\mathbf{D}_\omega^b\mathbf{SD}]^\ominus\big)\right) \tag{283}$$

where we have used Eq. (213) and inserted Eq. (161) in the resulting expression. We then make the replacements in Eqs. (277)-(278) for $\mathbf{D}_\omega^b$ and ω_b,

$$\mathbf{D}_\omega^b \;\to\; \mathbf{D}_\omega^{b\to q} \tag{284}$$

$$\omega_b \;\to\; \omega_q \tag{285}$$

For the $\mathbf{DG}^{KS}(\mathbf{D}_H^b)\mathbf{D}$ term, we have already eliminated the particular component of $\mathbf{D}_\omega^b$, see Eqs. (161)-(162), and we therefore make the replacement $\mathbf{D}_H^b \to \mathbf{D}_\omega^{b\to q}$ which then is equivalent to Eq. (284). Making this replacement and the replacements in Eqs. (284)-(285) gives the residue

$$\lim_{\omega_b\to\omega_q}(\omega_b-\omega_q)\langle\langle A;B,\rangle\rangle_{\omega_b} \overset{\mathrm{Tr}}{=}$$

$$\mathcal{E}_\omega^{1,a}\mathbf{D}_\omega^{b\to q} - \mathbf{S}_\omega^a\big([\mathbf{D}_\omega^{b\to q}\mathbf{FD}]^\oplus + \mathbf{DG}^{KS}(\mathbf{D}_\omega^{b\to q})\mathbf{D} + \tfrac{1}{2}\omega_q[\mathbf{D}_\omega^{b\to q}\mathbf{SD}]^\ominus\big) \tag{286}$$

where from Eqs. (275)-(276) and Eq. (165) we obtain

$$\mathbf{D}_\omega^{b\to q} \;=\; [\mathbf{D},\mathbf{X}^{b\to q}]_S \tag{287}$$

$$\mathbf{X}^{b\to q} \;=\; -\mathbf{X}_q\mathrm{Tr}(\mathbf{X}_q^*\mathbf{M}_{RHS}^{b\to q}) \tag{288}$$

$$\mathbf{M}_{RHS}^{b\to q} \;=\; \big[\breve{\mathcal{F}}_\omega^b\mathbf{DS} + \mathbf{FD}_P^b\mathbf{S} + \mathbf{FDS}_\omega^b\big]^\ominus$$
$$-\tfrac{1}{2}\omega_q\big[\mathbf{SD}_P^b\mathbf{S} + \mathbf{SDS}_\omega^b\big]^\oplus \tag{289}$$

where ω_q and $\boldsymbol{X}_q$ are determined from Eq. (272). The residue in Eq. (286) may be equated with $\langle 0|A|q\rangle\langle q|B|0\rangle$ in Eq. (264). We cannot determine the sign of the individual transition matrix elements but this is not important as molecular properties obtained from response function residues are always written in terms of products of transition matrix elements.

For perturbation-independent basis sets, the residue takes a much simpler form. First, in Eq. (286) only $\mathrm{Tr}\,\boldsymbol{\mathcal{E}}_\omega^{1,a}\mathbf{D}_\omega^{b\to q}$ contribute. From Eq. (94) and (203) it follows that for perturbation-independent basis sets

$$\boldsymbol{\mathcal{E}}_\omega^{1,a} = \left.\frac{\partial\boldsymbol{\mathcal{F}}}{\partial\varepsilon_a}\right|_{\{\varepsilon\}=0} = \mathbf{A} \tag{290}$$

To identify an expression for $\mathbf{D}_\omega^{b\to q}$ for perturbation-independent basis sets, we consider $\mathbf{M}_{RHS}^{b\to q}$ in Eq. (289), which can then be simplified significantly. Only the $\breve{\boldsymbol{\mathcal{F}}}_\omega^b$ term may survive as $\mathbf{D}_P^b$ may be written in terms of perturbed overlap matrices, see Eqs. (153) and (126). $\breve{\boldsymbol{\mathcal{F}}}_\omega^b$ reduces to $\mathbf{B}$ for perturbation-independent basis sets, see Eq. (162). Therefore $\mathbf{M}_{RHS}^{b\to q}$ is given by

$$\mathbf{M}_{RHS}^{b\to q} = [\mathbf{B}, \mathbf{S}]_D \tag{291}$$

Inserting Eq. (291) into Eqs. (287)-(288) yields

$$\mathbf{D}_\omega^{b\to q} = -[\mathbf{D}, \mathbf{X}_q]_S \mathrm{Tr}(\mathbf{X}_q^*[\mathbf{B}, \mathbf{S}]_D) \tag{292}$$

Finally, inserting Eqs. (290) and (292) into Eq. (286) and removing the $-\mathbf{S}_\omega^a(\ldots)$ term, we obtain the residue for perturbation-independent basis sets,

$$\lim_{\omega_b\to\omega_q}(\omega_b - \omega_q)\langle\langle A; B, \rangle\rangle_{\omega_b} = -\mathrm{Tr}\big([\mathbf{A}, \mathbf{S}]_D\mathbf{X}_q\big)\mathrm{Tr}\big(\mathbf{X}_q^*[\mathbf{B}, \mathbf{S}]_D\big) \tag{293}$$

in accordance with the expression in Ref. [45].

V. CONCLUSION

We have presented a generalization of response theory at the HF and KS levels of theory to include frequency- and perturbation-dependent basis sets. The derivations are formulated exclusively in terms of variations in the density matrix in the AO basis with the idempotency relation for the density matrix as a constraint. Response equations of arbitrary order are obtained by differentiation of the time-dependent SCF equation, Eq. (217), and the idempotency constraint, Eq. (218). Using the *particular-homogeneous* separation of the density matrix contributions described in Section IV D, these two contributions are decoupled and may be calculated successively. Response functions to arbitrary order are obtained by straightforward differentiation of the variational time-averaged quasienergy derivative Lagrangian in Eq. (216), and residues are obtained from the corresponding response function expressions by replacing the density matrix by a "residue density matrix" as described in Section IV H. Response functions may be evaluated by applying the $2n+1$ rule, the $n+1$ rule, or alternative "rules" that are intermediate between these as described in Section IV G. The choice of rule will depend on the number of components in the various perturbations in order to minimize the number of response equations to be solved. For certain classes of large molecules the density matrix becomes *sparse*. As only matrix multiplications and additions in the AO basis are involved, this sparsity can be utilized to obtain *linear scaling* for large molecules.

The major advantage of the present formalism—where the idempotency of the density matrix is treated as a constraint—compared to the exponential parameterization by Helgaker *et al.* [12, 13]—where an explicit parameterization is given for the density matrix—lies in the treatment of PDBS. For PDBS in the exponential parameterization, an additional constraint is introduced for the idempotency of the *reference* density matrix, whereas in our formulation, standard basis sets and PDBS are treated on an equal footing. When the $2n+1$ rule is applied in our formulation, the elements of the density matrix are the fundamental parameters, and compact formulas are obtained where higher-order perturbed density matrices are eliminated. In contrast, in the exponential parameterization, the X response parameters are the fundamental parameters, and the $2n+1$ rule is applied to these parameters. This means that the higher-order density matrix terms arising from differentiation of the reference density matrix must be considered also when the $2n+1$ rule is applied in the exponential parameterization. Our formulation avoids these higher-order density matrix terms, yielding simpler expressions for the response functions. Note that the structure of the linear response equations in both formulations is the same, and the same linear solver [5] may therefore be used.

Acknowledgments

Appendix A: Perturbation strength derivatives of the functional derivative matrix

1. Derivatives of the functional derivative matrix for response equations

The aim of Sections (A 1 a)–(A 1 c) is to identify perturbation-strength derivatives of the functional derivative matrix $\tilde{\mathbf{F}}_{xc}$ to first and second order, evaluated at zero perturbation strengths in the frequency domain ($\mathbf{F}^b_{xc,\omega}$ and $\mathbf{F}^{bc}_{xc,\omega}$) in order to isolate the terms containing the highest-order response parameters ($\mathbf{X}^b$ and $\mathbf{X}^{bc}$).

a. *Perturbation expansion of* $\tilde{\mathbf{F}}_{xc}$

$\tilde{\mathbf{F}}_{xc}$ in Eq. (67) is given as

$$\tilde{F}_{xc,\mu\nu} = \int \tilde{\Omega}_{\mu\nu} \tilde{v}_{xc} d\mathbf{x} \tag{A1}$$

where from Eqs. (44) and (66)

$$\tilde{\Omega}_{\mu\nu} = \tilde{\chi}^*_\mu \tilde{\chi}_\nu \tag{A2}$$

$$\tilde{v}_{xc}(\mathbf{r}, t) = \left. \frac{\delta \tilde{E}_{xc}}{\delta \rho(\mathbf{r})} \right|_{\rho(\mathbf{r}) = \tilde{\rho}(\mathbf{r}, t)} \tag{A3}$$

$\tilde{v}_{xc}$ may be expanded in terms of functional derivatives in the following manner

$$\tilde{v}_{xc}(\mathbf{r}, t) = v_{xc}(\mathbf{r}) + \int \frac{\delta v_{xc}(\mathbf{r})}{\delta \rho(\mathbf{r}_1)} \delta \tilde{\rho}(\mathbf{r}_1, t) d\mathbf{x}_1$$
$$+ \frac{1}{2} \int \int \frac{\delta^2 v_{xc}(\mathbf{r})}{\delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2)} \delta \tilde{\rho}(\mathbf{r}_1, t) \delta \tilde{\rho}(\mathbf{r}_2, t) d\mathbf{x}_1 d\mathbf{x}_2 \tag{A4}$$

where, due to the adiabatic approximation, the dependence of the external potential only occur in $\delta \tilde{\rho}(\mathbf{r}_i, t)$.

$\tilde{\mathbf{F}}_{xc}$ may now be expanded in orders of the perturbation strengths as

$$\tilde{\mathbf{F}}_{xc} = \mathbf{F}_{xc} + \tilde{\mathbf{F}}_{xc}^{(1)} + \tilde{\mathbf{F}}_{xc}^{(2)} + \dots \tag{A5}$$

where $\tilde{\mathbf{F}}_{xc}$ to second order is given by

$$F_{xc,\mu\nu} = \int \Omega_{\mu\nu}(\mathbf{r}) v_{xc}(\mathbf{r}) d\mathbf{x} \tag{A6}$$

$$\tilde{F}_{xc,\mu\nu}^{(1)} = \int \Omega_{\mu\nu}(\mathbf{r}) \tilde{v}_{xc}^{(1)}(\mathbf{r}, t) d\mathbf{x} + \int \tilde{\Omega}_{\mu\nu}^{(1)}(\mathbf{r}, t) v_{xc}(\mathbf{r}) d\mathbf{x} \tag{A7}$$

$$\tilde{F}_{xc,\mu\nu}^{(2)} = \int \Omega_{\mu\nu}(\mathbf{r}) \tilde{v}_{xc}^{(2)}(\mathbf{r}, t) d\mathbf{x} + \int \tilde{\Omega}_{\mu\nu}^{(1)}(\mathbf{r}, t) \tilde{v}_{xc}^{(1)}(\mathbf{r}, t) d\mathbf{x}$$
$$+ \int \tilde{\Omega}_{\mu\nu}^{(2)}(\mathbf{r}, t) v_{xc}(\mathbf{r}) d\mathbf{x} \tag{A8}$$

To obtain Eqs. (A6)-(A8) we have made a perturbation expansion of the overlap distribution matrix

$$\tilde{\boldsymbol{\Omega}} = \boldsymbol{\Omega} + \tilde{\boldsymbol{\Omega}}^{(1)} + \tilde{\boldsymbol{\Omega}}^{(2)} + \dots \tag{A9}$$

and introduced an expansion of the exchange-correlation potential,

$$\tilde{v}_{xc}(\mathbf{r}, t) = v_{xc}(\mathbf{r}) + \tilde{v}_{xc}^{(1)}(\mathbf{r}, t) + \tilde{v}_{xc}^{(2)}(\mathbf{r}, t) + \dots \tag{A10}$$

where the terms in Eq. (A10) are identified by inserting a perturbation expansion of $\delta \tilde{\rho}(\mathbf{r}_i, t)$,

$$\delta \tilde{\rho}(\mathbf{r}_i, t) = \tilde{\rho}^{(1)}(\mathbf{r}_i, t) + \tilde{\rho}^{(2)}(\mathbf{r}_i, t) + \dots \tag{A11}$$

into Eq. (A4), giving

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} \tag{A12}$$

$$\tilde{v}_{xc}^{(1)}(\mathbf{r}, t) = \int \frac{\delta v_{xc}(\mathbf{r})}{\delta \rho(\mathbf{r}_1)} \tilde{\rho}^{(1)}(\mathbf{r}_1, t) d\mathbf{x}_1 \tag{A13}$$

$$\tilde{v}_{xc}^{(2)}(\mathbf{r}, t) = \int \frac{\delta v_{xc}(\mathbf{r})}{\delta \rho(\mathbf{r}_1)} \tilde{\rho}^{(2)}(\mathbf{r}_1, t) d\mathbf{x}_1$$
$$+ \frac{1}{2} \int \int \frac{\delta^2 v_{xc}(\mathbf{r})}{\delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2)} \tilde{\rho}^{(1)}(\mathbf{r}_1, t) \tilde{\rho}^{(1)}(\mathbf{r}_2, t) d\mathbf{x}_1 d\mathbf{x}_2 \tag{A14}$$

The terms in Eq. (A11) may be obtained by expanding the electron density $\tilde{\rho}$ in Eq. (79)

$$\tilde{\rho} = \sum_{\mu\nu} \tilde{\Omega}_{\mu\nu} \tilde{D}_{\nu\mu} \overset{\text{Tr}}{=} \tilde{\boldsymbol{\Omega}} \tilde{\mathbf{D}} \tag{A15}$$

in orders of the perturbation strengths

$$\rho \stackrel{\text{Tr}}{=} \mathbf{D}\mathbf{\Omega} \tag{A16}$$

$$\tilde{\rho}^{(1)} \stackrel{\text{Tr}}{=} \mathbf{\Omega}\tilde{\mathbf{D}}^{(1)} + \tilde{\mathbf{\Omega}}^{(1)}\mathbf{D} \tag{A17}$$

$$\tilde{\rho}^{(2)} \stackrel{\text{Tr}}{=} \tilde{\mathbf{\Omega}}^{(2)}\mathbf{D} + \tilde{\mathbf{\Omega}}^{(1)}\tilde{\mathbf{D}}^{(1)} + \mathbf{\Omega}\tilde{\mathbf{D}}^{(2)} \tag{A18}$$

where ρ is the optimized electron density for the unperturbed system.

b. The first-order derivative $\mathbf{F}^b_{xc,\omega}$

The total first-order functional derivative in the frequency domain $\mathbf{F}^b_{xc,\omega}$, is given by, see Eq. (A7)

$$(F^b_{xc,\omega})_{\mu\nu} = \int \Omega_{\mu\nu}(\mathbf{r})v^b_{xc,\omega}(\mathbf{r})d\mathbf{x} + \int (\Omega^b_\omega)_{\mu\nu}(\mathbf{r})v_{xc}(\mathbf{r})d\mathbf{x} \tag{A19}$$

where $\mathbf{\Omega}^b_\omega$ may be determined once the specific perturbation dependency of the basis functions has been defined. From Eq. (A13) we obtain

$$v^b_{xc,\omega}(\mathbf{r}) = \int \frac{\delta v_{xc}(\mathbf{r})}{\delta\rho(\mathbf{r}_1)}\rho^b_\omega(\mathbf{r}_1)d\mathbf{x}_1 \tag{A20}$$

where the electron density derivative is found from Eq. (A17)

$$\rho^b_\omega(\mathbf{r}_1) \stackrel{\text{Tr}}{=} \mathbf{\Omega}^b_\omega(\mathbf{r}_1)\mathbf{D} + \mathbf{\Omega}(\mathbf{r}_1)\mathbf{D}^b_\omega \tag{A21}$$

$\mathbf{D}^b_\omega$ is written as a sum of $\mathbf{D}^b_P$ and $\mathbf{D}^b_H$, Eq. (152)

$$\mathbf{D}^b_\omega = \mathbf{D}^b_P + \mathbf{D}^b_H \tag{A22}$$

where only $\mathbf{D}^b_H$ contains the first-order response parameters X^b, see Eq. (154), whereas $\mathbf{D}^b_P$ is determined from Eq. (153). We now write $\mathbf{F}^b_{xc,\omega}$ in a form where the term containing the X^b parameters has been separated from the remaining terms. From Eqs. (A19)-(A22), it follows that the part of $(F^b_{xc,\omega})_{\mu\nu}$ containing $\mathbf{D}^b_H$ may be written as

$$\int \Omega_{\mu\nu}(\mathbf{r})\left(\int \frac{\delta v_{xc}(\mathbf{r})}{\delta\rho(\mathbf{r}_1)}\text{Tr}\big(\mathbf{\Omega}(\mathbf{r}_1)\mathbf{D}^b_H\big)d\mathbf{x}_1\right)d\mathbf{x} = G^{xc}_{\mu\nu}(\mathbf{D}^b_H) \tag{A23}$$

where we have introduced the contracted $\mathbf{G}^{xc}(\mathbf{M})$ matrix by

$$G^{xc}_{\mu\nu}(\mathbf{M}) = \sum_{\alpha\beta} M_{\beta\alpha} \int \Omega_{\mu\nu}(\mathbf{r})\left(\int \Omega_{\alpha\beta}(\mathbf{r}_1)\frac{\delta v_{xc}}{\delta\rho(\mathbf{r}_1)}d\mathbf{x}_1\right)d\mathbf{x} \tag{A24}$$

Thus, the total derivative $\mathbf{F}^b_{xc,\omega}$ may be written as a sum of $\mathbf{G}^{xc}_{\mu\nu}(\mathbf{D}^b_H)$ and a matrix containing the remaining terms which we denote as $\breve{\mathbf{F}}^b_{xc,\omega}$ and which does not contain the first-order response parameters X^b

$$\mathbf{F}^b_{xc,\omega} = \mathbf{G}^{xc}\big(\mathbf{D}^b_H\big) + \breve{\mathbf{F}}^b_{xc,\omega} \tag{A25}$$

where from Eqs. (A19)-(A22)

$$\begin{aligned}(\breve{F}^b_{xc,\omega})_{\mu\nu} &= \int \Omega_{\mu\nu}(\mathbf{r})\left(\int \frac{\delta v_{xc}(\mathbf{r})}{\delta\rho(\mathbf{r}_1)}\big[\text{Tr}\mathbf{\Omega}^b_\omega(\mathbf{r}_1)\mathbf{D} + \text{Tr}\mathbf{\Omega}(\mathbf{r}_1)\mathbf{D}^b_P\big]d\mathbf{x}_1\right)d\mathbf{x} \\ &+ \int (\Omega^b_\omega)_{\mu\nu}(\mathbf{r})v_{xc}(\mathbf{r})d\mathbf{x}\end{aligned} \tag{A26}$$

c. The second-order derivative $\mathbf{F}_{xc,\omega}^{bc}$

The second-order derivative $\mathbf{F}_{xc,\omega}^{bc}$ is treated in a similar manner as the first-order derivative $\mathbf{F}_{xc,\omega}^{b}$. From Eq. (A8) we obtain

$$
\begin{aligned}
(F_{xc,\omega}^{bc})_{\mu\nu} &= \int \Omega_{\mu\nu}(\mathbf{r})v_{xc,\omega}^{bc}(\mathbf{r})d\mathbf{x} + \int (\Omega_{\omega}^{b})_{\mu\nu}(\mathbf{r})v_{xc,\omega}^{c}(\mathbf{r})d\mathbf{x} \\
&+ \int (\Omega_{\omega}^{c})_{\mu\nu}(\mathbf{r})v_{xc,\omega}^{b}(\mathbf{r})d\mathbf{x} + \int (\Omega_{\omega}^{bc})_{\mu\nu}(\mathbf{r})v_{xc}(\mathbf{r})d\mathbf{x}
\end{aligned} \tag{A27}
$$

The aim is now to isolate terms containing $\mathbf{D}_{H}^{bc}$, as only these terms contain second-order response parameters X^{bc}, see Eq. (177). We thus focus on the terms containing $\mathbf{X}^{bc}$. The second-order exchange-correlation potential derivative $v_{xc,\omega}^{bc}(\mathbf{r})$ in the first term of Eq. (A27) may be identified from Eq. (A14) as

$$
\begin{aligned}
v_{xc,\omega}^{bc}(\mathbf{r}) &= \int \frac{\delta v_{xc}(\mathbf{r})}{\delta\rho(\mathbf{r}_1)}\rho_{\omega}^{bc}(\mathbf{r}_1)d\mathbf{x}_1 \\
&+ \int\int \frac{\delta^2 v_{xc}(\mathbf{r})}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)}\rho_{\omega}^{b}(\mathbf{r}_1)\rho_{\omega}^{c}(\mathbf{r}_2)d\mathbf{x}_1 d\mathbf{x}_2
\end{aligned} \tag{A28}
$$

where the second-order electron density derivative ρ_{ω}^{bc} is found from Eq. (A18)

$$
\rho_{\omega}^{bc} \overset{\mathrm{Tr}}{=} \mathbf{\Omega}_{\omega}^{bc}\mathbf{D} + \mathbf{\Omega}_{\omega}^{c}\mathbf{D}_{\omega}^{b} + \mathbf{\Omega}_{\omega}^{b}\mathbf{D}_{\omega}^{c} + \mathbf{\Omega}\mathbf{D}_{\omega}^{bc} \tag{A29}
$$

Only the last term in Eq. (A29) contains the $\mathbf{D}_{\omega}^{bc}$ matrix, which is written as, see Eq. (173)

$$
\mathbf{D}_{\omega}^{bc} = \mathbf{D}_{H}^{bc} + \mathbf{D}_{P}^{bc} \tag{A30}
$$

Comparing Eqs. (A27)-(A30) to Eqs. (A19)-(A22), we see that the $\mathbf{D}_{H}^{bc}$ matrix enters $\mathbf{F}_{xc,\omega}^{bc}$ in the same way that $\mathbf{D}_{H}^{b}$ entered $\mathbf{F}_{xc,\omega}^{b}$. We may thus write $\mathbf{F}_{xc,\omega}^{bc}$ in a form analogous to Eq. (A25)

$$
\mathbf{F}_{xc,\omega}^{bc} = \mathbf{G}^{xc}(\mathbf{D}_{H}^{bc}) + \breve{\mathbf{F}}_{xc,\omega}^{bc} \tag{A31}
$$

where $\breve{\mathbf{F}}_{xc,\omega}^{bc}$ contains the remaining terms of $\mathbf{F}_{xc,\omega}^{bc}$ which may be identified from Eqs. (A27)-(A30) and which only contains up to first-order response parameters.

Higher-order derivatives of $\tilde{\mathbf{F}}_{xc}$ may be identified in an analogous fashion and they all take the form of Eq. (A31).

2. Derivatives of the functional derivative matrix for response functions

In this section we consider the first-order derivative of $\tilde{\mathbf{F}}_{xc}^{\Omega^a}$, Eq. (83)

$$
(\tilde{F}_{xc}^{\Omega^a})_{\mu\nu} = \int \tilde{\Omega}_{\mu\nu}^{a}(\mathbf{r},t)\tilde{v}_{xc}(\mathbf{r},t)d\mathbf{x} \tag{A32}
$$

which is needed for the evaluation of response functions.

The exchange-correlation contribution to the linear response function is found by evaluating

$$
(\mathrm{Tr}\tilde{\mathbf{F}}_{xc}^{\Omega^a}\tilde{\mathbf{D}})^b = \sum_{\alpha\beta} \frac{\partial}{\partial\tilde{D}_{\alpha\beta}^{T}}\left(\sum_{\mu\nu}(\tilde{F}_{xc}^{\Omega^a})_{\mu\nu}\tilde{D}_{\nu\mu}\right)\tilde{D}_{\alpha\beta}^{bT} + \frac{\partial}{\partial\varepsilon_b}\sum_{\mu\nu}(\tilde{F}_{xc}^{\Omega^a})_{\mu\nu}\tilde{D}_{\nu\mu} \tag{A33}
$$

at zero field strengths in the frequency domain. We have split Eq. (A33) into two contributions—the first term arises from the perturbation strength dependency of the density matrix, whereas the second term is the partial derivative with respect to ε_b. For the first term in Eq. (A33) we obtain

$$\sum_{\alpha\beta} \frac{\partial}{\partial \tilde{D}_{\alpha\beta}^T} \left(\sum_{\mu\nu} (\tilde{F}_{xc}^{\Omega^a})_{\mu\nu} \tilde{D}_{\nu\mu} \right) \tilde{D}_{\alpha\beta}^{bT} = \sum_{\alpha\beta} (\tilde{F}_{xc}^{\Omega^a})_{\alpha\beta} \tilde{D}_{\beta\alpha}^b + \sum_{\mu\nu\alpha\beta} (\tilde{E}_{xc}^{2,a})_{\mu\nu\alpha\beta} \tilde{D}_{\nu\mu} \tilde{D}_{\beta\alpha}^b \quad (A34)$$

$$= \mathrm{Tr} \tilde{\mathbf{F}}_{xc}^{\Omega^a} \tilde{\mathbf{D}}^b + \sum_{\mu\nu} (\tilde{E}_{xc}^{2,a})_{\mu\nu} (\tilde{\mathbf{D}}^b) \tilde{D}_{\nu\mu}$$

$$= \mathrm{Tr} \tilde{\mathbf{F}}_{xc}^{\Omega^a} \tilde{\mathbf{D}}^b + \mathrm{Tr} \tilde{\mathbf{E}}_{xc}^{2,a} (\tilde{\mathbf{D}}^b) \tilde{\mathbf{D}}$$

$$= \mathrm{Tr} \tilde{\mathbf{F}}_{xc}^{\Omega^a} \tilde{\mathbf{D}}^b + \mathrm{Tr} \tilde{\mathbf{E}}_{xc}^{2,a} (\tilde{\mathbf{D}}) \tilde{\mathbf{D}}^b \quad (A35)$$

In Eq. (A35) we have used Eqs. (82) and (A32) to introduce the symmetric four-index matrix $\tilde{\mathbf{E}}_{xc}^{2,a}$ and the contracted two-index matrix $\tilde{\mathbf{E}}_{xc}^{2,a}(\mathbf{M})$, in analogy with the notation in Eqs. (204)-(205)

$$(\tilde{E}_{xc}^{2,a})_{\mu\nu\alpha\beta} = \frac{\partial \tilde{E}_{xc}^{0,a}}{\partial \tilde{D}_{\mu\nu}^T \partial \tilde{D}_{\alpha\beta}^T} = \frac{\partial (\tilde{F}_{xc}^{\Omega^a})_{\mu\nu}}{\partial \tilde{D}_{\alpha\beta}^T}$$

$$= \int \tilde{\Omega}_{\mu\nu}^a(\mathbf{r},t) \frac{\partial \tilde{v}_{xc}(\mathbf{r},t)}{\partial \tilde{D}_{\alpha\beta}^T} d\mathbf{x}$$

$$= \int \tilde{\Omega}_{\mu\nu}^a(\mathbf{r},t) \left(\int \frac{\delta v_{xc}(\mathbf{r})}{\delta \rho(\mathbf{r}_1)} \frac{\partial \tilde{\rho}(\mathbf{r}_1)}{\partial \tilde{D}_{\alpha\beta}^T} d\mathbf{x}_1 \right) d\mathbf{x}$$

$$= \int \tilde{\Omega}_{\mu\nu}^a(\mathbf{r},t) \left(\int \tilde{\Omega}_{\alpha\beta}(\mathbf{r}_1) \frac{\delta v_{xc}(\mathbf{r})}{\delta \rho(\mathbf{r}_1)} d\mathbf{x}_1 \right) d\mathbf{x} \quad (A36)$$

$$(\tilde{E}_{xc}^{2,a})_{\mu\nu}(\mathbf{M}) = \sum_{\alpha\beta} (\tilde{E}_{xc}^{2,a})_{\mu\nu\alpha\beta} M_{\beta\alpha} \quad (A37)$$

In the last line of Eq. (A35) we have made use of the relation

$$\mathrm{Tr} \tilde{\mathbf{E}}_{xc}^{2,a}(\mathbf{M}) \mathbf{N} = \mathrm{Tr} \tilde{\mathbf{E}}_{xc}^{2,a}(\mathbf{N}) \mathbf{M} \quad (A38)$$

which follows from the symmetry of $\tilde{\mathbf{E}}_{xc}^{2,a}$.

From the second term in Eq. (A33), which we denote as $\tilde{E}_{xc}^{0,ab}$, we obtain

$$\tilde{E}_{xc}^{0,ab} = \frac{\partial}{\partial \varepsilon_b} \sum_{\mu\nu} (\tilde{F}_{xc}^{\Omega^a})_{\mu\nu} \tilde{D}_{\nu\mu}$$

$$= \sum_{\mu\nu} \frac{\partial (\tilde{F}_{xc}^{\Omega^a})_{\mu\nu}}{\partial \varepsilon_b} \tilde{D}_{\nu\mu}$$

$$= \sum_{\mu\nu} \left[\int \tilde{\Omega}_{\mu\nu}^{ab}(\mathbf{r},t) \tilde{v}_{xc}(\mathbf{r},t) d\mathbf{x} \right.$$

$$+ \left. \int \tilde{\Omega}_{\mu\nu}^a(\mathbf{r},t) \left(\int \frac{\delta v_{xc}(\mathbf{r})}{\delta \rho(\mathbf{r}_1)} \left(\mathrm{Tr} \tilde{\mathbf{\Omega}}^b(\mathbf{r}_1) \tilde{\mathbf{D}} \right) d\mathbf{x}_1 \right) d\mathbf{x} \right] \tilde{D}_{\nu\mu} \quad (A39)$$

where we have used Eq. (79).

Thus, the total exchange-correlation contribution to the linear response function is found by evaluating Eqs. (A35) and (A39) at zero perturbation strengths and removing the phase factor $\exp(-i\omega_b t)$ common to all terms to arrive at an expression in the frequency domain.

Appendix B: Identification of the Lagrange multipliers $\tilde{\boldsymbol{\lambda}}_a$ and $\tilde{\boldsymbol{\zeta}}_a$

In the following subsections, we identify the $\tilde{\boldsymbol{\lambda}}_a$ and $\tilde{\boldsymbol{\zeta}}_a$ multipliers which satisfy the variational criteria in Eq. (219)

$$\frac{\partial}{\partial \tilde{\mathbf{D}}^T} \tilde{\mathcal{L}}^a \overset{\{\text{Tr}\}_T}{=} \frac{\partial}{\partial \tilde{\mathbf{D}}^T}\big(\tilde{\mathcal{E}}^{0,a} - \tilde{\mathbf{S}}^a\tilde{\mathbf{W}} - \tilde{\boldsymbol{\lambda}}_a\big[\tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}}\tilde{\mathbf{S}} - \tfrac{i}{2}\tilde{\mathbf{S}}(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}})\big]^{\ominus} - \tilde{\boldsymbol{\zeta}}_a(\tilde{\mathbf{D}}\tilde{\mathbf{S}}\tilde{\mathbf{D}} - \tilde{\mathbf{D}})\big) = \mathbf{0} \qquad (B1)$$

In Eq. (B1), we differentiate with respect to the *transposed* density matrix in order to avoid transpositions when differentiating trace products,

$$\frac{\partial}{\partial \mathbf{B}^T}\text{Tr}\mathbf{B}\mathbf{A} = \mathbf{A} \qquad (B2)$$

From the first two terms in Eq. (B1), when differentiating with respect to $\tilde{\mathbf{D}}^T$ and inserting Eq. (95), we get

$$\begin{aligned}
\frac{\partial}{\partial \tilde{\mathbf{D}}^T}\big\{\tilde{\mathcal{E}}^{0,a} - \text{Tr}\,\tilde{\mathbf{S}}^a\tilde{\mathbf{W}}\big\}_T =&\ \tilde{\mathcal{E}}^{1,a} - \tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}}\tilde{\mathbf{S}}^a - \tilde{\mathbf{S}}^a\tilde{\mathbf{D}}\tilde{\boldsymbol{\mathcal{F}}} - \tilde{\mathcal{E}}^2(\tilde{\mathbf{D}}\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}) \\
&+ \tfrac{i}{2}(\tilde{\mathbf{S}}\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}^a}) - \tfrac{i}{2}\tilde{\mathbf{S}}^a\dot{\tilde{\mathbf{D}}}\tilde{\mathbf{S}} + \tfrac{i}{2}\tilde{\mathbf{S}}\dot{\tilde{\mathbf{D}}}\tilde{\mathbf{S}}^a - \tfrac{i}{2}(\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}) \\
=&\ \tilde{\mathcal{E}}^{1,a} - \tilde{\mathcal{E}}^2(\tilde{\mathbf{D}}\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}) \\
&+ \big[-\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}\tilde{\boldsymbol{\mathcal{F}}} - \tfrac{i}{2}\tilde{\mathbf{S}}^a(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}) - \tfrac{i}{2}(\tilde{\mathbf{S}}^a\tilde{\mathbf{D}})\dot{\tilde{\mathbf{S}}}\big]^{\oplus} \qquad (B3)
\end{aligned}$$

where we have used Eqs. (204)-(205) to get

$$\frac{\partial}{\partial \tilde{\mathbf{D}}^T_{\mu\nu}}\text{Tr}\tilde{\boldsymbol{\mathcal{F}}}\mathbf{M} = \sum_{\alpha\beta}\frac{\partial \tilde{\boldsymbol{\mathcal{F}}}_{\alpha\beta}}{\partial \tilde{\mathbf{D}}^T_{\mu\nu}}M_{\beta\alpha} = \sum_{\alpha\beta}\tilde{\mathcal{E}}^2_{\mu\nu\alpha\beta}M_{\beta\alpha} = \tilde{\mathcal{E}}^2_{\mu\nu}(\mathbf{M}) \qquad (B4)$$

which is valid when $\mathbf{M}$ is independent of the density matrix. Furthermore, we have used the periodicity of the system, see Eq. (24)

$$\{\text{Tr}(\tilde{\mathbf{D}}\tilde{\mathbf{S}}\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}^a})\}_T = 0 \qquad (B5)$$

to obtain

$$\frac{\partial}{\partial \tilde{\mathbf{D}}^T}\{\text{Tr}\tilde{\mathbf{S}}^a\dot{\tilde{\mathbf{D}}}\tilde{\mathbf{S}}\tilde{\mathbf{D}}\}_T = -(\tilde{\mathbf{S}}\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}^a}) \qquad (B6)$$

From the $\tilde{\boldsymbol{\lambda}}_a$ term of Eq. (B1), we get

$$\begin{aligned}
\frac{\partial}{\partial \tilde{\mathbf{D}}^T}\big\{&-\text{Tr}\big(\tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}}\tilde{\mathbf{S}} - \tilde{\mathbf{S}}\tilde{\mathbf{D}}\tilde{\boldsymbol{\mathcal{F}}} - \tfrac{i}{2}\tilde{\mathbf{S}}(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}) - \tfrac{i}{2}(\tilde{\mathbf{S}}\tilde{\mathbf{D}})\dot{\tilde{\mathbf{S}}}\big)\tilde{\boldsymbol{\lambda}}_a\big\}_T \\
=&\ \tilde{\mathcal{E}}^2(\tilde{\boldsymbol{\lambda}}_a\tilde{\mathbf{S}}\tilde{\mathbf{D}} - \tilde{\mathbf{D}}\tilde{\mathbf{S}}\tilde{\boldsymbol{\lambda}}_a) + \tilde{\boldsymbol{\mathcal{F}}}\tilde{\boldsymbol{\lambda}}_a\tilde{\mathbf{S}} - \tilde{\mathbf{S}}\tilde{\boldsymbol{\lambda}}_a\tilde{\boldsymbol{\mathcal{F}}} \\
&+ \tfrac{i}{2}\dot{\tilde{\mathbf{S}}}\tilde{\boldsymbol{\lambda}}_a\tilde{\mathbf{S}} - \tfrac{i}{2}(\tilde{\mathbf{S}}\tilde{\boldsymbol{\lambda}}_a\dot{\tilde{\mathbf{S}}}) - \tfrac{i}{2}(\dot{\tilde{\mathbf{S}}}\tilde{\boldsymbol{\lambda}}_a\tilde{\mathbf{S}}) + \tfrac{i}{2}\tilde{\mathbf{S}}\tilde{\boldsymbol{\lambda}}_a\dot{\tilde{\mathbf{S}}} \\
=&\ \tilde{\mathcal{E}}^2([\tilde{\boldsymbol{\lambda}}_a\tilde{\mathbf{S}}\tilde{\mathbf{D}}]^{\oplus}) + \big[\tilde{\boldsymbol{\mathcal{F}}}\tilde{\boldsymbol{\lambda}}_a\tilde{\mathbf{S}} - \tfrac{i}{2}\tilde{\mathbf{S}}(\tilde{\boldsymbol{\lambda}}_a\dot{\tilde{\mathbf{S}}})\big]^{\oplus} \qquad (B7)
\end{aligned}$$

and from the $\tilde{\boldsymbol{\zeta}}_a$ term

$$\begin{aligned}
\frac{\partial}{\partial \tilde{\mathbf{D}}^T}\big\{-\text{Tr}\,\tilde{\boldsymbol{\zeta}}_a(\tilde{\mathbf{D}}\tilde{\mathbf{S}}\tilde{\mathbf{D}} - \tilde{\mathbf{D}})\big\} =&\ -\tilde{\boldsymbol{\zeta}}_a\tilde{\mathbf{D}}\tilde{\mathbf{S}} - \tilde{\mathbf{S}}\tilde{\mathbf{D}}\tilde{\boldsymbol{\zeta}}_a + \tilde{\boldsymbol{\zeta}}_a \\
=&\ -\big[\tilde{\boldsymbol{\zeta}}_a(\tilde{\mathbf{D}}\tilde{\mathbf{S}} - \tfrac{1}{2})\big]^{\oplus} \qquad (B8)
\end{aligned}$$

Thus, the sum of Eqs. (B3), (B7), and (B8) should be zero. The aim of the following three subsections is to rewrite the sum of Eqs. (B3), (B7), and (B8) into Eq. (223)

$$\begin{aligned}
\mathbf{0} =&\ \big[\big[\tilde{\boldsymbol{\mathcal{F}}}^a\tilde{\mathbf{D}}\tilde{\mathbf{S}} + \tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}}^a\tilde{\mathbf{S}} - \tfrac{i}{2}\tilde{\mathbf{S}}(\tilde{\mathbf{D}}^a\dot{\tilde{\mathbf{S}}}) + \tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}}\tilde{\mathbf{S}}^a - \tfrac{i}{2}\tilde{\mathbf{S}}^a(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}) - \tfrac{i}{2}\tilde{\mathbf{S}}(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}^a})\big]^{\ominus}\tilde{\mathbf{D}}\tilde{\mathbf{S}}\big]^{\oplus} \\
&+ \big[\big(\big[\tilde{\boldsymbol{\mathcal{F}}}^a(\tilde{\mathbf{D}}\tilde{\mathbf{S}} - \tfrac{1}{2}) - (\tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}} - \tfrac{i}{2}\dot{\tilde{\mathbf{S}}}\tilde{\mathbf{D}} - i\tilde{\mathbf{S}}\dot{\tilde{\mathbf{D}}})\tilde{\mathbf{S}}^a\big]^{\oplus} - \tilde{\boldsymbol{\zeta}}_a\big)(\tilde{\mathbf{D}}\tilde{\mathbf{S}} - \tfrac{1}{2})\big]^{\oplus} \qquad (B9)
\end{aligned}$$

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by using the ansatz for the $\tilde{\boldsymbol{\lambda}}_a$ multiplier in Eq. (220)

$$\tilde{\boldsymbol{\lambda}}_a = \tilde{\mathbf{D}}^a\tilde{\mathbf{S}}\tilde{\mathbf{D}} - \tilde{\mathbf{D}}\tilde{\mathbf{S}}\tilde{\mathbf{D}}^a = [\tilde{\mathbf{D}}^a\tilde{\mathbf{S}}\tilde{\mathbf{D}}]^\ominus \tag{B10}$$

In this way we may determine $\tilde{\boldsymbol{\zeta}}_a$ as, see Eq. (221)

$$\tilde{\boldsymbol{\zeta}}_a = \left[\tilde{\boldsymbol{\mathcal{F}}}^a(\tilde{\mathbf{D}}\tilde{\mathbf{S}}-\tfrac{1}{2}) - (\tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}} - \tfrac{i}{2}\dot{\tilde{\mathbf{S}}}\tilde{\mathbf{D}} - i\tilde{\mathbf{S}}\dot{\tilde{\mathbf{D}}})\tilde{\mathbf{S}}^a\right]^\oplus \tag{B11}$$

since the upper line in Eq. (B9) is zero by Eq. (221). The $\tilde{\boldsymbol{\zeta}}_a$ term is written in the same form in Eq. (B9) as in Eq. (B8), whereas the terms of Eqs. (B3) and (B7) must be rewritten to arrive at the remaining terms of Eq. (B9).

a.   Terms with $\tilde{\boldsymbol{\mathcal{F}}}^a$

Inserting $\tilde{\boldsymbol{\lambda}}_a$ as given by Eq. (B10) and using the idempotency relation in Eq. (218), together with Eq. (222), the matrix $[\tilde{\boldsymbol{\lambda}}_a\tilde{\mathbf{S}}\tilde{\mathbf{D}}]^\oplus$ which appears in Eq. (B7), can be rewritten as

$$\begin{aligned}
[\tilde{\boldsymbol{\lambda}}_a\tilde{\mathbf{S}}\tilde{\mathbf{D}}]^\oplus &= \left[(\tilde{\mathbf{D}}^a\tilde{\mathbf{S}}\tilde{\mathbf{D}} - \tilde{\mathbf{D}}\tilde{\mathbf{S}}\tilde{\mathbf{D}}^a)\tilde{\mathbf{S}}\tilde{\mathbf{D}}\right]^\oplus = \left[(\tilde{\mathbf{D}}^a - \tilde{\mathbf{D}}\tilde{\mathbf{S}}\tilde{\mathbf{D}}^a)\tilde{\mathbf{S}}\tilde{\mathbf{D}}\right]^\oplus \\
&= \left[(\tilde{\mathbf{D}}^a\tilde{\mathbf{S}}\tilde{\mathbf{D}} + \tilde{\mathbf{D}}\tilde{\mathbf{S}}^a\tilde{\mathbf{D}})\tilde{\mathbf{S}}\tilde{\mathbf{D}}\right]^\oplus = \left[\tilde{\mathbf{D}}^a\tilde{\mathbf{S}}\tilde{\mathbf{D}} + \tilde{\mathbf{D}}\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}\right]^\oplus \\
&= \tilde{\mathbf{D}}^a\tilde{\mathbf{S}}\tilde{\mathbf{D}} + 2\tilde{\mathbf{D}}\tilde{\mathbf{S}}^a\tilde{\mathbf{D}} + \tilde{\mathbf{D}}\tilde{\mathbf{S}}\tilde{\mathbf{D}}^a = \tilde{\mathbf{D}}^a + \tilde{\mathbf{D}}\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}
\end{aligned} \tag{B12}$$

From this we may combine the following three terms from Eqs. (B3) and (B7) into $\tilde{\boldsymbol{\mathcal{F}}}^a$

$$\tilde{\boldsymbol{\mathcal{E}}}^{1,a} - \tilde{\boldsymbol{\mathcal{E}}}^2(\tilde{\mathbf{D}}\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}) + \tilde{\boldsymbol{\mathcal{E}}}^2([\tilde{\boldsymbol{\lambda}}_a\tilde{\mathbf{S}}\tilde{\mathbf{D}}]^\oplus) = \tilde{\boldsymbol{\mathcal{E}}}^{1,a} + \tilde{\boldsymbol{\mathcal{E}}}^2(\tilde{\mathbf{D}}^a) = \tilde{\boldsymbol{\mathcal{F}}}^a \tag{B13}$$

where we have used Eqs. (202)-(205). Using idempotency, we manipulate $\tilde{\boldsymbol{\mathcal{F}}}^a$ into the first term of the lower line and the first term of the upper line in Eq. (B9)

$$\begin{aligned}
\tilde{\boldsymbol{\mathcal{F}}}^a &= \tilde{\boldsymbol{\mathcal{F}}}^a - [\tilde{\boldsymbol{\mathcal{F}}}^a\tilde{\mathbf{D}}\tilde{\mathbf{S}}]^\oplus + [\tilde{\boldsymbol{\mathcal{F}}}^a\tilde{\mathbf{D}}\tilde{\mathbf{S}}]^\oplus = -\left[\tilde{\boldsymbol{\mathcal{F}}}^a(\tilde{\mathbf{D}}\tilde{\mathbf{S}}-\tfrac{1}{2})\right]^\oplus + [\tilde{\boldsymbol{\mathcal{F}}}^a\tilde{\mathbf{D}}\tilde{\mathbf{S}}]^\oplus \\
&= -\left[\tilde{\boldsymbol{\mathcal{F}}}^a(\tilde{\mathbf{D}}\tilde{\mathbf{S}}-\tfrac{1}{2})\right]^\oplus + \left[(2\tilde{\boldsymbol{\mathcal{F}}}^a\tilde{\mathbf{D}}\tilde{\mathbf{S}} - \tilde{\boldsymbol{\mathcal{F}}}^a + \tilde{\mathbf{S}}\tilde{\mathbf{D}}\tilde{\boldsymbol{\mathcal{F}}}^a - \tilde{\mathbf{S}}\tilde{\mathbf{D}}\tilde{\boldsymbol{\mathcal{F}}}^a)\tilde{\mathbf{D}}\tilde{\mathbf{S}}\right]^\oplus \\
&= -\left[\tilde{\boldsymbol{\mathcal{F}}}^a(\tilde{\mathbf{D}}\tilde{\mathbf{S}}-\tfrac{1}{2})\right]^\oplus + \left[\left(\left[\tilde{\boldsymbol{\mathcal{F}}}^a(\tilde{\mathbf{D}}\tilde{\mathbf{S}}-\tfrac{1}{2})\right]^\oplus + [\tilde{\boldsymbol{\mathcal{F}}}^a\tilde{\mathbf{D}}\tilde{\mathbf{S}}]^\ominus\right)\tilde{\mathbf{D}}\tilde{\mathbf{S}}\right]^\oplus \\
&= \left[\left[\tilde{\boldsymbol{\mathcal{F}}}^a(\tilde{\mathbf{D}}\tilde{\mathbf{S}}-\tfrac{1}{2})\right]^\oplus(\tilde{\mathbf{D}}\tilde{\mathbf{S}}-\tfrac{1}{2})\right]^\oplus + \left[[\tilde{\boldsymbol{\mathcal{F}}}^a\tilde{\mathbf{D}}\tilde{\mathbf{S}}]^\ominus\tilde{\mathbf{D}}\tilde{\mathbf{S}}\right]^\oplus
\end{aligned} \tag{B14}$$

b.   Terms with $\tilde{\mathbf{D}}^a$

Inserting $\tilde{\boldsymbol{\lambda}}_a$ from Eq. (B10) into the remaining terms of Eq. (B7) and expanding, we obtain

$$\begin{aligned}
\left[\tilde{\boldsymbol{\mathcal{F}}}\tilde{\boldsymbol{\lambda}}_a\tilde{\mathbf{S}} - \tfrac{i}{2}\tilde{\mathbf{S}}(\tilde{\boldsymbol{\lambda}}_a\tilde{\mathbf{S}})\dot{}\,\right]^\oplus &= \left[\tilde{\boldsymbol{\mathcal{F}}}(\tilde{\mathbf{D}}^a\tilde{\mathbf{S}}\tilde{\mathbf{D}} - \tilde{\mathbf{D}}\tilde{\mathbf{S}}\tilde{\mathbf{D}}^a)\tilde{\mathbf{S}} - \tfrac{i}{2}\tilde{\mathbf{S}}\big((\tilde{\mathbf{D}}^a\tilde{\mathbf{S}}\tilde{\mathbf{D}} - \tilde{\mathbf{D}}\tilde{\mathbf{S}}\tilde{\mathbf{D}}^a)\mathbf{S}\big)\dot{}\,\right]^\oplus \\
&= \left[\tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}}^a\tilde{\mathbf{S}}\tilde{\mathbf{D}}\tilde{\mathbf{S}} - \tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}}\tilde{\mathbf{S}}\tilde{\mathbf{D}}^a\tilde{\mathbf{S}} - \tfrac{i}{2}\tilde{\mathbf{S}}(\tilde{\mathbf{D}}^a\tilde{\mathbf{S}})\dot{}\,\tilde{\mathbf{D}}\tilde{\mathbf{S}} \right. \\
&\quad \left. - \tfrac{i}{2}\tilde{\mathbf{S}}\tilde{\mathbf{D}}^a\tilde{\mathbf{S}}(\tilde{\mathbf{D}}\tilde{\mathbf{S}})\dot{} + \tfrac{i}{2}\tilde{\mathbf{S}}(\tilde{\mathbf{D}}\tilde{\mathbf{S}})\dot{}\,\tilde{\mathbf{D}}^a\tilde{\mathbf{S}} + \tfrac{i}{2}\tilde{\mathbf{S}}\tilde{\mathbf{D}}\tilde{\mathbf{S}}(\tilde{\mathbf{D}}^a\tilde{\mathbf{S}})\dot{}\,\right]^\oplus
\end{aligned} \tag{B15}$$

Reversing the order of the matrices in the second, fifth and sixth terms (allowed in $[\ldots]^\oplus$ when the non-differentiated matrices are Hermitian), and combining the second, fourth and fifth terms we get

$$\begin{aligned}
\left[\tilde{\boldsymbol{\mathcal{F}}}\tilde{\boldsymbol{\lambda}}_a\tilde{\mathbf{S}} - \tfrac{i}{2}\tilde{\mathbf{S}}(\tilde{\boldsymbol{\lambda}}_a\tilde{\mathbf{S}})\dot{}\,\right]^\oplus &= \left[\big(\tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}}^a\tilde{\mathbf{S}} - \tfrac{i}{2}\tilde{\mathbf{S}}(\tilde{\mathbf{D}}^a\tilde{\mathbf{S}})\dot{} - \tfrac{i}{2}(\tilde{\mathbf{S}}\tilde{\mathbf{D}}^a)\dot{}\,\tilde{\mathbf{S}}\big)\tilde{\mathbf{D}}\tilde{\mathbf{S}} \right. \\
&\quad \left. + \tilde{\mathbf{S}}\tilde{\mathbf{D}}^a\big(-\tilde{\mathbf{S}}\tilde{\mathbf{D}}\tilde{\boldsymbol{\mathcal{F}}} - \tfrac{i}{2}(\tilde{\mathbf{S}}\tilde{\mathbf{D}})\dot{}\,\tilde{\mathbf{S}} - \tfrac{i}{2}\tilde{\mathbf{S}}(\tilde{\mathbf{D}}\tilde{\mathbf{S}})\dot{}\big)\right]^\oplus
\end{aligned} \tag{B16}$$

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We may substitute the last terms using the TDSCF equation, Eq. (217),

$$
\begin{aligned}
\left[\tilde{\boldsymbol{\mathcal{F}}}\tilde{\boldsymbol{\lambda}}_a\tilde{\mathbf{S}}-\tfrac{i}{2}\tilde{\mathbf{S}}(\dot{\tilde{\boldsymbol{\lambda}}}_a\tilde{\mathbf{S}})\right]^{\oplus}
&= \left[(\tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}}^a\tilde{\mathbf{S}} - \tfrac{i}{2}\tilde{\mathbf{S}}(\tilde{\mathbf{D}}^a\tilde{\mathbf{S}}) - \tfrac{i}{2}(\tilde{\mathbf{S}}\dot{\tilde{\mathbf{D}}}{}^a\tilde{\mathbf{S}})\tilde{\mathbf{D}}\tilde{\mathbf{S}} + \tilde{\mathbf{S}}\tilde{\mathbf{D}}^a(-\tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}}\tilde{\mathbf{S}})\right]^{\oplus} \\
&= \left[\left[\tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}}^a\tilde{\mathbf{S}} - \tfrac{i}{2}\tilde{\mathbf{S}}(\tilde{\mathbf{D}}^a\tilde{\mathbf{S}})\right]^{\ominus}\tilde{\mathbf{D}}\tilde{\mathbf{S}}\right]^{\oplus} \quad (B17)
\end{aligned}
$$

where we recognize the second and third terms in the upper line of Eq. (B9).

c. The terms with $\tilde{\mathbf{S}}^a$

From the remaining terms in Eq. (B3), by using the idempotency and expanding, we obtain

$$
\left[-\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}\tilde{\boldsymbol{\mathcal{F}}} - \tfrac{i}{2}\tilde{\mathbf{S}}^a(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}) - \tfrac{i}{2}(\tilde{\mathbf{S}}^a\dot{\tilde{\mathbf{D}}})\tilde{\mathbf{S}}\right]^{\oplus} \quad (B18)
$$

$$
\begin{aligned}
&= \left[-\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}\tilde{\mathbf{S}}\tilde{\mathbf{D}}\tilde{\boldsymbol{\mathcal{F}}} - \tfrac{i}{2}\tilde{\mathbf{S}}^a(\tilde{\mathbf{D}}\tilde{\mathbf{S}}\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}) - \tfrac{i}{2}(\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}\tilde{\mathbf{S}}\dot{\tilde{\mathbf{D}}})\tilde{\mathbf{S}}\right]^{\oplus} \\
&= \left[-\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}\tilde{\mathbf{S}}\tilde{\mathbf{D}}\tilde{\boldsymbol{\mathcal{F}}} - \tfrac{i}{2}\tilde{\mathbf{S}}^a(\tilde{\mathbf{D}}\tilde{\mathbf{S}})\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}} - \tfrac{i}{2}\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}\tilde{\mathbf{S}}(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}})\right. \\
&\qquad\left. - \tfrac{i}{2}(\tilde{\mathbf{S}}^a\dot{\tilde{\mathbf{D}}})\tilde{\mathbf{S}}\tilde{\mathbf{D}}\tilde{\mathbf{S}} - \tfrac{i}{2}\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}(\tilde{\mathbf{S}}\dot{\tilde{\mathbf{D}}})\tilde{\mathbf{S}}\right]^{\oplus} \quad (B19)
\end{aligned}
$$

Combining the first, third and fifth terms, and substituting with the TDSCF equation, this becomes

$$
\left[-\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}\tilde{\boldsymbol{\mathcal{F}}} - \tfrac{i}{2}\tilde{\mathbf{S}}^a(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}) - \tfrac{i}{2}(\tilde{\mathbf{S}}^a\dot{\tilde{\mathbf{D}}})\tilde{\mathbf{S}}\right]^{\oplus}
$$

$$
\begin{aligned}
&= \left[\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}\left(-\tilde{\mathbf{S}}\tilde{\mathbf{D}}\tilde{\boldsymbol{\mathcal{F}}} - \tfrac{i}{2}(\mathbf{S}\dot{\mathbf{D}})\mathbf{S} - \tfrac{i}{2}\tilde{\mathbf{S}}(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}})\right)\right. \\
&\qquad\left. - \left(\tfrac{i}{2}\tilde{\mathbf{S}}^a(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}) + \tfrac{i}{2}(\tilde{\mathbf{S}}^a\dot{\tilde{\mathbf{D}}})\tilde{\mathbf{S}})\tilde{\mathbf{D}}\tilde{\mathbf{S}}\right]^{\oplus} \\
&= \left[\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}\left(-\tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}}\tilde{\mathbf{S}}\right) + \left(-\tfrac{i}{2}\tilde{\mathbf{S}}^a(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}) - \tfrac{i}{2}(\tilde{\mathbf{S}}^a\dot{\tilde{\mathbf{D}}})\tilde{\mathbf{S}})\tilde{\mathbf{D}}\tilde{\mathbf{S}}\right]^{\oplus} \\
&= \left[\left(-\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}\tilde{\boldsymbol{\mathcal{F}}} - \tfrac{i}{2}\tilde{\mathbf{S}}^a(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}) - \tfrac{i}{2}(\tilde{\mathbf{S}}^a\dot{\tilde{\mathbf{D}}})\tilde{\mathbf{S}})\tilde{\mathbf{D}}\tilde{\mathbf{S}}\right]^{\oplus} \quad (B20)
\end{aligned}
$$

Comparing with the first line of Eq. (B19), a factor $\tilde{\mathbf{D}}\tilde{\mathbf{S}}$ has appeared at the end of the bracket. This means that the corresponding term with $\tilde{\mathbf{D}}\tilde{\mathbf{S}}{-}\mathbf{1}$ is zero. Adding this zero term

$$
\left[-\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}\tilde{\boldsymbol{\mathcal{F}}} - \tfrac{i}{2}\tilde{\mathbf{S}}^a(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}) - \tfrac{i}{2}(\tilde{\mathbf{S}}^a\dot{\tilde{\mathbf{D}}})\tilde{\mathbf{S}}\right]^{\oplus}
$$

$$
\begin{aligned}
&= \left[(-\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}\tilde{\boldsymbol{\mathcal{F}}} - \tfrac{i}{2}\tilde{\mathbf{S}}^a(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}) - \tfrac{i}{2}(\tilde{\mathbf{S}}^a\dot{\tilde{\mathbf{D}}})\tilde{\mathbf{S}})\tilde{\mathbf{D}}\tilde{\mathbf{S}}\right]^{\oplus} \\
&\quad + \left[(-\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}\tilde{\boldsymbol{\mathcal{F}}} - \tfrac{i}{2}\tilde{\mathbf{S}}^a(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}) - \tfrac{i}{2}(\tilde{\mathbf{S}}^a\dot{\tilde{\mathbf{D}}})\tilde{\mathbf{S}})(\tilde{\mathbf{D}}\tilde{\mathbf{S}}{-}\mathbf{1})\right]^{\oplus} \quad (B21)
\end{aligned}
$$

followed by addition and subtraction

$$
\left[-\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}\tilde{\boldsymbol{\mathcal{F}}} - \tfrac{i}{2}\tilde{\mathbf{S}}^a(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}) - \tfrac{i}{2}(\tilde{\mathbf{S}}^a\dot{\tilde{\mathbf{D}}})\tilde{\mathbf{S}}\right]^{\oplus}
$$

$$
\begin{aligned}
&= \left[(-\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}\tilde{\boldsymbol{\mathcal{F}}} - \tfrac{i}{2}\tilde{\mathbf{S}}^a(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}) - \tfrac{i}{2}(\tilde{\mathbf{S}}^a\dot{\tilde{\mathbf{D}}})\tilde{\mathbf{S}})\tilde{\mathbf{D}}\tilde{\mathbf{S}}\right]^{\oplus} \\
&\quad + \left[(-\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}\tilde{\boldsymbol{\mathcal{F}}} - \tfrac{i}{2}\tilde{\mathbf{S}}^a(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}) - \tfrac{i}{2}(\tilde{\mathbf{S}}^a\dot{\tilde{\mathbf{D}}})\tilde{\mathbf{S}})(\tilde{\mathbf{D}}\tilde{\mathbf{S}}{-}\mathbf{1})\right]^{\oplus} \\
&\quad + \left[(\tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}}\tilde{\mathbf{S}}^a - \tfrac{i}{2}(\tilde{\mathbf{S}}\dot{\tilde{\mathbf{D}}})\tilde{\mathbf{S}}^a - \tfrac{i}{2}\tilde{\mathbf{S}}(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}{}^a))\tilde{\mathbf{D}}\tilde{\mathbf{S}}\right]^{\oplus} \\
&\quad - \left[(\tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}}\tilde{\mathbf{S}}^a - \tfrac{i}{2}(\tilde{\mathbf{S}}\dot{\tilde{\mathbf{D}}})\tilde{\mathbf{S}}^a - \tfrac{i}{2}\tilde{\mathbf{S}}(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}{}^a))\tilde{\mathbf{D}}\tilde{\mathbf{S}}\right]^{\oplus} \quad (B22)
\end{aligned}
$$

we can collect the terms into two double brackets,

$$
\left[-\tilde{\mathbf{S}}^a\tilde{\mathbf{D}}\tilde{\boldsymbol{\mathcal{F}}} - \tfrac{i}{2}\tilde{\mathbf{S}}^a(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}) - \tfrac{i}{2}(\tilde{\mathbf{S}}^a\dot{\tilde{\mathbf{D}}})\tilde{\mathbf{S}}\right]^{\oplus}
$$

$$
\begin{aligned}
&= \left[\left[\tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}}\tilde{\mathbf{S}}^a - \tfrac{i}{2}\tilde{\mathbf{S}}^a(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}) - \tfrac{i}{2}\tilde{\mathbf{S}}(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}{}^a)\right]^{\ominus}\tilde{\mathbf{D}}\tilde{\mathbf{S}}\right]^{\oplus} \\
&\quad - \left[\left[\tilde{\boldsymbol{\mathcal{F}}}\tilde{\mathbf{D}}\tilde{\mathbf{S}}^a - \tfrac{i}{2}(\tilde{\mathbf{S}}\dot{\tilde{\mathbf{D}}})\tilde{\mathbf{S}}^a - \tfrac{i}{2}\tilde{\mathbf{S}}(\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}{}^a)\right]^{\oplus}(\tilde{\mathbf{D}}\tilde{\mathbf{S}}{-}\tfrac{\mathbf{1}}{\mathbf{2}})\right]^{\oplus} \quad (B23)
\end{aligned}
$$

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in which all terms appear in Eq. (B9), except

$$
\begin{aligned}
\left[\left[\tfrac{i}{2}\tilde{\mathbf{S}}\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}^{a}\right]^{\oplus}(\tilde{\mathbf{D}}\tilde{\mathbf{S}}-\tfrac{1}{2})\right]^{\oplus} &= \left[\left[\tfrac{i}{2}\tilde{\mathbf{S}}\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}^{a}\right]^{\oplus}(\tilde{\mathbf{D}}\tilde{\mathbf{S}}-1)\right]^{\oplus} + \left[\tfrac{i}{2}\tilde{\mathbf{S}}\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}^{a}\right]^{\oplus} \\
&= \left[\tfrac{i}{2}(\tilde{\mathbf{S}}\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}^{a} - \dot{\tilde{\mathbf{S}}}^{a}\tilde{\mathbf{D}}\tilde{\mathbf{S}})(\tilde{\mathbf{D}}\tilde{\mathbf{S}}-1)\right]^{\oplus} + \left[\tfrac{i}{2}\tilde{\mathbf{S}}\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}^{a}\right]^{\oplus} \\
&= \left[\tfrac{i}{2}\tilde{\mathbf{S}}\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}^{a}(\tilde{\mathbf{D}}\tilde{\mathbf{S}}-1)\right]^{\oplus} + \left[\tfrac{i}{2}\tilde{\mathbf{S}}\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}^{a}\right]^{\oplus} = \left[\tfrac{i}{2}\tilde{\mathbf{S}}\tilde{\mathbf{D}}\dot{\tilde{\mathbf{S}}}^{a}\tilde{\mathbf{D}}\tilde{\mathbf{S}}\right]^{\oplus} \\
&= \mathbf{0}
\end{aligned}
\tag{B24}
$$

which after some manipulations turns out to be zero.

With this we have identified all terms in Eq. (B9), and thus verified that $\tilde{\boldsymbol{\lambda}}_a$ and $\tilde{\boldsymbol{\zeta}}_a$ given by Eqs. (B10) and (B11) indeed solve Eq. (B1).

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