Hartree-Fock and Kohn-Sham time-dependent response theory in a second-quantization atomic-orbital formalism suitable for linear scaling

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We present a second-quantization based atomic-orbital method for the computation of time-dependent response functions within Hartree-Fock and Kohn-Sham density-functional theories. The method is suited for linear scaling. Illustrative results are presented for excitation energies, one- and two-photon transition moments, polarizabilities, and hyperpolarizabilities for hexagonal BN sheets with up to 180 atoms. © 2008 American Institute of Physics. [DOI: 10.1063/1.2961039]

I. INTRODUCTION

Response-function theory describes how an observable responds when a molecular system is subjected to an external field. If the field is time dependent and oscillates with a given frequency, it causes the observable to oscillate and to become frequency dependent. The response of the observable may be expanded in powers of the field strength: the linear response of the system is determined by the linear response function, the quadratic response by the quadratic response function, and so on.1

Molecular response properties may be calculated from the response functions by specifying operators for the observable and for the applied fields. For example, the frequency-dependent polarizability and hyperpolarizability may be evaluated from the linear and quadratic response functions, respectively, by specifying the electric dipole-moment operator for both the observable and the oscillating electric fields (lasers). From the poles and residues of the response functions, additional molecular properties can be obtained, including excitation energies to electronically excited states, strength parameters for (multiphoton) transitions to these states, and excited-state properties.2 In view of the wealth of molecular information afforded by the response functions, it is important that they are evaluated efficiently. This is further substantiated by the fact that in density-functional theory—no doubt the method of choice nowadays for large systems—information about electronically excited states is only available through the response functions as these states cannot be obtained directly by an energy optimization.

In this paper, we describe how molecular response functions may be derived for Kohn-Sham density-functional theory3 using an atomic-orbital (AO) basis representation and the formalism of second quantization. In the derivation, we focus first on the response function for a Hartree-Fock state and then introduce the generalizations that are required for Kohn-Sham theory.

Time-dependent perturbation theory for Hartree-Fock states has a long history. The theory of first-order molecular properties was first given by Ball and McLacland, using the time-dependent Hartree-Fock approximation.4,5 Second- and higher-order molecular properties in Hartree-Fock theory were subsequently evaluated.6,7 Response-function theory as it is used today—where response functions are subjected to a pole and residue analysis to determine molecular properties for both ground and excited states and for transitions between these states—was developed in the 1980s (Ref. 2) and has since been used to calculate a large variety of molecular properties. The quasienery approach that was developed in the 1990s (Refs. 8 and 9) has tied response-function theory closely to energy-derivative techniques. Through the quasienery approach, response functions may be straightforwardly derived for both variational and nonvariational wave functions and used to calculate molecular properties for both ground and excited states, as well as transition properties between these states.2,9

The linear response eigenvalue equations exhibit, in general, a paired structure with pairs of eigenvalues with identical magnitude and opposite signs. Furthermore, it is sufficient to calculate the eigenvector for one eigenvalue of such a pair, as the eigenvector for the other eigenvalue may be obtained by a simple rearrangement.5 A method has previ-
ously been developed to exploit this pairing to obtain a fast
and reliable iterative scheme for solving linear response
equations.\textsuperscript{10}

Using an AO parametrization, Hartree-Fock and Kohn-
Sham response-function theory was described by Larsen
et al.\textsuperscript{11} in the language of first quantization. Here we present
the second-quantization analog of the derivation by Larsen
et al.\textsuperscript{11} correcting at the same time some inconsistencies
in their derivation concerning the pairing properties of the
generalized Hessian and metric matrices. The derivation of
Larsen et al.\textsuperscript{11} was recently used by Coriani et al.\textsuperscript{12} to obtain
a linear-scaling algorithm for solving the response eigen-
value and linear equations and for evaluating second-order
molecular properties. We extend the linear-scaling develop-
ment of Ref. 12 to the description of molecular properties
that may be obtained from the quadratic response function
and its residues. We furthermore analyze the involved mat-
rices and eigenvectors in detail to show how the eigenvector
pairing may be used to obtain effective iterative schemes in
the AO basis.

A linearly scaling time-independent response theory has
been presented by Niklasson, and co-workers\textsuperscript{13,14} within a
purification framework, and recently, Kussmann and Ochsen-
feld have also reported time-dependent Hartree-Fock and
Kohn-Sham calculations of the frequency-dependent polariz-
ability and hyper-polarizability using a linear-scaling
framework.\textsuperscript{15}

The theoretical foundation for time-dependent perturba-
tion theory as a means to obtain information about electroni-
cally excited states in Kohn-Sham density-functional theory
has been discussed by several authors.\textsuperscript{16–18} and a large variety
of molecular properties calculated—see, for example, Refs.
19–23. Accepting the standard approach, only minor modifi-
cations must be made to generalize time-dependent Hartree-
Fock theory to Kohn-Sham theory. Using the response-
function approach, the generalization has been described in
detail for properties that relate to linear, quadratic, and cubic
response functions in Refs. 24 and 25. We describe here the
modifications that are required in an AO-based parameteriza-
tion.

In the next section, we summarize those aspects of sec-
ond quantization that are relevant for deriving response func-
tions within a second-quantization AO-based formalism. In
Sec. III, we identify response functions with terms in the
expansion of the expectation value of a general observable.
Next, in Sec. IV, we derive equations for the first- and
second-order corrections to the wave function. In Sec. V, we
discuss the linear and quadratic response functions, their
residues, and their poles—in particular, we examine the pair-
ing of the excitation energies obtained from the linear re-
sponse function. In Sec. VI, the expressions required for a
linear-scaling implementation are derived. In Sec. VIII, the
Hartree-Fock theory is generalized to Kohn-Sham theory. Fi-
ally, features of the theory are illustrated by calculations on
boron nitride.

II. SECOND-QUANTIZATION-BASED AO THEORY

A. The density matrix

Consider a set of nonorthogonal atomic spin orbitals $\chi_{\mu}$
with the Hermitian metric $S$. The creation and annihilation
operators of the AOs fulfill the anticommutation relations:\textsuperscript{26}

\begin{equation}
[a_{\mu}^{\dagger}a_{\nu}]_{k} = 0,
\end{equation}

\begin{equation}
[a_{\mu}, a_{\nu}]_{k} = 0,
\end{equation}

\begin{equation}
[a_{\mu}^{\dagger}a_{\nu}]_{k} = S_{\nu\mu}.
\end{equation}

For a single-determinant state $|0\rangle$, the expectation values of
the creation and annihilation operators are given by

\begin{equation}
\Delta_{\mu\nu} = \langle 0 | a_{\mu}^{\dagger} a_{\nu} | 0 \rangle,
\end{equation}

where

\begin{equation}
|0\rangle = a_{1}^{\dagger}a_{2}^{\dagger}\cdots a_{n}^{\dagger}|\text{vac}\rangle
\end{equation}

and $a_{1}^{\dagger}a_{2}^{\dagger}\cdots a_{n}^{\dagger}$ refer to the set of orthonormal molecular spin
orbitals that are occupied in $|0\rangle$. Roman letters are used here
for the orthonormal molecular spin orbitals and Greek letters
for their atomic counterparts. The orthonormal spin orbitals
may be expanded in the AO basis as

\begin{equation}
a_{i}^{\dagger} = \sum_{\alpha} C_{\alpha i} a_{\alpha}^{\dagger},
\end{equation}

The elements of the density matrix $D$ are in the AO repre-
sentation given as

\begin{equation}D_{\mu\nu} = \sum_{i=1}^{n} C_{\mu i} C_{\nu i}^{\dagger},
\end{equation}

where the summation is over all occupied spin orbitals and
where the expansion coefficients are normalized over the
metric:

\begin{equation}C^{\dagger}SC = I.
\end{equation}

The density matrix $D$ is related to $\Delta$ by the transforma-
tion

\begin{equation}\Delta = S^{\dagger}D S^{\dagger}.
\end{equation}

To prove this transformation, we use

\begin{equation}[a_{\mu}^{\dagger}a_{\nu}]_{k} = \sum_{\alpha} C_{\nu\alpha} S_{\nu\alpha},
\end{equation}

\begin{equation}[a_{\mu}, a_{\nu}]_{k} = \sum_{\alpha} C_{\nu\alpha}^{\dagger} S_{\nu\alpha}
\end{equation}

to show that

\begin{equation}\langle \text{vac}| a_{1}^{\dagger} a_{2}^{\dagger} a_{3}^{\dagger} a_{4}^{\dagger} a_{5}^{\dagger} a_{6}^{\dagger} a_{6}^{\dagger} a_{5}^{\dagger} a_{4}^{\dagger} a_{3}^{\dagger} a_{2}^{\dagger} a_{1}^{\dagger}|\text{vac}\rangle
\end{equation}

\begin{equation}\quad = \langle \text{vac}| a_{1}^{\dagger} a_{2}^{\dagger} a_{3}^{\dagger} a_{4}^{\dagger} a_{5}^{\dagger} a_{6}^{\dagger} a_{6}^{\dagger} a_{5}^{\dagger} a_{4}^{\dagger} a_{3}^{\dagger} a_{2}^{\dagger} a_{1}^{\dagger}|\text{vac}\rangle + \sum_{\alpha\beta} C_{\alpha\beta} S_{\nu\alpha} C_{\nu\beta} S_{\nu\beta}.
\end{equation}
Repeated use of Eq. (11) shows that Eq. (9) is valid. Thus, the AO density-matrix element \( D_{\mu\nu} \) is only identical to the matrix element \( \Delta_{\mu\nu} \) in an orthonormal basis.

Turning our attention to the two-electron case, we show in Appendix A that the two-electron expectation value

\[
\Gamma_{\mu\nu\rho\sigma} = \langle 0 | a_{\mu}^\dagger a_{\rho}^\dagger a_{\sigma} a_{\nu} | 0 \rangle
\]  

(12)
decouples into products of expectation values of one-electron operators,

\[
\Gamma_{\mu\nu\rho\sigma} = \Delta_{\mu\nu} \Delta_{\rho\sigma} - \Delta_{\mu\nu} \Delta_{\rho\sigma}
\]  

(13)
This decoupling is similar to the decoupling of the two-electron density matrix in the molecular spin-orbital basis. It may therefore be argued that \( \Delta \) and \( \Gamma \) should be called the AO one- and two-electron density matrices, respectively. However, in keeping with standard nomenclature, we shall refer to \( D \) as the AO density matrix, and to \( \Delta \) and \( \Gamma \) as the matrices of expectation values of the one- and two-electron operators, respectively.

From the symmetry, trace, and idempotency properties of the one-electron density matrix, \(^{26,27}\)

\[
D^\dagger = D,
\]  

(14)
\[
\text{Tr} \, D S = N_{el},
\]  

(15)
\[
D S D = D,
\]  

(16)
we straightforwardly obtain the following relations for \( \Delta \):

\[
\Delta^\dagger = \Delta,
\]  

(17)
\[
\text{Tr} \, \Delta S^{-1} = N_{el},
\]  

(18)
\[
\Delta S^{-1} \Delta = \Delta.
\]  

(19)
Although Eqs. (15) and (16) are formally equivalent to Eqs. (18) and (19), the relations for the standard AO density matrix \( D \) are somewhat simpler to use as they contain the metric \( S \) as opposed to the relations for \( \Delta \), which contain the inverted metric \( S^{-1} \). We note that Eqs. (14)–(19) are necessary and sufficient conditions for a density matrix to represent a normalized single-determinant wave function.

**B. Transformations of the density matrix**

Next, we consider how \( \Delta \) changes for a corresponding change in the reference wave function \( |0\rangle \) in Eq. (5) described by the exponential operator

\[
\hat{T} = \exp(i \hat{k}),
\]  

(20)
where \( \hat{k} \) is a Hermitian one-electron operator,

\[
\hat{k} = \sum_{\mu\nu} \kappa_{\mu\nu} a_{\mu}^\dagger a_{\nu},
\]  

(21)
and \( \kappa \) is a Hermitian matrix. The transformed wave function may be expressed as

\[
|\tilde{0}\rangle = \exp(i \hat{k}) |0\rangle = \exp(i \hat{k}) a_{j}^\dagger \cdots a_{i}^\dagger |\text{vac}\rangle
\]
\[
= a_{i}^\dagger a_{j}^\dagger \cdots a_{r}^\dagger |\text{vac}\rangle,
\]  

(22)
where we have introduced the transformed creation operators

\[
\tilde{a}_{\mu}^\dagger = \exp(i \hat{k}) a_{\mu}^\dagger \exp(-i \hat{k})
\]  

(23)
which satisfy the same anticommutation relations as the untransformed operators

\[
[\tilde{a}_{\mu}, \tilde{a}_{\nu}] = [\exp(i \hat{k}) a_{\mu}^\dagger \exp(-i \hat{k}), \exp(i \hat{k}) a_{\nu} \exp(-i \hat{k})] = \exp(i \hat{k}) [a_{\mu}^\dagger a_{\nu}, \exp(-i \hat{k})] = \delta_{\mu\nu},
\]  

(24)
The exponential operators of Eq. (20) therefore represent the manifold of operators that conserve the metric \( S \).

Using the Hausdorff expansion\(^{26}\) and the anticommutation relation of Eq. (1), the transformed creation operators can be related to the untransformed ones as

\[
\tilde{a}_{\mu}^\dagger = a_{\mu}^\dagger + i [\hat{k}, a_{\mu}^\dagger] = \frac{1}{2} [\hat{k}, [\hat{k}, a_{\mu}^\dagger]] + \cdots
\]
\[
= a_{\mu}^\dagger + i \sum_{\nu} (\kappa S)_{\mu\nu} a_{\nu}^\dagger - \frac{1}{2} \sum_{\nu} (\kappa S)_{\mu\nu}^2 a_{\nu}^\dagger + \cdots
\]
\[
= \sum_{\nu} \exp(i \kappa S)_{\mu\nu} a_{\nu}^\dagger,
\]  

(25)
In the special case where \( S = I \), \( \exp(i \kappa) \) represents a unitary transformation of the orbitals.

The expectation value of \( a_{\mu}^\dagger a_{\nu} \) for the transformed state becomes

\[
\tilde{\Delta}_{\mu\nu} = \langle \tilde{0} | \tilde{a}_{\mu}^\dagger \tilde{a}_{\nu} | \tilde{0} \rangle = \langle 0 | \exp(-i \hat{k}) a_{\mu}^\dagger \exp(i \hat{k}) \exp(-i \hat{k}) a_{\nu} \exp(i \hat{k}) | 0 \rangle.
\]  

(26)
Using Eqs. (23) and (25), we straightforwardly obtain

\[
\exp(-i \hat{k}) a_{\mu}^\dagger \exp(i \hat{k}) = \sum_{\sigma} \exp(-i \kappa S)_{\sigma\mu} a_{\sigma}^\dagger,
\]  

(27a)
\[
\exp(-i \hat{k}) a_{\nu} \exp(i \hat{k}) = \sum_{\sigma} \exp(i \kappa S)_{\nu\sigma} a_{\sigma}.
\]  

(27b)
The insertion of these expressions into Eq. (26) gives

\[
\tilde{\Delta} = \exp(-i S^T \kappa^T) \Delta \exp(i S^T \kappa^T),
\]  

(28)
which describes how \( \Delta \) transforms for a transformation of the reference state. If \( \Delta \) fulfills Eqs. (17)–(19), then so does \( \tilde{\Delta} \) defined in Eq. (26), as demonstrated in Appendix B. We conclude that \( \Delta \) fulfills Eqs. (17)–(19) and that \( \exp(i \hat{k}) |0\rangle \) is a normalized single-determinant wave function. It may also be shown that all matrices fulfilling Eqs. (17)–(19) may be obtained by an appropriate choice of \( \kappa \), so the transformation of Eq. (22) constitutes a complete parametrization. Note that the matrix \( \kappa \) should comply with the projection relation \( \kappa = \mathbb{P} (\kappa) = \mathbb{P} \kappa \mathbb{Q}^\dagger + \mathbb{Q} \kappa \mathbb{P}^\dagger \), where \( \mathbb{P} = DS \) and \( \mathbb{Q} = I - DS \), so as to eliminate redundancies—that is, sets of nonvanishing parameters for which \( \tilde{\Delta}(\kappa) = \Delta \).
III. TIME-DEPENDENT EQUATIONS IN SECOND QUANTIZATION

A. Time-dependent wave functions and Hamiltonian

The electronic system is described by the Hamiltonian

\[ \hat{H} = \hat{H}_0 + \hat{V}(t) + \hat{W}(t), \]  

where \( \hat{H}_0 \) is the unperturbed operators, whereas \( \hat{V}(t) \) and \( \hat{W}(t) \) are first- and second-order perturbations that describe how the system interacts with the applied field. At \( t = -\infty \), no field is present and no perturbations appear in the Hamiltonian. For \( t > -\infty \), the fields are slowly applied according to the adiabatic approximation

\[ \hat{V}(t) = \int_{-\infty}^{\infty} \hat{V}(\omega) \exp[-i\omega t] d\omega, \]  

\[ \hat{W}(t) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \hat{W}(\omega_1, \omega_2) \times \exp[-i(\omega_1 + \omega_2 + 2\epsilon)t] d\omega_1 d\omega_2, \]

where \( \epsilon \) is a real positive infinitesimal that ensures \( \hat{V}(t = -\infty) = 0 \). The perturbations are required to be Hermitian, so we have the relations

\[ \hat{V}(\omega)^\dagger = \hat{V}(-\omega), \]  

\[ \hat{W}(\omega_1, \omega_2)^\dagger = \hat{W}(\omega_2, \omega_1). \]

We further require that \( \hat{W} \) is symmetric in the two frequencies:

\[ \hat{W}(\omega_1, \omega_2) = \hat{W}(\omega_2, \omega_1). \]

In response to these perturbations, the wave function changes,

\[ |\tilde{0}\rangle = \exp(i\hat{\kappa}(t))|0\rangle, \]

and we shall use this dependence to calculate the time dependence of expectation values induced by the perturbations. We assume that the unperturbed system is described by an optimized single-determinant wave function \( |0\rangle \), for which the first-order variation of the energy \( \langle 0|\hat{H}_0|0\rangle \) vanishes. Expansion of the expectation value of the Hamiltonian operator as

\[ \langle \tilde{0}|\hat{H}_0|\tilde{0}\rangle = \langle 0|\hat{H}_0|0\rangle - i\{\langle 0|\hat{\kappa}, \hat{H}_0|0\rangle + \frac{\hbar^2}{2}\{\langle 0|\hat{\kappa}, \hat{\kappa}, \hat{H}_0|0\rangle\} \]

\[ - \frac{\hbar^3}{3!}\{\langle 0|\hat{\kappa}, \hat{\kappa}, \hat{\kappa}, \hat{H}_0|0\rangle\} + O(\hat{\kappa}^4) \]

then yields that the optimized state satisfies the stationary condition

\[ \frac{d}{d\kappa_{\mu\nu}} \langle \tilde{0}|\hat{H}_0|\tilde{0}\rangle \mid_{\kappa = 0} = i(0)|\hat{H}_0, a^\dagger_\mu a_\nu|0\rangle = 0. \]

We shall now consider how expectation values are affected by time-dependent perturbations.

B. The linear and quadratic response functions

The linear and quadratic response functions describe the first- and second-order correction to the expectation value of a given (time-independent) operator \( \hat{A} \) when the system is subjected to a perturbation. To determine the linear and quadratic response functions, we begin by considering the time dependence of the expectation value \( \langle \tilde{0}|\hat{A}|\tilde{0}\rangle \) of a one-electron operator \( \hat{A} \), noting that, for this purpose, we only need to expand the wave function \( |\tilde{0}\rangle \) of Eq. (22) to second order in the external perturbation:

\[ \hat{\kappa}(t) = \hat{\kappa}^{(1)}(t) + \hat{\kappa}^{(2)}(t) + \cdots. \]

The zero-order term \( \hat{\kappa}^{(0)} \) does not contribute since the unperturbed wave function \( |0\rangle \) satisfies the stationarity conditions Eq. (35). To second order, we obtain the expansion

\[ \langle \tilde{0}|\hat{A}|\tilde{0}\rangle = \langle 0|\hat{A}|0\rangle - i\{\langle 0|\hat{\kappa}^{(1)}(t), \hat{A}|0\rangle \}
\]

\[ - \frac{1}{2}\{\langle 0|\hat{\kappa}^{(1)}(t), \hat{\kappa}^{(1)}(t), \hat{A}|0\rangle \}
\]

\[ - i\{\langle 0|\hat{\kappa}^{(2)}(t), \hat{A}|0\rangle \}. \]

Since the response functions are defined in the frequency domain, we introduce the wave-function corrections in the frequency domain. By analogy with Eq. (30), we write

\[ \hat{\kappa}^{(1)}(t) = \int_{-\infty}^{\infty} \hat{\kappa}^{(1)}(\omega) \exp[-i\omega t] d\omega, \]

\[ \hat{\kappa}^{(2)}(t) = \int \int_{-\infty}^{\infty} \hat{\kappa}^{(2)}(\omega_1, \omega_2) \times \exp[-i(\omega_1 + \omega_2 + 2\epsilon)t] d\omega_1 d\omega_2, \]

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

\[ \hat{\kappa}^{(2)}(\omega_1, \omega_2) = \hat{\kappa}^{(2)}(\omega_2, \omega_1). \]

Inserting the frequency expansions of the wave-function corrections of Eq. (38) into Eq. (37), we obtain

\[ \langle \tilde{0}|\hat{A}|\tilde{0}\rangle = \langle 0|\hat{A}|0\rangle - i \int_{-\infty}^{\infty} \{\langle 0|\hat{\kappa}^{(1)}(\omega), \hat{A}|0\rangle \}
\]

\[ \times \exp[-i(\omega + \epsilon)t] d\omega \]

\[ - \frac{1}{2} \int \int_{-\infty}^{\infty} \{\langle 0|\hat{\kappa}^{(1)}(\omega_1), \hat{\kappa}^{(1)}(\omega_2), \hat{A}|0\rangle \}
\]

\[ \times \exp[-i(\omega_1 + \omega_2 + 2\epsilon)t] d\omega_1 d\omega_2 \]

\[ - i \int \int_{-\infty}^{\infty} \{\langle 0|\hat{\kappa}^{(2)}(\omega_1, \omega_2), \hat{A}|0\rangle \}
\]

\[ \times \exp[-i(\omega_1 + \omega_2 + 2\epsilon)t] d\omega_1 d\omega_2. \]

The integrand in the double commutator expression of Eq. (40) may be symmetrized in the integration variables \( \omega_1 \) and \( \omega_2 \), using the operator \( P_{12} \), which creates the different permutations of the frequencies \( \omega_1 \) and \( \omega_2 \).
and second-order corrections are derived. Comparing Eq. (40) with the formal expansion of an expectation value in terms of response functions,1

\[
\langle 0 | \hat{A} | 0 \rangle = \langle 0 | \hat{A} | 0 \rangle + \int \int_{-\infty}^{\infty} \langle \hat{A} ; \hat{V}(\omega) \rangle_{\omega} \exp[(-i\omega + e)t]d\omega + \int \int_{-\infty}^{\infty} \langle \hat{A} ; \hat{W}(\omega_1, \omega_2) \rangle_{\omega_1, \omega_2} \times \exp[(-i(\omega_1 + \omega_2) + 2e)t]d\omega_1 d\omega_2 + \frac{1}{2} \int \int_{-\infty}^{\infty} \langle \hat{A} ; \hat{V}(\omega_1, \hat{V}(\omega_2)) \rangle_{\omega_1, \omega_2} \times \exp[(-i(\omega_1 + \omega_2) + 2e)t]d\omega_1 d\omega_2,
\]

we may identify the linear response function,

\[
\langle \hat{A} ; \hat{V}(\omega) \rangle_{\omega} = -i\langle 0 | [\hat{A}^{(1)}(\omega) , \hat{A}^{(1)}] | 0 \rangle,
\]

and the sum of a linear response function and a quadratic response function,

\[
\langle \hat{A} ; \hat{W}(\omega_1, \omega_2) \rangle_{\omega_1, \omega_2} + \frac{1}{2} \langle \hat{A} ; \hat{V}(\omega_1, \hat{V}(\omega_2)) \rangle_{\omega_1, \omega_2} = -\frac{1}{2} P_{12}(0[[\hat{A}^{(1)}(\omega_1) , [\hat{A}^{(1)}(\omega_2) , \hat{A}^{(1)}]] | 0) - i\langle 0 | [\hat{A}^{(2)}(\omega_1, \omega_2) , \hat{A}^{(1)}] | 0 \rangle.
\]

We shall later see how the linear and quadratic response functions in Eq. (43) may be separated. The response of the system to a given perturbation can be determined from the wave-function correction of \( \hat{k} \). In the next section, the first- and second-order corrections are derived.

**IV. FORM AND SOLUTION OF THE TIME-DEPENDENT EQUATIONS**

**A. Equations for the time development of the reference state**

In this section, we first discuss the equations for determining the time-dependent parameters \( \kappa(t) \) and then derive the equations for determining the first- and second-order corrections of Eq. (36). We begin by rewriting \( \hat{k} \) in component form,

\[
\hat{k} = \sum_{\mu > \nu} (\kappa_{\mu \nu} a^{\dagger}_{\mu} a_{\nu} + \kappa^{\dagger}_{\mu \nu} a^{\dagger}_{\nu} a_{\mu}) + \sum_{\mu} \kappa_{\mu \mu} a^{\dagger}_{\mu} a_{\mu},
\]

where the single-excitation operators \( a^{\dagger}_{\mu} a_{\nu} \) have been divided into a set of AO excitations \( \mu > \nu \) and a set of AO deexcitations \( \mu < \nu \). As the AO excitations and deexcitations are formally equivalent, this division has no physical significance but will prove important when the paired structure of the response equations is investigated. Note that, in the AO representation, it is not possible to omit the diagonal operators \( a^{\dagger}_{\mu} a_{\mu} \) (the number operators) as done in the molecular-orbital (MO) representation, where these operators may be viewed as providing phase factors to be absorbed in the MO coefficients.2 In Ref. 11, the diagonal operators were mistakenly assumed to vanish although, when the code was written,12 no such assumption was made and the working equations and results are therefore valid.

For the further development, it is convenient to collect the operators of \( \hat{k} \) in a vector:

\[
\Lambda = \begin{pmatrix} Q \\ D \\ \bar{Q} \end{pmatrix}, \quad \Lambda^{\dagger} = (Q^{\dagger} D^{\dagger} \bar{Q}),
\]

where the three classes of operators are defined as

\[
Q^{\mu}_{\nu} = a^{\dagger}_{\mu} a_{\nu}, \quad \mu > \nu,
\]

\[
D^{\mu}_{\nu} = a^{\dagger}_{\mu} a_{\nu},
\]

\[
\bar{Q} = a^{\dagger}_{\mu} a_{\mu}, \quad \mu > \nu.
\]

The parameters of \( \kappa \) may similarly be arranged in a vector

\[
\alpha^{(i)} = \begin{pmatrix} \kappa^{(i)}_{\mu \nu} \\ \kappa^{(i)}_{\mu \nu} \\ \kappa^{(i)}_{\mu \nu} \end{pmatrix}, \quad \mu > \nu,
\]

such that \( \kappa^{(i)} = \alpha^{(i)} , \Lambda = \Lambda^{\dagger} \cdot \alpha^{(i)} \). The superscript \((i)\) here indicates the order of the external perturbation, see Eq. (36). The diagonal elements \( \kappa_{\mu \mu} \) have only a real component due to the Hermiticity of \( \kappa \).

Likewise, to study the time evolution of \( |\bar{0}\rangle \) in the presence of the time-dependent perturbation, we introduce the transformed operator basis

\[
\bar{\Lambda} = \begin{pmatrix} \bar{Q} \\ \bar{D} \\ \bar{\bar{Q}} \end{pmatrix}, \quad \bar{\Lambda} = (\bar{Q}^{\dagger} \bar{D}^{\dagger} \bar{\bar{Q}}),
\]

where

\[
\bar{Q}^{\mu}_{\nu} = \exp(i\kappa(t))Q^{\mu}_{\nu} \exp(-i\kappa(t))
\]

and similarly for \( \bar{D}^{\mu}_{\nu}, \bar{\bar{Q}}^{\mu}_{\nu} \). The time evolution of \( |\bar{0}\rangle \) may now be determined by invoking Ehrenfest’s theorem for the transformed operators of \( \bar{\Lambda} \),

\[
\frac{d}{dt} \langle \bar{0} | \bar{\Lambda} | \bar{0} \rangle = i\langle \bar{0} | \frac{d}{dt} \bar{\Lambda} | \bar{0} \rangle + \langle \bar{0} | [\bar{\Lambda} , \bar{\bar{H}} + \bar{\bar{V}}(t) + \bar{\bar{W}}(t)] | \bar{0} \rangle.
\]

This choice of operator simplifies the Ehrenfest theorem since the expectation value of \( \bar{\Lambda} \) is time independent:

\[
\frac{d}{dt} \langle \bar{0} | \bar{\Lambda} | \bar{0} \rangle = \frac{d}{dt} \langle \bar{0} | \Lambda | \bar{0} \rangle = 0
\]

yielding
The Ehrenfest theorem results in a set of nonlinear equations that determine the time evolution of $\vec{r}(t)$. In the next section, we solve the Ehrenfest equations order by order in the parameters $\hat{r}(t)$. However, we first make a comment on notation. The supermatrix notation introduced above for collecting all AO excitation operators into a vector is essential for simplifying our subsequent derivations. In the remainder of this paper, we adopt Italic boldface type to represent vectors and matrices in the supermatrix notation, keeping Roman boldface type to describe vectors and matrices in conventional matrix-vector notation. For example, $\mathbf{b}$ and $\mathbf{c}$ represent two vectors in the supermatrix notation, whereas $\mathbf{b}^T \mathbf{c} = \Sigma_{\mu j} \rho_{\mu \nu}^{j} = \Sigma_{\mu} \rho_{\mu \nu} \rho_{\nu \mu} = \text{Tr}(\mathbf{b}^T \mathbf{c})$.

### B. Expansion of the time-dependent equations in the external perturbation

To obtain an order-by-order expansion of Eq. (54), we first recognize that the time-derivative term in Eq. (54) may be expressed as

$$i\langle 0 | \left( \frac{\partial}{\partial t} \hat{\Lambda} \right) | \vec{0} \rangle = -\langle 0 | [\hat{\Lambda}, \hat{\Lambda}] | 0 \rangle - \frac{i}{2} \langle 0 | [\hat{\Lambda}^2] | 0 \rangle + \mathcal{O}(\hat{r}^3) \tag{55}$$

as shown in Appendix C. Expanding Eq. (54) in orders of the external perturbation, using Eq. (36), and collecting the terms linear in the perturbation, we obtain the first-order time-dependent equations

$$i\langle 0 | \left[ \hat{\Lambda}, \hat{\rho}^{(1)} \right] | 0 \rangle - \langle 0 | [\hat{\Lambda}, \hat{\rho}^{(1)}] | \vec{0} \rangle = -i\langle 0 | [\hat{\Lambda}, \hat{w}(t)] | 0 \rangle. \tag{56}$$

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

$$\frac{i}{2} \langle 0 | [\hat{\Lambda}, \hat{\rho}^{(2)}] | 0 \rangle - \langle 0 | [\hat{\Lambda}, \hat{\rho}^{(2)}] | \vec{0} \rangle \tag{57}$$

$$= i\langle 0 | [\hat{\Lambda}, \hat{w}(t)] | 0 \rangle - \frac{1}{2} \langle 0 | [\hat{\Lambda}, [\hat{\Lambda}, \hat{\rho}^{(1)}]] | 0 \rangle + \langle 0 | [\hat{\Lambda}, \hat{w}(t)] | 0 \rangle + i\langle 0 | [\hat{\Lambda}, \hat{w}(t)] | \vec{0} \rangle \langle \vec{0} | [\hat{\Lambda}, \hat{w}(t)] | 0 \rangle.$$

### C. The first-order equations

The time-dependent equations, Eqs. (56) and (57), may be straightforwardly solved in frequency space. Using Eqs. (30) and (38), we obtain the first-order equation

$$\int_{-\infty}^{\infty} \exp[-i\omega + \epsilon t] \langle 0 | [\hat{\Lambda}, \hat{\rho}^{(1)}(\omega)] | 0 \rangle \, d\omega$$

$$= -\langle 0 | [\hat{\Lambda}, [\hat{\Lambda}, \hat{\rho}^{(1)}(\omega)]] | 0 \rangle \langle 0 | [\hat{\Lambda}, [\hat{\Lambda}, \hat{\rho}^{(1)}(\omega)]] | 0 \rangle \, d\omega \tag{58}$$

which gives the first-order response equations in the frequency space,

$$\omega \langle 0 | [\hat{\Lambda}, \hat{\rho}^{(1)}(\omega)] | 0 \rangle - \langle 0 | [\hat{\Lambda}, [\hat{\Lambda}, \hat{\rho}^{(1)}(\omega)]] | 0 \rangle \tag{59}$$

Inserting $\rho^{(1)} = \Lambda_{1} \cdot \mathbf{a}^{(1)}$, we obtain

$$\langle 0 | [\Lambda_{1}, [\hat{\Lambda}, \mathbf{a}^{(1)}(\omega)]] | 0 \rangle \tag{60}$$

Introducing the generalized Hessian and metric matrices

$$E_{ij}^{[2]} = \langle 0 | [\Lambda_{i}, [\hat{\Lambda}, \Lambda_{j}^{\dagger}]] | 0 \rangle \tag{61}$$

$$S_{ij}^{[2]} = \langle 0 | [\Lambda_{i}, \Lambda_{j}^{\dagger}] | 0 \rangle \tag{62}$$

and the property gradient vector

$$V_{j}^{[1]}(\omega) = \langle 0 | [\Lambda_{j}, \hat{\omega}(\omega)] | 0 \rangle \tag{63}$$

the first-order response equations [Eq. (60)] may, in (super) matrix notation, be expressed as

$$\mathbf{E}^{[2]} - \omega \mathbf{S}^{[2]} \mathbf{a}^{(1)} = i \mathbf{V}^{[1]}(\omega). \tag{64}$$

Note that $\mathbf{E}^{[2]}$ is the second derivative of the energy with respect to the electronic-structure parameters [see the second-order term in Eq. (34)] and thus positive definite for an optimized ground state.

### D. The second-order equations

Invoking Eqs. (30) and (38), we may express the second-order equations in the frequency domain as
Using the definitions of $E^{[2]}$ and $S^{[2]}$ from Eqs. (61) and (62), together with $\kappa^{[2]}(\omega_1, \omega_2) = \Lambda^{[2]} \alpha^{[2]}(\omega_1, \omega_2)$, we obtain

$$E^{[2]} = \begin{pmatrix}
\frac{1}{2} & 0 & 0 & 0 \\
0 & \frac{1}{2} & 0 & 0 \\
0 & 0 & \frac{1}{2} & 0 \\
0 & 0 & 0 & \frac{1}{2}
\end{pmatrix}$$

and

$$S^{[2]} = \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}$$

In Eq. (66), we have performed a symmetrization of the integration variables to obtain response parameters $\kappa^{[2]} \times (\omega_1, \omega_2)$ that are symmetric in the frequency indices.

The second-order equations may be expressed in a more compact form, inserting $\kappa^{(1)}(\omega) = \Lambda^{[2]} \alpha^{[1]}(\omega)$ and introducing the three-index supermatrices $E^{[3]}$ and $S^{[3]}$,

$$E^{[3]} = \begin{pmatrix}
\frac{1}{2} & 0 & 0 & 0 \\
0 & \frac{1}{2} & 0 & 0 \\
0 & 0 & \frac{1}{2} & 0 \\
0 & 0 & 0 & \frac{1}{2}
\end{pmatrix}$$

and

$$S^{[3]} = \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}$$

We furthermore introduce $V^{[2]}(\omega)$, obtained from $E^{[2]}$ in Eq. (61) by replacing $\hat{H}_0$ with $\hat{V}(\omega)$, and $W^{[1]}(\omega_1, \omega_2)$ obtained by replacing $\hat{V}(\omega)$ by $\hat{W}(\omega_1, \omega_2)$ in Eq. (63). The second-order equations can then be written as

$$\sum_j \left[ E^{[2]}_{ij} \right. - \left. (\omega_1 + \omega_2) S^{[2]}_{ij} \alpha^{[2]}(\omega_1, \omega_2) \right] = P_{12} \sum_k \left[ -iE^{[3]}_{ijk} - i\omega_1 S^{[3]}_{ijk} \alpha^{[1]}(\omega_1) \alpha^{[1]}(\omega_2) - V^{[2]}_{ij} \times (\omega_1) \alpha^{[1]}(\omega_1) \alpha^{[1]}(\omega_2) + iW^{[1]}_{ij}(\omega_1, \omega_2) \right].$$

We obtain

$$\langle \hat{A} \hat{B} \rangle_\omega = - A^{[1]}(\omega) B^{[1]}(\omega).$$

The linear response function may thus be calculated by solving one set of linear equations at each frequency,

$$N^{[\omega]}(\omega) = (E^{[2]} - \omega S^{[2]})^{-1} B^{[1]}.$$

B. Pairing of the excitation energies obtained from the linear response function

The excitation energies are identified as the poles of the linear response function of Eq. (71). The excitation energies are therefore solutions to the generalized eigenvalue problem

$$E^{[2]} X_\omega = S^{[2]} X_\omega \omega.$$

In the standard formulation of response theory in the MO basis, it is has been shown that the excitation energies are paired—that is, if $\omega_j$ is an eigenvalue, then $-\omega_j$ is also an eigenvalue. The standard MO proof of pairing cannot be applied directly in the AO basis due to the presence of the diagonal operators $D_j$. We first analyze here the structure of $E^{[2]}$ and $S^{[2]}$ and then show how the pairing is obtained in the AO basis. Note that when pairing was discussed in Ref. 11, consideration was not given to the diagonal operators $D_j$.

Partitioning of $\Lambda$ into the three classes [Eq. (46)–(48)], we may write $E^{[2]}$ as

$$E^{[2]} = \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}$$

The nine blocks in Eq. (74) can all be written in terms of the following four matrices:

$$A_{ij} = \langle 0 | [Q_j, \hat{H}_0, Q_i] | 0 \rangle,$$

$$B_{ij} = \langle 0 | [Q_j, \hat{H}_0, Q_i] | 0 \rangle,$$

$$C_{ij} = \langle 0 | [Q_j, \hat{H}_0, Q_i] | 0 \rangle,$$

$$D_{ij} = \langle 0 | [Q_j, \hat{H}_0, Q_i] | 0 \rangle.$$
To rewrite the blocks \( \langle 0 | [Q_f, \hat{H}_0, Q_f] | 0 \rangle \) and \( \langle 0 | [D_f, \hat{H}_0, Q_f] | 0 \rangle \), the Jacobi identity [see Eq. (C9)] and the stationarity condition Eq. (35) are used,

\[
\langle 0 | [D_f, \hat{H}_0, Q_f] | 0 \rangle = \langle 0 | [Q_f, \hat{H}_0, D_f] | 0 \rangle \quad \text{for} \quad f = 1, 2.
\]

Rewriting the remaining blocks in a similar way, we obtain

\[
\langle 0 | [D_f, \hat{H}_0, Q_f] | 0 \rangle = L^* f, \quad \text{for} \quad f = 1, 2.
\]

The matrix \( S^{[2]} \) may, in a similar way, be written as

\[
S^{[2]} = \begin{pmatrix}
\Sigma & \theta & \Delta \\
\theta^T & \epsilon & -\theta^T \\
-\Delta^* & -\theta^* & -\Sigma^*
\end{pmatrix},
\]

where

\[
\Sigma_{ij} = \langle 0 | [Q_f, Q_f] | 0 \rangle, \\
\Delta_{ij} = \langle 0 | [Q_f, D_f] | 0 \rangle, \\
T_{ij} = \langle 0 | [D_f, D_f] | 0 \rangle, \\
\epsilon_{ij} = \langle 0 | [D_f, D_f] | 0 \rangle.
\]

The block \( \epsilon \) containing two diagonal operators vanishes for real orbitals,

\[
\epsilon_{ij} = \langle 0 | [D_f, D_f] | 0 \rangle = 0.
\]

Note that \( E^{[2]} \) and \( S^{[2]} \) are both Hermitian. For \( E^{[2]} \), Hermiticity follows from the fact that \( A^\dagger = A, B^\dagger = B \), and \( N \) is real and symmetric. For \( S^{[2]} \), it occurs since \( \Sigma^\dagger = \Sigma, \Delta^\dagger = -\Delta^* \), and \( \epsilon \) is imaginary and antisymmetric.

Let us now assume that the vector

\[
X_f = \begin{pmatrix} Z \\ U \\ Y \end{pmatrix}
\]

is an eigenvector for Eq. (73) with eigenvalue \( \omega_f \),

\[
\begin{pmatrix}
A \\ L \\ B
\end{pmatrix} \begin{pmatrix} Z \\ U \\ Y \end{pmatrix} + \begin{pmatrix} \Sigma & \theta & \Delta \\ \theta^T & \epsilon & -\theta^T \\ -\Delta^* & -\theta^* & -\Sigma^* \end{pmatrix} \begin{pmatrix} Z \\ U \\ Y \end{pmatrix} = \omega_f \begin{pmatrix} Z \\ U \\ Y \end{pmatrix}
\]

We may now express Eq. (90) in component form as three sets of equations,

\[
AZ + LU + BY = \omega_f (\Sigma Z + \theta U + \Delta Y),
\]

\[
L^* Z + NU + L^* Y = \omega_f (\theta^* Z + \epsilon U - \theta^* Y),
\]

\[
B^* Z + L^* U + A^* Y = \omega_f (-\Delta^* Z - \theta^* U - \Sigma^* Y).
\]

We will now prove that the paired vector \( X_{-f} \) given as

\[
X_{-f} = \begin{pmatrix} Y^* \\ U^* \\ Z^* \end{pmatrix}
\]

is an eigenvector for Eq. (73) with eigenvalue \(-\omega_f \),

\[
\begin{pmatrix}
A \\ L \\ B
\end{pmatrix} \begin{pmatrix} Y^* \\ U^* \\ Z^* \end{pmatrix} - \begin{pmatrix} \Sigma & \theta & \Delta \\ \theta^* & \epsilon & -\theta^* \\ -\Delta^* & -\theta^* & -\Sigma^* \end{pmatrix} \begin{pmatrix} Y^* \\ U^* \\ Z^* \end{pmatrix} = -\omega_f \begin{pmatrix} Y^* \\ U^* \\ Z^* \end{pmatrix}
\]

In component form, Eq. (93) becomes

\[
AY^* + LU^* + BZ^* = -\omega_f (\Sigma Y^* + \theta U^* + \Delta Z^*),
\]

\[
L^* Y^* + NU^* + L^* Z^* = -\omega_f (\theta^* Y^* + \epsilon U^* - \theta^* Z^*),
\]

\[
B^* Y^* + L^* U^* + A^* Z^* = -\omega_f (-\Delta^* Y^* - \theta^* U^* - \Sigma^* Z^*).
\]

Complex conjugation of Eq. (94) reveals the equivalence of Eqs. (91a) and (94c), of Eqs. (91b) and (94b), and of Eqs. (91c) and (94a). Therefore, if \( X_f \) is an eigenvector with eigenvalue \( \omega_f \),

\[
E^{[2]} X_f = \omega_f S^{[2]} X_f,
\]

then \( X_{-f} \) is an eigenvector with eigenvalue \(-\omega_f \),

\[
E^{[2]} X_{-f} = -\omega_f S^{[2]} X_{-f}.
\]

C. The residue of the linear response functions

In the previous section, the solution vectors to the generalized eigenvalue problem [Eq. (73)] were shown to appear in pairs and Eqs. (96) and (95) may be combined as

\[
\frac{1}{\omega_f} E^{[2]} X_f = \text{sgn}(f) S^{[2]} X_f.
\]
For the molecular ground state, \( E^2 \) is positive definite and Eq. (97) may be viewed as a generalized Hermitian eigenvalue problem with \( E^2 \) as the metric. The eigenvectors \( X_f \) may therefore be chosen to be orthogonal with respect to the inner product induced by \( E^2 \),

\[
X^*_f E[X^2]X_f = \omega_f \delta_{gf}. \tag{98}
\]

From Eq. (97), we further obtain

\[
X^*_f S^{[2]} X_f = \text{sgn}(f) \delta_{gf}. \tag{99}
\]

The excitation vectors can be collected as the columns of an eigenvector matrix \( X \) with the positive-sign eigenvectors collected first, followed by the negative-sign eigenvectors,

\[
X = (\cdots \ X_f \cdots \ X_{-f} \cdots).
\]

In matrix form, Eqs. (98) and (99) become

\[
X^* E^{[2]} X = \begin{pmatrix} \omega_f & 0 \\ 0 & \omega_f \end{pmatrix},
\tag{101}
\]

\[
X^* S^{[2]} X = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix},
\tag{102}
\]

where \( \omega_f \) is a diagonal matrix with elements \( \omega_f, \omega_f, \cdots \) and \( I \) is the identity matrix. With this knowledge, we can write

\[
X^*[E^2 - \omega S^{[2]}] X = \begin{pmatrix} \omega_f - \omega I & 0 \\ 0 & \omega_f + \omega I \end{pmatrix},
\tag{103}
\]

Inversion of Eq. (103) gives

\[
X^{-1} [E^2 - \omega S^{[2]}]^{-1} (X^*)^{-1} = \begin{pmatrix} (\omega_f - \omega I)^{-1} & 0 \\ 0 & (\omega_f + \omega I)^{-1} \end{pmatrix}.
\tag{104}
\]

Multiplication from the left with \( X \) and from the right with \( X^* \) gives the diagonal representation

\[
(E^2 - \omega S^{[2]})^{-1} = X \begin{pmatrix} (\omega_f - \omega I)^{-1} & 0 \\ 0 & (\omega_f + \omega I)^{-1} \end{pmatrix} X^*,
\tag{105}
\]

which, in component form, may be expressed as

\[
(E^2 - \omega S^{[2]})^{-1} = \sum_f (X_f(\omega_f - \omega)^{-1} X_f^* + X_{-f}(\omega_f + \omega)^{-1} X_{-f}^*).
\tag{106}
\]

The residue may be calculated by inserting Eq. (105) into the linear response function [Eq. (71)] and taking the limit

\[
\lim_{\omega \to \omega_f} (\omega - \omega_f) \langle \hat{A} \hat{B} \rangle = - \sum_f A^{[1]} X_f (\omega_f - \omega)^{-1} X_f^* B^{[1]} + \sum_f A^{[1]} X_{-f} (\omega_f + \omega)^{-1} X_{-f}^* B^{[1]}.
\tag{107}
\]

From exact theory, \(^2\) we can identify the square of the transition-matrix element as

\[
\lim_{\omega \to \omega_f} (\omega - \omega_f) \langle \hat{A} \hat{B} \rangle = 0 \langle \hat{A} | g \rangle \langle g | \hat{B} \rangle. \tag{109}
\]

D. The quadratic response function

The quadratic response function is obtained by inserting the first- and second-order corrections [Eqs. (64) and (69)] into the expression for the quadratic response function in Eq. (43). The linear response function of Eq. (43) may be separated since

\[
\langle \langle \hat{A} \hat{V} \rangle \rangle_{\omega_1 + \omega_2} = - A^{[1]}(E^2 + (\omega_1 + \omega_2) S^{[2]})^{-1} W^{[1]}.
\tag{110}
\]

We next rename \( \hat{V}(\omega_1) \) and \( \hat{V}(\omega_2) \) as \( \hat{B} \) and \( \hat{C} \), respectively, and introduce the vector \( C^{[1]} \) in analogy with \( B^{[1]} \) of Eq. (70b). Finally, we generate \( B^{[2]} \) and \( C^{[2]} \) from the original definition of \( E^2 \) in Eq. (61) by replacing \( \hat{H}_0 \) with \( \hat{B} \) and \( \hat{C} \), respectively. Introducing further the matrix

\[
A^{[2]} = \frac{1}{2} \langle 0 | [A^1, [A^1, \hat{A}]] | 0 \rangle,
\tag{111}
\]

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

\[
\langle \langle \hat{A} \hat{B} \hat{C} \rangle \rangle_{\omega_1 + \omega_2} = \sum_{IJKL} A^{[2]}_{IJK} + A^{[2]}_{KLI} (E^2 + (\omega_1 + \omega_2) S^{[2]})^{-1} B^{[1]}_{IJK} (E^2 + (\omega_1 + \omega_2) S^{[2]})^{-1} C^{[1]}_{KLI}
\]

\[
+ \sum_{IJKL} A^{[1]}_{IJK} (E^2 + (\omega_1 + \omega_2) S^{[2]})^{-1} B^{[1]}_{IJK} (E^2 + (\omega_1 + \omega_2) S^{[2]})^{-1} C^{[1]}_{KLI}
\]

\[
+ \sum_{IJKL} A^{[1]}_{IJK} (E^2 + (\omega_1 + \omega_2) S^{[2]})^{-1} C^{[1]}_{IJKL} (E^2 + (\omega_1 + \omega_2) S^{[2]})^{-1} B^{[1]}_{KLI}
\]

\[
- \sum_{IJKLNM} A^{[1]}_{IJK} (E^2 + (\omega_1 + \omega_2) S^{[2]})^{-1} L^{[3]}_{KLI} + E^{[1]}_{KLI} - \omega_1 S^{[3]}_{KIJ} - \omega_2 S^{[3]}_{NLM} - \omega_3 S^{[3]}_{KLI} - \omega_4 S^{[3]}_{NLM} B^{[1]}_{KLI} - \omega_5 S^{[3]}_{LKM} B^{[1]}_{KLI} - \omega_6 S^{[3]}_{NLM} B^{[1]}_{KLI} - \omega_7 S^{[3]}_{LKM} B^{[1]}_{KLI}.
\tag{112}
\]
For a given pair of frequencies $\omega_1$ and $\omega_2$, the quadratic response function may thus be evaluated by solving three sets of first-order equations,

$$\begin{align*}
N^\circ(\omega_1 + \omega_2)^2 &= (E^{[2]} - (\omega_1 + \omega_2)S^{[2]})^{-1}A^{[1]}, \\
N^\circ(\omega_1) &= (E^{[2]} - \omega_1S^{[2]})^{-1}B^{[1]}, \\
N^\circ(\omega_2) &= (E^{[2]} - \omega_2S^{[2]})^{-1}C^{[1]},
\end{align*}
$$

which allow us to write the quadratic response function as

$$\left<\langle \hat{A}; \hat{B}, \hat{C} \rangle \right>_{\omega_1, \omega_2} = \sum_{IJ} (A_{iJ}^{[2]} + A_{Ji}^{[2]})N^\circ_i(\omega_1)N^\circ_j(\omega_2)$$

$$ + \sum_{IJ} N^\circ_i(\omega_1 + \omega_2)B_{iJ}^{[2]}N^\circ_j(\omega_2)$$

$$ + \sum_{IJ} N^\circ_i(\omega_1 + \omega_2)C_{iJ}^{[2]}N^\circ_j(\omega_1)$$

$$ - \sum_{IJK} N^\circ_i(\omega_1 + \omega_2)(E_{iJK}^{[3]})$$

$$ - \omega_1S_{iJK}^{[3]}N^\circ_j(\omega_1)N^\circ_k(\omega_2)$$

$$ - \sum_{IJK} N^\circ_i(\omega_1 + \omega_2)(E_{iJK}^{[3]} - \omega_2S_{iJK}^{[3]})N^\circ_j(\omega_2)N^\circ_k(\omega_1).$$

Equations similar to Eq. (114) have been reported in Refs. 2 and 28 for self-consistent field and multiconfiguration self-consistent field (MCSCF) wave functions.

The main challenge in the computation of quadratic response functions is the solution of the linear sets of response equations in Eq. (113). Coriani et al. have presented a linear-scaling implementation for solving response equations using an AO-based, preconditioned-conjugate-gradient method equivalent to the one that has previously been successfully used in the MO basis. The method exploits paired trial vectors to ensure that complex eigenvalues do not arise during the solution of the response equations. The response equations are preconditioned in the orthogonalized AO basis so as to reduce the conditioning number of $E^{[2]}$ and to make it more diagonal dominant.

### E. Residues of the quadratic response functions

The quadratic response function has simple poles where either the absolute value of the frequency parameters or their sum match an excitation energy, which is apparent from the singularity of the response vectors in Eq. (113). The residue of the response vectors may be obtained by introducing Eq. (106) in the singular response vector—for example, for $N^\circ(\omega_2)$ in Eq. (113c), we obtain

$$N^\circ(\omega_2) = \sum_g \left( X_g(\omega_g - \omega_2)^{-1}X^\dagger_g + X_{-g}(\omega_g + \omega_2)^{-1}X^\dagger_{-g} \right)C^{[1]}_g$$

(115)

giving the residue

$$\lim_{\omega_2 \to \omega} (\omega_2 - \omega_j)N^\circ(\omega_2) = -X_jX^\dagger_jC^{[1]}_j.$$  

We may therefore determine the residue of the quadratic response function,

$$\lim_{\omega_2 \to \omega_j} (\omega_2 - \omega_j)\langle \langle \hat{A}; \hat{B}, \hat{C} \rangle \rangle_{\omega_1, \omega_2} = -\sum_{IJ} (A_{iJ}^{[2]} + A_{Ji}^{[2]})N^\circ_i(\omega_1)\langle X_j \rangle_f(X^\dagger_j)_{C^{[1]}} - \sum_{IJ} N^\circ_i(\omega_j - \omega_1)B_{iJ}^{[2]}(X_j)_{f(X^\dagger_j)_{C^{[1]}}}

+ \sum_{IJ} N^\circ_i(\omega_j - \omega_1)(E_{iJK}^{[3]}) + \omega_1S_{iJK}^{[3]}N^\circ_j(\omega_1)\langle X_j \rangle_{K(X^\dagger)_{C^{[1]}}}

+ \sum_{IJK} N^\circ_i(\omega_j - \omega_1)(E_{iJK}^{[3]} - \omega_2S_{iJK}^{[3]})\langle X_j \rangle_{K(X^\dagger)_{C^{[1]}}}N^\circ_k(\omega_1).$$  

(117)

The residue may be used to obtain, for instance, the two-photon transition matrix element between the ground state $|0\rangle$ and an excited state $|f\rangle$.

$$\Gamma_{0-f}^{AB} = -\left[ \langle 0|\hat{A}|j(\hat{B} - (0)\hat{B}|0)\rangle_f + \langle 0|\hat{B}|j(\hat{A} - (0)\hat{A}|0)\rangle_f \right]_{\omega_j - \omega_1}$$

$$ = -\sum_{IJ} (A_{iJ}^{[2]} + A_{Ji}^{[2]})N^\circ_i(\omega_1)\langle X_j \rangle_f - \sum_{IJ} N^\circ_i(\omega_j - \omega_1)B_{iJ}^{[2]}(X_j)_{f} + \sum_{IJK} N^\circ_i(\omega_j - \omega_1)(E_{iJK}^{[3]}) + \omega_1S_{iJK}^{[3]}N^\circ_j(\omega_1)\langle X_j \rangle_{K}$$

$$ + \sum_{IJK} N^\circ_i(\omega_j - \omega_1)(E_{iJK}^{[3]} - \omega_2S_{iJK}^{[3]})\langle X_j \rangle_{K}N^\circ_k(\omega_1),$$  

(118)

where $\omega_j = \omega_1 + \omega_2$ and $\hat{A}$ and $\hat{B}$ refer to Cartesian components of the electronic dipole operator.
Double residues can also be calculated in a similar manner and allow for the identification of transition matrix elements between two excited states. Since

$$\lim_{\omega_1 \to -\omega_0} (\omega_1 + \omega_0) N^i(\omega_1) = X_{g}^i X_{g}^{\dagger i}$$,  

(119)

we can write a double residue of the quadratic response function as

$$\lim_{\omega_1 \to -\omega_0} (\omega_1 + \omega_0) \left[ \lim_{\omega_2 \to -\omega_0} (\omega_2 - \omega_0)(\tilde{\mathbf{A}}; \tilde{\mathbf{B}}, \tilde{\mathbf{C}})_{\omega_1, \omega_2} \right]$$

$$= - \sum_{IJ} (A^{[2]}_{ij} + A^{[3]}_{ij})(X_{g}^i X_{g}^{\dagger j})(X_{g}^{\dagger j} X_{g}^i) C^{(1)}(t) + \sum_{IJK} N^i_{ij}(\omega_j - \omega_g)(E^{[3]}_{IJK})$$

$$+ \omega_S^{[3]}(X_{g}^i X_{g}^{\dagger j})(X_{g}^{\dagger j} X_{g}^i) C^{(1)}(t) + \sum_{IJK} N^i_{ij}(\omega_j - \omega_g)(E^{[3]}_{IJK} - \omega_g S^{[3]}_{IJK})(X_{g}^{\dagger j} X_{g}^i) (X_{g}^{\dagger j} X_{g}^i)$$

(120)

and carry out the identification

$$\langle g|\tilde{\mathbf{A}}|f \rangle - \delta_{gf}(0)\langle \tilde{\mathbf{A}}|0 \rangle = \sum_{IJ} (A^{[2]}_{ij} + A^{[3]}_{ij})(X_{g}^i X_{g}^{\dagger j})(X_{g}^{\dagger j} X_{g}^i) - \sum_{IJK} N^i_{ij}(\omega_j - \omega_g)(E^{[3]}_{IJK}) + \omega_g S^{[3]}_{IJK}(X_{g}^{\dagger j} X_{g}^i)(X_{g}^{\dagger j} X_{g}^i)$$

$$- \sum_{IJK} N^i_{ij}(\omega_j - \omega_g)(E^{[3]}_{IJK} - \omega_g S^{[3]}_{IJK})(X_{g}^{\dagger j} X_{g}^i) (X_{g}^{\dagger j} X_{g}^i)$$.

(121)

VI. LINEAR-SCALING EXPRESSIONS FOR RESPONSE-FUNCTION EVALUATION

The linear and quadratic response functions and their residues derived in the previous sections are expressed in terms of derivatives with respect to the electronic-structure parameters of the energy ($E^{[1]}$, $E^{[2]}$, $E^{[3]}$), the metric ($\chi^{[2]}$, $\chi^{[3]}$), and property matrix elements ($A^{[1]}$, $A^{[2]}$, $B^{[1]}$, $B^{[2]}$). While the first derivatives are simple to evaluate and store on a computer, the evaluation and storage of the higher derivatives become more demanding. To avoid the evaluation and storage of these higher derivatives, it may be recognized that the higher derivatives themselves are not needed, only the transformation of these higher derivatives on trial vectors. These transformations may be evaluated at a cost similar to that for first derivatives. Furthermore, since the derivatives are expressed in the local AO basis, we may achieve linear scaling by exploiting the sparsity of the matrices when carrying out the matrix operations that enter the evaluation of the response functions. The technique has previously been used to achieve linear scaling when evaluating the linear response function and when solving the response eigenvalue and linear sets of equations.  

A. The first energy derivative

The derivatives with respect to the electronic-structure parameters of the energy ($E^{[1]}$, $E^{[2]}$, $E^{[3]}$) introduced in this paper are not derivatives obtained from a traditional Taylor expansion of the expectation value $\langle 0 | \hat{H}_0 | 0 \rangle$, but are rather defined through the expansion

$$\langle 0 | [\Delta_\mu, \hat{H}_0] | 0 \rangle = i \langle 0 | [\Delta_\mu, \hat{H}_0] | 0 \rangle + i \langle 0 | [\Delta_\mu, [\hat{H}_0, \tilde{k}]] | 0 \rangle$$

$$+ \frac{i^2}{2} \langle 0 | [\Delta_\mu, [[\hat{H}_0, \tilde{k}], \tilde{k}]] | 0 \rangle + \cdots$$

(122)

The first derivative

$$E^{[1]}_\mu = \langle 0 | [\Delta_\mu, \hat{H}_0] | 0 \rangle = 0$$

(124)

is zero according to the stationary condition, Eq. (35). For further development, we derive an explicit expression for $E^{[1]}_\mu$, which we may express as

$$E^{[1]}_\mu = \langle 0 | [\Delta_\mu, \hat{H}_0] | 0 \rangle = \langle 0 | [\Delta_\mu, \hat{H}_0] | 0 \rangle$$

$$+ \langle 0 | [\Delta_\mu, \hat{H}_0] | 0 \rangle$$

(125)

Introducing the generalized Fock matrix

$$\tilde{f}_{\alpha \beta} = \langle 0 | [\Delta_\mu, \hat{H}_0] | \alpha \beta \rangle$$

(126)

we obtain

$$E^{[1]}_\mu = \tilde{f}_{\alpha \beta} - \tilde{f}_{\alpha \beta}^*$$

(127)

In the nonorthogonal AO basis, $\hat{H}_0$ may be expressed as

$$\hat{H}_0 = \sum_{\mu \nu} (S^{-1} h S^{-1})_{\mu \nu} a_\mu^i a_\nu^j$$

$$+ \frac{1}{2} \sum_{\mu \nu \rho \sigma} \left( \sum_{\gamma \lambda} (S^{-1})_{\mu} (S^{-1})_{\nu} (S^{-1})_{\rho} (S^{-1})_{\sigma} \right)$$

$$\times a_\mu^i a_\nu^j a_\rho^k a_\sigma^l$$

(128)

where $h_{\gamma \lambda}$ (i.e., the elements of the matrix $h$) and $g_{\gamma \lambda}$ are given by

$$h_{\gamma \lambda} = \int \chi_\gamma^*(r) \left( -\frac{1}{2} \nabla^2 - \sum_A \frac{Z_A}{|r - r_A|} \right) \chi_\lambda(r) d\tau$$

(129)
$$g_{c_{\gamma\lambda}} = \int \int \chi_{c_{\gamma}^*}(r_1) \chi_{c_{\lambda}}(r_2) \chi_{c_{\gamma}^*}(r_1) \chi_{c_{\lambda}}(r_2) \frac{d \tau_1 d \tau_2}{r_{12}}. \quad (130)$$

Note that although the Hamiltonian contains the inverse metric $S^{-1}$, the working equations do not. Using the commutation relations

$$a_{\gamma}^\dagger [a_{\lambda} a_{\gamma}^\dagger a_{\mu} a_{\nu}] = S_{\gamma\lambda} a_{\mu}^\dagger a_{\nu}, \quad (131)$$

$$a_{\lambda}^\dagger [a_{\gamma} a_{\mu} a_{\lambda}^\dagger a_{\nu}] = S_{\lambda\gamma} a_{\mu}^\dagger a_{\nu} - S_{\gamma\lambda} a_{\mu}^\dagger a_{\nu}, \quad (132)$$

and Eq. (13), we may express the generalized Fock matrix as

$$f_{c} = \langle 0 | [a_{\gamma}^\dagger \hat{H}_0 a_{\lambda}] | 0 \rangle = (S^T D^T F^T)_{c}, \quad (133)$$

with the Fock matrix $F_0$ defined as

$$F_0 = F_0(D) = h + G(D) \quad (134)$$

and

$$G_{\mu\nu}(M) = \sum_{\rho\tau} M_{\rho\tau}(g_{\mu\rho\nu} - g_{\mu\nu\rho}). \quad (135)$$

The first derivative may therefore be written as

$$E^{[1]} = S^T D^T F_0^T - F_0^T D^T S^T = E^{[1]}.$$

**B. The second energy derivative**

The matrix $E^{[2]}$ by itself is not needed, only the linear transformations of $E^{[2]}$ on a trial vector $b$ are required,

$$\sigma_t = \sum_j E^{[2]}_{j} b_{j} = \sum_j \langle 0 | [\Lambda_{t} [\hat{H}_0, \Lambda_{j}^T]] | 0 \rangle b_{j}$$

$$= \langle 0 | [\Lambda_{t} [\hat{H}_0, \hat{b}]] | 0 \rangle. \quad (137)$$

To obtain the last equality, we have introduced the operator

$$\hat{b} = \sum_j \Lambda_{j}^T b_{j} = \sum_{\mu\nu} b_{\mu} a_{\nu}^\dagger a_{\nu}. \quad (138)$$

The commutator $[\hat{H}_0, \hat{b}]$ can be calculated using Eqs. (131) and (132) to obtain the one-index transformed Hamilton operator

$$\hat{H}^b = [\hat{H}_0, \hat{b}] = \sum_{\mu\nu} (S^{-1} \tilde{h} S^{-1})_{\mu\nu} a_{\mu}^\dagger a_{\nu}$$

$$+ \frac{1}{2} \sum_{\mu\nu\rho\tau} \left( \sum_{c_{\gamma\lambda}} (S^{-1})_{\mu\nu} (S^{-1})_{\gamma\lambda} (S^{-1})_{\rho\tau} (S^{-1})_{\lambda\sigma} \tilde{g}_{c_{\gamma\lambda}} \right)$$

$$\times a_{\mu}^\dagger a_{\rho}^\dagger a_{\sigma} a_{\nu}, \quad (139)$$

where $\tilde{h}_{c_{\gamma\lambda}}$ and $\tilde{g}_{c_{\gamma\lambda}}$ are one-index transformed integrals,

$$\tilde{h}_{c_{\gamma\lambda}} = \sum_a (-S_b)_{c_{\gamma}a} h_{a\gamma} + h_{\mu\nu}(b)_{a\gamma}, \quad (140)$$

$$\tilde{g}_{c_{\gamma\lambda}} = \sum_a (-S_b)_{c_{\gamma}a} g_{a\gamma\lambda} + g_{c_{\gamma}a\lambda}(b)_{a\gamma} + (-S_b)_{c_{\lambda}a\gamma}$$

$$+ g_{c_{\gamma}a\lambda}(b)_{a\lambda} \lambda \cdot \gamma \lambda. \quad (141)$$

A matrix expression for Eq. (137) may therefore be obtained by using Eqs. (139) and (140), recognizing that the Fock matrix in Eq. (136) should be replaced by the Fock matrix with one-index transformed integrals $\tilde{F}$, giving

$$\sigma = \langle 0 | [\Lambda_{t} [\hat{H}_0, \hat{b}]] | 0 \rangle = S^T D^T \tilde{F}^T - F^T D^T S^T = [S^T \tilde{F}^T]_{c}.$$ 

Note above the implicit definition of a “generalized” commutator

$$[A, B]_c = A C B - B A C. \quad (143)$$

Insertion of the one-index transformed integrals into $\tilde{F}$ gives

$$\tilde{F} = [F_0 S]_b + G([b, D]_c). \quad (144)$$

The linear transformation in Eq. (142) therefore becomes

$$\sigma = [S^T, [S^T, F^T_0 b]]_{c T} + [S^T, G]([b, D]_c)]_{c T}$$

$$= F^T_0 [b^T D^T]_{c T} S^T - S^T [b^T D^T]_{c T} F^T_0$$

$$+ G([D, b]_c) D^T S^T - S^T D^T G([D, b]_c), \quad (146)$$

where the stationarity condition $S^T D^T F_0^T - F_0^T D^T S^T = 0$ has been used to obtain the last equation.

Let us consider now the linear transformation of the paired vector—that is, of the $b^\dagger$ matrix. Using the identity

$$G(t)(M) = (G(M))^t = G(M)^t,$$

we see from Eq. (145) that

$$\langle \sigma^t \rangle_j = \sum_j E^{[2]}(b^\dagger)_{j}. \quad (148)$$

Therefore, if the linear transformation on a trial vector $b$ is known, then it is also known for the paired trial vector. This fact is used in the preconditioned-conjugate-gradient method to solve the linear equations Eq. (113) in an efficient way, see Ref. 12.

**C. The third energy derivative**

As for $E^{[2]}$, the matrix elements of $E^{[3]}$ are not required; we only need to evaluate the effect of $E^{[3]}$ on two trial vectors $b$ and $c$,

$$\sum_{JK} E^{[3]}_{jK} b_{j} c_{K} = \frac{1}{2} \sum_{JK} \langle 0 | [\Lambda_{t} [[[\hat{H}_0, \Lambda_j^T], \Lambda_K^T]] | 0 \rangle b_{j} c_{K}$$

$$= \frac{1}{2} \sum_{JK} \langle 0 | [\Lambda_{t} [[[\hat{H}_0, \hat{b}]], \hat{c}]] | 0 \rangle. \quad (149)$$

To facilitate its calculation, the two-index transformed Hamilton operator $\hat{H}^{bc}$ is introduced,

$$\hat{H}^{bc} = [[[\hat{H}_0, \hat{b}], \hat{c}]]$$

$$= \sum_{\mu\nu} (S^{-1} \tilde{h} S^{-1})_{\mu\nu} a_{\mu}^\dagger a_{\nu}$$

$$+ \frac{1}{2} \sum_{\mu\nu\rho\tau} \left( \sum_{c_{\gamma\lambda}} (S^{-1})_{\mu\nu} (S^{-1})_{\gamma\lambda} (S^{-1})_{\rho\tau} (S^{-1})_{\lambda\sigma} \tilde{g}_{c_{\gamma\lambda}} \right)$$

$$\times a_{\mu}^\dagger a_{\rho}^\dagger a_{\sigma} a_{\nu}, \quad (150)$$

with two-index transformed integrals.
\[ \tilde{h}_{\alpha \gamma} = \sum_{\alpha} (-S\mathbf{c})_{\alpha \gamma} + \tilde{h}_{\alpha \gamma}(\mathbf{c})_{\alpha \gamma}, \]  
\[ \tilde{g}_{\gamma \lambda \alpha} = \sum_{\alpha} (-S\mathbf{c})_{\alpha \gamma \lambda} + \tilde{g}_{\alpha \gamma \lambda}(\mathbf{c})_{\alpha \gamma \lambda}. \]  

Hence,
\[ \sum_{j,k} E_{j,k}^3 b_{j,k} = \frac{1}{2} \langle 0 | [\Lambda_1, \hat{H}_c^\alpha] | 0 \rangle \]

and
\[ E_{j,k}^3 b_{j,k} = \frac{1}{2} S^T \mathbf{D}' \mathbf{F}' - \mathbf{F}' \mathbf{D}' S^T = \frac{1}{2} [S^T, \mathbf{F}']_{D^T}, \]

where
\[ \bar{F} = [\bar{F}, S]_c + \tilde{G}([\mathbf{c}, \mathbf{D})_b, S]_c + [G([\mathbf{b}, \mathbf{D})_b, S]_c + [G([\mathbf{b}, \mathbf{D})_b, S]_c, \]

\[ E_{j,k}^3 b_{j,k} = \frac{1}{2} S^T [S^T, \mathbf{F}']_{D^T} + \frac{1}{2} S^T [S^T, \mathbf{G}([\mathbf{b}, \mathbf{D})_b, S]_c + \frac{1}{2} S^T [S^T, \mathbf{D}'_{[\mathbf{b}, \mathbf{D})_b, S]_c)_D^T. \]

\[ A_{\alpha}^1 = \mathbf{A}^T \mathbf{D}' \mathbf{S}^T - \mathbf{S}^T \mathbf{D}' \mathbf{A}^T, \]

\[ A_{\alpha}^2 = \frac{1}{2} [S^T, \mathbf{A}^T]_{D^T}. \]

The second and third derivatives of the metric matrix require multiple use of Eq. (131) but are otherwise straightforward,
\[ S^{(2)} b = S^T \mathbf{D}' b_{\alpha}^\gamma S^T, \]

\[ S^{(3)} b c = \frac{1}{2} S^T (P^T \mathbf{c}^T b_{\gamma}^\alpha S^T - [c^T b_{\gamma}^\alpha S^T P] S^T. \]

Note that both trial vectors are projected according to, for example, \[ \mathcal{P}(\mathbf{b}) = \mathbf{P}Q^\dagger + \mathbf{Q}P^\dagger. \] By exploiting the relationships \[ \mathbf{P}^\dagger \mathbf{P} = \mathbf{P}^\dagger \mathbf{P} = \mathbf{P}, \] \[ \mathbf{Q}^\dagger \mathbf{P} = \mathbf{P} \mathbf{Q}^\dagger = 0, \] and \[ \mathbf{Q}^\dagger \mathbf{P} \mathbf{S} = \mathbf{P} \mathbf{S} \mathbf{Q}^\dagger = 0, \] it can be shown that \[ S^{(2)} b c = 0. \] 

The transformations described above are the key computational steps of the response theory and consist entirely of matrix-algebra operations. Linear scaling can therefore be achieved for sufficiently large systems by exploiting sparsity.
\[
\langle 0 | [\hat{\mathcal{A}}, \hat{\mathcal{F}}] | 0 \rangle = \exp(i S^T \kappa^T) (\Delta (S^{-1})^T F^T - F (S^{-1})^T \Delta) \times \exp(-i \kappa^T S^T).
\]

To evaluate the left-hand side of Eq. (164), we first recognize that the transformed expectation value of the two-electron operator,

\[
\tilde{\Gamma}_{\mu \nu \rho \sigma} = \langle 0 | \hat{\mathcal{a}}_\mu \hat{\mathcal{a}}_\rho \hat{\mathcal{a}}_\sigma \hat{\mathcal{a}}_\nu | 0 \rangle = \Delta_{\mu \nu} \Delta_{\rho \sigma} - \Delta_{\mu \rho} \Delta_{\nu \sigma},
\]

decouples as \( \tilde{\Gamma} \). To see this, write \( \tilde{\Gamma} \) in terms of transformed operators as in Eq. (26), after which Eqs. (27a), (27b), and (13) can be used to obtain Eq. (167). Using Eq. (167), the left-hand side of Eq. (164) becomes

\[
\langle 0 | [\hat{\mathcal{A}}, \hat{\mathcal{H}}_0] | 0 \rangle = \exp(i S^T \kappa^T) (\Delta (S^{-1})^T h^T - h (S^{-1})^T \Delta) \times \exp(-i \kappa^T S^T) + i \kappa^T S^T \times \Delta (S^{-1})^T G^T(D) - G^T(D) (S^{-1}) \Delta \times \exp(-i \kappa^T S^T).
\]

Therefore, Eq. (164) is satisfied if the matrix elements of the Fock operator are identified as

\[
\mathbf{F}(\hat{\mathbf{D}}) = \mathbf{h} + \mathbf{G}(\hat{\mathbf{D}}).
\]

The Fock operator thus depends on the perturbation through the density matrix. In the absence of the perturbation, the Fock matrix in Eq. (169) is identical to Eq. (134), justifying the use of subscript 0 in Eq. (134).

### A. Order expansion of the Fock operator

To solve the Ehrenfest theorem order by order, we need to carry out an order expansion of \( \langle 0 | [\hat{\mathcal{A}}, \hat{\mathcal{F}}(\hat{\mathcal{D}})] | 0 \rangle \) where the Fock operator is defined through Eqs. (163) and (169). We therefore need to expand the Fock matrix Eq. (169) in orders of the perturbation. We therefore first expand the expectation value of the one-electron operator in orders of \( \kappa \),

\[
\tilde{\Delta}_J = \langle 0 | \Lambda_J | 0 \rangle + i \langle 0 | [\Lambda_J, \hat{\kappa}(t)] | 0 \rangle + \frac{i^2}{2} \langle 0 | [[\Lambda_J, \hat{\kappa}(t)], \hat{\kappa}(t)] | 0 \rangle + O(\kappa^3).
\]

Using \( \hat{\kappa}(t) = \sum J \lambda_J \alpha_J(t) \) (see Sec. IV), we then obtain

\[
\tilde{\Delta} = \Delta^{(0)} + i \sum J \Delta^{(1)}_J \alpha_J(t) + \frac{i^2}{2} \sum J K \Delta^{(2)}_{JK} \alpha_J(t) \alpha_K(t) + O(\kappa^3),
\]

where

\[
\Delta^{(0)} = \Delta = \langle 0 | \Lambda | 0 \rangle,
\]

\[
\Delta^{(1)}_J = \langle 0 | [\Lambda, \Lambda_J] | 0 \rangle,
\]

\[
\Delta^{(2)}_{JK} = \frac{i}{2} \left( \langle 0 | [[\Lambda, \Lambda_J], \Lambda_K] | 0 \rangle + \langle 0 | [[\Lambda, \Lambda_K], \Lambda_J] | 0 \rangle \right).
\]

Note that \( \Delta^{(2)}_{JK} \) is symmetric in the indices \( J \) and \( K \). The density matrix satisfies

\[
\mathbf{D} = \mathbf{S}^\dagger \mathbf{S}^{-1}.
\]

Introducing the notation

\[
\mathbf{D}^{(n)} = \mathbf{S}^{-1} \Delta^{(n)} \mathbf{S}^{-1}
\]

and expressing the density expansion in the frequency domain, we may write Eq. (175) as

\[
\tilde{\mathbf{D}} = \mathbf{D} + i \sum J \mathbf{D}^{(1)}_J \alpha_J^{(1)}(\omega) + i \sum J \mathbf{D}^{(1)}_J \alpha_J^{(2)}(\omega) + \frac{i^2}{2} \sum J K \mathbf{D}^{(2)}_{JK} \alpha_J^{(1)}(\omega_1) \alpha_K^{(1)}(\omega_2) + \cdots,
\]

where we have used Eq. (171). Insertion of \( \tilde{\mathbf{D}} \) in the Fock matrix in Eq. (169) then gives, to second order,

\[
\mathbf{F}(\tilde{\mathbf{D}}) = \mathbf{F}_0 + i \sum J \mathbf{G}(\mathbf{D}^{(1)}_J) \alpha_J^{(1)}(\omega) + \sum J \mathbf{G}(\mathbf{D}^{(1)}_J) \alpha_J^{(2)}(\omega_1, \omega_2) + \frac{i^2}{2} \sum J K \mathbf{G}(\mathbf{D}^{(2)}_{JK}) \alpha_J^{(1)}(\omega_1) \alpha_K^{(1)}(\omega_2) + \cdots,
\]

with \( \mathbf{F}_0 \) given in Eq. (134).

In conclusion, we have shown that an order expansion of Eq. (164) may be expressed as

\[
\langle 0 | [\hat{\mathcal{A}}, \hat{\mathcal{H}}_0] | 0 \rangle = \sum \langle 0 | [\hat{\mathcal{A}}, \hat{\mathcal{F}}^{(n)}] | 0 \rangle,
\]

where

\[
\hat{\mathcal{F}}^{(0)} = \sum_{\mu \nu} (S^{-1} \mathbf{F}_0(D) (S^{-1})_{\mu \nu} \alpha_{\mu} \alpha_{\nu},
\]

\[
\hat{\mathcal{F}}^{(1)} = i \sum_{\mu \nu J} (S^{-1} \mathbf{G}(\mathbf{D}_J^{(1)}) (S^{-1})_{\mu \nu} \alpha_J^{(1)}(\omega) \alpha_{\mu} \alpha_{\nu},
\]

\[
\hat{\mathcal{F}}^{(2)} = i \sum_{\mu \nu J K} (S^{-1} \mathbf{G}(\mathbf{D}_J^{(2)}) (S^{-1})_{\mu \nu} \alpha_J^{(1)}(\omega_1) \alpha_K^{(1)}(\omega_2) \alpha_{\mu} \alpha_{\nu} + \frac{i^2}{2} \sum_{\mu \nu J K} (S^{-1} \mathbf{G}(\mathbf{D}_J^{(2)}) (S^{-1})_{\mu \nu} \alpha_J^{(1)}(\omega_1) \alpha_K^{(1)}(\omega_2) \alpha_{\mu} \alpha_{\nu},
\]

In the absence of the perturbation, Eq. (179) reduces to the stationarity condition of Eq. (35),

\[
\langle 0 | [\hat{\mathcal{H}}_0, \alpha^\dagger J \alpha_J] | 0 \rangle = \langle 0 | [\hat{\mathcal{F}}_0(D), \alpha^\dagger J \alpha_J] | 0 \rangle = 0,
\]

with the Fock matrix \( \mathbf{F}_0(D) \) given in Eq. (134). The Fock matrix may also be obtained as the first derivative of the energy with respect to the density matrix:

\[
(\mathbf{F}_0(D))_{\mu \nu} = \frac{\partial E}{\partial D_{\mu \nu}} = \h_{\mu \nu} + \mathbf{G}_{\mu \nu}(\mathbf{D}).
\]

Note the order of the indices, which is significant for complex AO's. To prove Eq. (184), we write the first derivative of the energy with respect to the orbital parameter as

\[
\frac{\partial E}{\partial \lambda_J} = \int \mathbf{F}_0(D) \lambda_J \phi_{\lambda J} | \phi_{\lambda J} \rangle.
\]
\[
\frac{dE}{d\kappa_{\mu\nu}} = i\langle 0|\left[\hat{H}_0, a_{\mu}^\dagger a_{\nu}\right]|0\rangle \\
= i\langle 0|\left[,\hat{F}_0(D), a_{\mu}^\dagger a_{\nu}\right]|0\rangle \\
= i\sum_{\alpha\beta} (S^{-1}F_0\langle D|S^{-1}\rangle_{\alpha\beta})(0|[a_{\alpha}^\dagger a_{\beta}^\dagger a_{\mu} a_{\nu}]|0) 
\]

or, alternatively,

\[
\frac{dE}{d\kappa_{\mu\nu}} = \sum_{\alpha\beta} \left(\frac{\partial}{\partial D_{\rho\sigma}}\right)\left(\frac{\partial D_{\rho\sigma}}{\partial \Delta_{\alpha\beta}}\right)\left(\frac{\partial \Delta_{\alpha\beta}}{\partial \kappa_{\mu\nu}}\right) \\
= \sum_{\alpha\beta} \left(\frac{\partial}{\partial D_{\rho\sigma}}\right)\left((S^{-1})^{\top}_{\rho\sigma}(S^{-1})_{\alpha\beta}\right) \\
\times (i\langle 0|[a_{\alpha}^\dagger a_{\beta}^\dagger a_{\mu} a_{\nu}]|0\rangle) \\
= i\sum_{\alpha\beta} \left(S^{-1}\frac{\partial}{\partial D}S^{-1}\right)_{\beta\alpha} \left(0|[a_{\alpha}^\dagger a_{\beta}^\dagger a_{\mu} a_{\nu}]|0\rangle\right). 
\]

Comparison of Eqs. (185) and (186) then shows that Eq. (184) is valid.

The development of this section may thus be summarized as follows. The Fock operator \(\hat{F}_0(D)\) in Eq. (180), with matrix elements defined according to Eq. (184), satisfies the stationarity condition [Eq. (183)] for the Hartree-Fock energy. When a perturbation is applied, the density in the Fock matrix in Eq. (184) evolves in time as described by the Fock matrix in Eq. (169). The density matrix may then be expanded in orders of the perturbation, leading to the expansion of \(0|\hat{A},\hat{F}(D)|0\rangle\) given in Eq. (179). The time evolution of the density matrix is then formally determined by solving the Ehrenfest theorem order by order in the perturbation, and the order expansion of Eq. (179) is used to accomplish this goal. An similar approach will be used to determine the time evolution of the density matrix in Kohn-Sham theory.

VIII. KOHN-SHAM RESPONSE THEORY

A. The Kohn-Sham energy

The AO second-quantization formulation of linear and quadratic response theory has so far been developed at the Hartree-Fock level of theory. In this section, we extend the development to Kohn-Sham (KS) density-functional theory.

In Kohn-Sham theory, the total electronic energy

\[
\]

is expressed as a functional of the electron density

\[
\rho(\mathbf{r}) = \langle 0|\hat{\rho}(\mathbf{r})|0\rangle = \sum_{\mu\nu} \chi_\mu^\dagger(\mathbf{r})\chi_\nu(\mathbf{r})D_{\nu\mu}, 
\]

where \(\hat{\rho}\) is the a second-quantized density operator in the AO basis,

\[
\hat{\rho}(\mathbf{r}) = \sum_{\rho\sigma} \sum_{l} (S^{-1})_{l\rho}(r)\chi_\rho^\dagger(\mathbf{r})\chi_\nu(\mathbf{r})a_{l\rho}^\dagger a_{l\nu}. 
\]

The first and second terms in the Kohn-Sham energy represent the kinetic energy and the external potential arising from the static nuclear potential,

\[
T_\rho[\rho] + V_N[\rho] = \sum_{\mu\nu} (S^{-1}\hbar S^{-1})_{\mu\nu}(0)|a_{\mu}^\dagger a_{\nu}|0\rangle \\
= \sum_{\mu\nu} \hbar\mu D_{\nu\mu}, 
\]

where the elements \(h_{\mu\nu}\) are given in Eq. (129). The third and fourth terms are the Coulomb and exact-exchange contributions to the KS energy, respectively,

\[
J[\rho] = \frac{1}{2} \sum_{\mu\nu} g_{\mu\nu} D_{\nu\mu} D_{\nu\mu}, \\
K[\rho] = \frac{1}{2} \sum_{\mu\nu} g_{\mu\nu} D_{\nu\mu} D_{\nu\mu}. 
\]

The scaling factor \(w_s\) in front of \(K[\rho]\) is nonzero for hybrid theories only and vanishes in pure density-functional theory. \(E_{xc}[\rho]\) is the exchange-correlation energy functional.

The optimization of the Kohn-Sham energy may be expressed in terms of the stationarity condition

\[
\langle 0|\hat{A},\hat{F}^{KS}(D)|0\rangle = 0, 
\]

where the Kohn-Sham operator is given as

\[
\hat{F}^{KS}(D) = \sum_{\mu\nu} (S^{-1}F^{KS}(D)S^{-1})_{\mu\nu} a_{\mu}^\dagger a_{\nu}. 
\]

The Kohn-Sham matrix is the derivative of the Kohn-Sham energy with respect to the density matrix,

\[
(F^{KS}(D))_{\mu\nu} = \frac{\partial E^{KS}[\rho]}{\partial D_{\nu\mu}} = h_{\mu\nu} + G^{HF}(D)_{\mu\nu} + \frac{\partial E_{xc}[\rho]}{\partial D_{\nu\mu}}, 
\]

where

\[
G^{HF}_{\mu\nu}(D) = \sum_{\rho\sigma} D_{\rho\sigma}(g_{\rho\sigma} - w_s g_{\mu\rho} g_{\nu\sigma}). 
\]

differs from Eq. (135) used in the Fock matrix in Eq. (184) in the presence of the scaling factor \(w_s\). The third term in the Kohn-Sham matrix is the derivative of the exchange-correlation functional,

\[
\frac{\partial E_{xc}[\rho]}{\partial D_{\nu\mu}} = \int \frac{\delta E_{xc}[\hat{\rho}]}{\delta \rho(\mathbf{r})} \frac{\delta \rho(\mathbf{r})}{\partial D_{\nu\mu}} d\mathbf{r} = \int \chi_\rho^\dagger(\mathbf{r})u_{xc}(\mathbf{r})\chi_\mu(\mathbf{r}) d\mathbf{r}, 
\]

where we have used Eq. (188) and introduced the exchange-correlation potential

\[
u_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}. 
\]

B. Order expansion of the exchange-correlation potential

When the time-dependent perturbation is applied to our molecular system, we will adopt here the adiabatic approximation, assuming that the time dependence of the exchange-correlation potential may be fully described through the time evolution of the density, keeping the functional form of the exchange-correlation potential unchanged. The time evolu-
tion of the density is determined from Ehrenfest’s theorem as in Hartree-Fock theory, replacing the Fock operator by the Kohn-Sham operator \( \langle 0 | [ \hat{A} , F^{KS}(\hat{D}) ] | 0 \rangle \). In the absence of the perturbation, Ehrenfest’s theorem simplifies to the Kohn-Sham stationarity condition [Eq. (192)].

As in Hartree-Fock theory, we need to carry out an order expansion of \( F^{KS}(\hat{D}) \). We therefore need to evaluate, in addition to the terms entering in Hartree-Fock theory, the contributions from the exchange-correlation potential. As in the time-independent case, we have

\[
\frac{\partial E_{xc}[\rho]}{\partial \tilde{\rho}_{\mu\nu}} = \tilde{v}_{xc,\mu\nu} = \int \chi_{\mu}^*(r) \tilde{v}_{xc}(r,t) \chi_{\nu}(r) d\mathbf{r},
\]

(198)

where the exchange-correlation potential

\[
\tilde{v}_{xc}(r,t) = \frac{\delta E_{xc}[\tilde{\rho}]}{\delta \tilde{\rho}(\mathbf{r},t)}
\]

(199)

depends on the electron density

\[
\tilde{\rho}(\mathbf{r},t) = \langle 0 | \tilde{\rho}(\mathbf{r}) | 0 \rangle = \sum_{\mu\nu} \chi_{\mu}^*(\mathbf{r}) \chi_{\nu}(\mathbf{r}) \tilde{D}_{\mu\nu}.
\]

(200)

We shall now determine the perturbation expansion of the exchange-correlation potential [Eq. (199)] and its matrix elements [Eq. (198)], noting that both are functionals of \( \tilde{\rho}(\mathbf{r},t) \). We recall that \( \tilde{v}_{xc}(r,t) \) is assumed to have the same functional form as in the absence of the perturbation, depending on the perturbation only through the density.

Expanding the exchange-correlation potential \( \tilde{v}_{xc} \) to second order in the rotation parameters \( \kappa_j \) in Eq. (21), we obtain

\[
\tilde{v}_{xc} = v_{xc} + \int \frac{\delta v_{xc}(r,t)}{\delta \tilde{\rho}(\mathbf{r'},t)} \sum_{\mu} \frac{\partial \tilde{\rho}(\mathbf{r'},t)}{\partial \kappa_j} \alpha_j(\mathbf{t}) d\mathbf{r'}
\]

\[
+ \frac{1}{2} \int \frac{\delta^2 v_{xc}(r,t)}{\delta \tilde{\rho}(\mathbf{r'},t) \delta \tilde{\rho}(\mathbf{r''},t)} \sum_{J,K} \frac{\partial \tilde{\rho}(\mathbf{r'},t)}{\partial \kappa_j} \frac{\partial \tilde{\rho}(\mathbf{r''},t)}{\partial \kappa_k} \alpha_j(\mathbf{t}) \alpha_k(\mathbf{t}) d\mathbf{r'} d\mathbf{r''} + \cdots .
\]

(201)

Collecting terms to the same order in the perturbation, we may express the exchange-correlation potential to second order in the perturbation as

\[
\tilde{v}_{xc}(r,t) = v_{xc}(r,0) + v_{xc}^{(1)}(r,t) + v_{xc}^{(2)}(r,t) + \cdots ,
\]

(202)

where \( v_{xc}(r,0) \) was given in Eq. (197) and the first- and second-order terms are given by

\[
v_{xc}^{(1)}(r,t) = \int \frac{\delta v_{xc}(r,t)}{\delta \tilde{\rho}(\mathbf{r'},t)} \rho^{(1)}(\mathbf{r'},t) d\mathbf{r'} ,
\]

(203)

\[
v_{xc}^{(2)}(r,t) = \int \frac{\delta^2 v_{xc}(r,t)}{\delta \tilde{\rho}(\mathbf{r'},t) \delta \tilde{\rho}(\mathbf{r''},t)} \rho^{(1)}(\mathbf{r'},t) \rho^{(1)}(\mathbf{r''},t) d\mathbf{r'} d\mathbf{r''} + \frac{1}{2} \int \frac{\delta^2 v_{xc}(r,t)}{\delta \tilde{\rho}(\mathbf{r'},t) \delta \tilde{\rho}(\mathbf{r''},t)} \rho^{(1)}(\mathbf{r'},t) \rho^{(1)}(\mathbf{r''},t) d\mathbf{r'} d\mathbf{r''} .
\]

(204)

The first- and second-order variations of the density [Eq. (200)] that appear in these expressions are given by

\[
\rho^{(1)}(r,t) = i \sum_{\mu \nu} \chi_{\mu}^*(\mathbf{r}) \chi_{\nu}(\mathbf{r}) D_{\nu \mu}^{(1)}(\mathbf{r},t),
\]

(205)

\[
\rho^{(2)}(r,t) = i \sum_{\mu \nu} \chi_{\mu}^*(\mathbf{r}) \chi_{\nu}(\mathbf{r}) D_{\nu \mu}^{(1)}(\mathbf{r},t) D_{\nu \mu}^{(1)}(\mathbf{r},t)
\]

\[
+ i^2 P_{JK} \sum_{\mu \nu \kappa \lambda} \chi_{\mu}^*(\mathbf{r}) \chi_{\nu}(\mathbf{r}) D_{\nu \mu \kappa}^{(1)}(\mathbf{r},t) D_{\nu \mu \lambda}^{(1)}(\mathbf{r},t).
\]

(206)

Inserting the perturbed densities, we obtain, in the frequency domain,

\[
v_{xc}^{(1)}(\mathbf{r}) = i \sum_{\rho \sigma} \sum_{\kappa \lambda} \int \chi_{\rho}^*(\mathbf{r'}) S_{\rho \sigma}^{-1} \chi_{\sigma}(\mathbf{r'}) S_{\sigma \kappa}^{-1} \frac{\delta v_{xc}(\mathbf{r})}{\delta \tilde{\rho}(\mathbf{r})} \langle 0 | [ a_{\rho \kappa}^1, \Lambda^\dagger ] | 0 \rangle \alpha^1(\omega) d\mathbf{r'},
\]

(207)

\[
v_{xc}^{(2)}(\mathbf{r}) = i \sum_{\rho \sigma} \sum_{\kappa \lambda} \int \chi_{\rho}^*(\mathbf{r'}) S_{\rho \sigma}^{-1} \chi_{\sigma}(\mathbf{r'}) S_{\sigma \kappa}^{-1} \frac{\delta v_{xc}(\mathbf{r})}{\delta \tilde{\rho}(\mathbf{r})} \langle 0 | [ a_{\rho \kappa}^1, \Lambda^\dagger ] | 0 \rangle \alpha^1(\omega) d\mathbf{r'}
\]

\[
+ i^2 \sum_{\rho \sigma} \sum_{\kappa \lambda} \int \chi_{\rho}^*(\mathbf{r'}) S_{\rho \sigma}^{-1} \chi_{\sigma}(\mathbf{r'}) S_{\sigma \kappa}^{-1} \chi_{\rho}^*(\mathbf{r''}) S_{\rho \lambda}^{-1} \chi_{\lambda}(\mathbf{r''}) S_{\lambda \kappa}^{-1} \frac{\delta^2 v_{xc}(\mathbf{r})}{\delta \tilde{\rho}(\mathbf{r}) \delta \tilde{\rho}(\mathbf{r''})} \langle 0 | [ a_{\rho \kappa}^1, \Lambda^\dagger ] | 0 \rangle \alpha^1(\omega_1) \alpha^1(\omega_2) d\mathbf{r'} d\mathbf{r''}
\]

\[
+ \frac{i^2}{2} \sum_{\rho \sigma \kappa \lambda \gamma \delta} \int \chi_{\rho}^*(\mathbf{r'}) S_{\rho \sigma}^{-1} \chi_{\sigma}(\mathbf{r'}) S_{\sigma \kappa}^{-1} \chi_{\rho}^*(\mathbf{r''}) S_{\rho \lambda}^{-1} \chi_{\lambda}(\mathbf{r''}) S_{\lambda \kappa}^{-1} \frac{\delta^2 v_{xc}(\mathbf{r})}{\delta \tilde{\rho}(\mathbf{r}) \delta \tilde{\rho}(\mathbf{r''})} \langle 0 | [ a_{\rho \kappa}^1, \Lambda^\dagger ] | 0 \rangle \alpha^1(\omega_1) \langle 0 | [ a_{\rho \kappa}^1, \Lambda^\dagger ] | 0 \rangle \alpha^1(\omega) d\mathbf{r'} d\mathbf{r''} .
\]

(208)
Defining the functions
\[ G^{\text{xc}}_{\phi\delta}(\mathbf{M}) = \sum_{\rho\sigma} M_{\rho\sigma} \int \chi^{\rho}_{\phi}(r) \chi^{\sigma}_{\delta}(r') \frac{\partial^{2} \psi_{\phi\delta}(\mathbf{r})}{\partial \rho(r')} dr' dr, \]
\[ T^{\text{xc}}(N, \mathbf{M}) = \sum_{\rho\sigma\eta\iota} M_{\rho\sigma} N_{\eta\iota} \int \chi^{\rho}_{\phi}(r) \chi^{\sigma}_{\delta}(r') \chi^{\eta}_{\iota}(r') \chi^{\iota}_{\rho}(r) \]
\[ \times \frac{\partial^{2} \psi_{\phi\delta}(\mathbf{r})}{\partial \rho(r')} \frac{\partial \psi_{\phi\delta}(\mathbf{r})}{\partial \rho(r')} \frac{\partial \psi_{\phi\delta}(\mathbf{r})}{\partial \rho(r')} \frac{\partial \psi_{\phi\delta}(\mathbf{r})}{\partial \rho(r')} dr' dr' dr \] (209)
then gives
\[ v_{\text{xc},\phi\delta}^{(1)}(\mathbf{r}) = i \sum_{J} G^{\text{xc}}_{\phi\delta}(\mathbf{D}^{(1)}) \alpha_{J}^{(1)}(\omega), \] (211)
\[ v_{\text{xc},\phi\delta}^{(2)}(\mathbf{r}) = i \sum_{J} G^{\text{xc}}_{\phi\delta}(\mathbf{D}^{(1)}) \alpha_{J}^{(2)}(\omega) + i^{2} P_{JK} \sum_{JK} G^{\text{xc}}_{\phi\delta}(\mathbf{D}^{(2)}) \alpha_{J}^{(1)} \alpha_{K}^{(1)} \]
\[ \times (\omega_{1}) \alpha_{K}^{(1)}(\omega_{2}) + i^{2} \sum_{JK} T^{\text{xc}}_{\phi\delta}(\mathbf{D}^{(1)}, \mathbf{D}^{(1)}) \alpha_{J}^{(1)} \]
\[ \times (\omega_{1}) \alpha_{K}^{(1)}(\omega_{2}) \] (212)

**C. Order expansion of the Kohn-Sham operator**

Having determined the expansion of the exchange-correlation potential, we may now write the Ehrenfest theorem of Kohn-Sham theory in the form
\[ \langle 0 | [\mathbf{H}, \hat{P}^{\text{KS}}(\mathbf{D})] | 0 \rangle = \sum_{n} \langle 0 | [\mathbf{H}, (\hat{P}^{\text{KS}})^{(n)}] | 0 \rangle, \] (213)
where
\[ (\hat{P}^{\text{KS}})^{(0)} = \sum_{\mu\nu} (\mathbf{S}^{-1} \mathbf{F}^{\text{KS}}_{\mu} \mathbf{S}^{-1})_{\mu\nu} a_{\mu}^{\dagger} a_{\nu}, \] (214)
functions and their residues may also be evaluated. Below, the symmetrized form of quadratic expressions give equivalent molecular property expressions. For Hartree-Fock theory, Eq. (156) becomes

\[ E^{[3]}_{bc} = \left[ \frac{1}{2} \left( S^T [S^T (G^{xc})^T (b, D)_l]_r \right) \right]_{D^T} + \frac{1}{2} \left[ S^T (G^{xc})^T (b, [c, D]_l) \right]_{D^T} + \frac{1}{2} \left[ S^T (G^{xc})^T (c, [b, D]_l) \right]_{D^T} + \frac{1}{2} \left[ S^T (T^{xc})^T (b, [c, D]_l) \right]_{D^T}, \] (221)

which is slightly different from the expression obtained in Eq. (156),

\[ E^{[3]}_{bc} = \frac{1}{2} \left[ S^T [S^T (F)^T (b, D)_l]_r \right]_{D^T} + \frac{1}{2} \left[ S^T (G^{xc})^T (b, [c, D]_l) \right]_{D^T} + \frac{1}{2} \left[ S^T (G^{xc})^T (c, [b, D]_l) \right]_{D^T} + \frac{1}{2} \left[ S^T (T^{xc})^T (b, [c, D]_l) \right]_{D^T}. \] (222)

However, since the \( E^{[3]}_{bc} \) contributions always appear in a symmetrized form \( E^{[3]}_{bc} + E^{[3]}_{cb} \) when molecular properties are evaluated from quadratic response functions, the two expressions give equivalent molecular property expressions.

**IX. IMPLEMENTATION AND ILLUSTRATIVE RESULTS**

The theory presented has been implemented for Hartree-Fock and Kohn-Sham theories in a development version of the DALTON code.\(^3\) The present code contains a linear-scaling implementation of all molecular properties that may be obtained from the linear and quadratic response functions, their poles, and residues.

The linear-scaling implementation of the response eigenvalue equations and linear sets of equations together with the calculation of the linear response function were presented in Ref. 12. Within the same linear-scaling framework, molecular properties that may be obtained from quadratic response functions and their residues may also be evaluated. Below, we report sample calculations on boron nitride sheets.

**A. Boron nitride**

Boron nitride is a white solid consisting of layers of hexagonal boron nitride sheets. It is the “combo” equivalent of graphite but, contrary to graphite, it is not an electrical conductor. Furthermore, it is much less reactive than graphite. It is often used as a replacement for graphite wherever the electrical conductivity or the reactivity of graphite is undesired.

We examine in this section the electronic structure and molecular properties of a single layer of a hexagonal boron nitride sheet by carrying out electronic-structure calculations on borazine (B\(_3\)N\(_3\)H\(_6\)) and its circular extensions containing 7, 19, 37, and 61 hexagonal B\(_3\)N\(_3\) units (see Fig. 1). Free valences on B and N are saturated with H atoms to obtain a closed-shell system. The geometries of the molecular fragments were obtained from a geometry optimized structure, at the B3LYP/6-31G(d,p) level, of the seven-unit \( D_{3h} \) fragment by simple extensions with center- and border-unit geometries. The bond lengths are given in Table I.

We report the results of calculations on the molecular fragments of the lowest excitation energies, the strengths of the one- and two-photon transitions to the excited states and of selected components of the frequency-dependent dipole polarizability and hyperpolarizability.

**1. The polarizability and hyperpolarizability**

A naive implementation of local density approximation or simple hybrid functionals results in an overestimation of the polarizability and hyperpolarizability for large molecules. The overestimation, which increases with the size of the molecular systems, is caused by the inability of the conventional exchange functionals to describe long-range interactions. The optimized effective potential\(^{31-34}\) alleviates this problem.

![FIG. 2. The \(zzz\) component of the hyperpolarizability tensor vs the number of units in the sheet.](image-url)
Although the extra computational cost and technical complications make this approach less accessible for applications on large molecules.

An alternative approach is to use long-range corrected or Coulomb-attenuated hybrid functionals. We use the hybrid CAMB3LYP functional,\(^35,36\) where a generalized Ewald partitioning technique of the electron-electron repulsion is used to obtain an improved long-range interaction. Successful calculations of hyperpolarizabilities have previously been reported using an Ewald partitioning technique of the electron-electron repulsion to obtain the correct long-range interaction.\(^37-40\)

It is well known that calculated polarizabilities and, in particular, hyperpolarizabilities are very sensitive to the representation of the one-electron space. The basis sets we use are much smaller than those usually employed for quantitative reproduction of polarizabilities and hyperpolarizabilities of small molecules. For larger molecules, however, the polarizabilities and even the hyperpolarizabilities are not nearly as sensitive to the choice of the basis set as for smaller molecules, since basis functions on other centers improve the flexibility of the description of the response to the applied electric field.

2. Linear and quadratic response functions

In Tables II, we report the results for the dipole polarizability component \(\alpha_{zz}(\omega)\) and the dipole hyperpolarizability component \(\beta_{zzz}(2\omega,\omega,\omega)\) obtained using the 6-31G* and cc-pVDZ basis sets. Both total values and values per unit of BN units are listed. The frequency chosen is 0.065 648 7 a.u., corresponding to a standard ruby laser (694.3 nm). For the polarizability, \(\alpha_{zz}(\omega)\) is the dominant component, whereas \(\beta_{zzz}(2\omega,\omega,\omega)\), \(\beta_{zxx}(2\omega,\omega,\omega)\), \(\beta_{xzz}(2\omega,\omega,\omega)\), and \(\beta_{zzx}(2\omega,\omega,\omega)\) are all important for the hyperpolarizability. To reduce the computational cost, we only report here \(\beta_{zzz}(2\omega,\omega,\omega)\).

Table II shows that the \(zz\) polarizability component is much larger for a single borazine molecule than for a single \(B_3N_3\) unit in the sheet. This is not surprising as the hydrogen atoms of borazine are expected to make the borazine molecule more easily polarizable. Note also that the deficiency in the basis set is expected to diminish when the BN sheet fragment is increased in size and the description of the larger fragments is improved.

Both \(\beta_{zzz}(2\omega,\omega,\omega)/\text{unit}\) and \(\alpha_{zz}(\omega)/\text{unit}\) approach finite values as expected for an infinite two-dimensional insulator. While \(\alpha_{zz}(\omega)/\text{unit}\) is fairly close to a converged result, \(\beta_{zzz}(2\omega,\omega,\omega)/\text{unit}\) is still slightly off. The convergence is more clearly seen in Fig. 2.

3. Excitation energies and oscillator strengths

In Table III, we report the computed excitation energies for excitations to the five lowest states of the BN sheet fragments. Oscillator strengths \(f_{0j}\) (in atomic units) are also reported, indicating that the first transitions are forbidden for all fragments,

\[
f_{0j} = \frac{2}{3} \omega_j \sum_{\alpha=x,y,z} \sum_{j} |\langle 0|\mu_{\alpha,j}|j\rangle|^2.
\]

As symmetry is not implemented in our code, the symmetry labels for the smaller fragments have been assigned using the latest released version of the Dalton code.\(^30\) Only allowed electronic transitions have been assigned for the larger fragments.

As the size of the system increases, the energy difference between the excited states decreases until, in the limit of an infinite layer, the excitation spectrum may be viewed as a continuous band. In borazine, the difference between the first and fifth excited states is 0.0526 a.u., which decreases to 0.0158 a.u. for the 37-unit sheet. Going from a single borazine molecule to a 37-unit fragment, there is a significant reordering of the excitation energies; although the lowest excited state is expected to remain the \(A_1^2\).

As a crude approximation to the band gap, we may use HOMO-LUMO gap—that is, the difference between the orbital energies of the highest occupied MO (HOMO) and lowest unoccupied MO (LUMO). The HOMO and LUMO orbital energies are obtained in an iterative manner from the occupied and unoccupied projections, respectively, of the Fock/Kohn-Sham matrix as described in Ref. 12. Table IV reports the HOMO-LUMO gap for our BN fragments.

<table>
<thead>
<tr>
<th>(B_3N_3)</th>
<th>HOMO-LUMO gap</th>
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<tr>
<td>1</td>
<td>0.4710</td>
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<tr>
<td>7</td>
<td>0.3590</td>
</tr>
<tr>
<td>19</td>
<td>0.3442</td>
</tr>
<tr>
<td>37</td>
<td>0.3368</td>
</tr>
<tr>
<td>61</td>
<td>0.3320</td>
</tr>
</tbody>
</table>

TABLE IV. HOMO-LUMO gap (in a.u.) of BN fragments of increasing size (in a.u.).
4. Two-photon transition moments

In Sec. V E, we derived expressions for the two-photon transition tensor elements $\Gamma_{0\rightarrow i}^{BA}(\omega)$, where $\omega_1$ and $\omega_2$ fulfill the matching rule $\omega_f = \omega_1 + \omega_2$ and A and B indicate Cartesian components of the electric dipole moment operator $\hat{\mu}$. The two-photon transition moments can be regarded as a transition moment perturbed by an electric field. We therefore expect the two-photon transition moment of an electronically forbidden transition to be small and solely due to second-order effects.

In Table V, we report the two-photon transition tensor $\Gamma_{0\rightarrow i}$ relative to the transition to the first excited state for the various fragments of increasing size. As indicated in Table III, the first excited state for a single borazine is an electronically forbidden transition, and the tensor elements are small as expected. As the BN fragment grows to seven rings, the density decreases close to the energy of the first excited state. Equation (119) shows that the energy difference does play an important role and we expect the contribution to the two-photon transition moment to increase, which is also what we see.

5. Transition moments between excited states

Transition moments between the reference state and an excited state can be determined from the single residue of the linear response function. Transition moments between excited states can only be determined from the double residue of the quadratic response function. This includes the expectation values on the excited state(s) of one-electron operators such as, for instance, the dipole moments of the excited states.

Transition moments between excited states can be used to calculate a number of properties and have, for instance, been used in the sum-over-states procedure of Seth et al.\textsuperscript{41}

We expect the lowest excited state to be of $A_1^+$ symmetry for all fragments under investigation. In Table VI, we report the calculated dipole transition moment between this first excited state and the first $E'$ degenerate state.

We see that all transition dipole moments in the y direction are zero, while the dipole moment in the x and z direction grows steadily.

X. SUMMARY

We have described a second-quantization formulation of time-dependent molecular response function theory in an AO basis representation for Hartree-Fock and Kohn-Sham theories. We have followed the outline of Ref. 2, where a second quantization formulation was described for MCSCF theory in the MO representation. An equivalent formulation of response function theory using first quantization was given for Hartree-Fock theory in Ref. 11. We have described the generalizations required for extending the Hartree-Fock development to Kohn-Sham theory. Explicit expressions are given for evaluating the linear and quadratic response functions and their residues. The computationally expensive step consists of evaluating Fock/Kohn-Sham matrices with generalized density matrices. Splitting the Fock/Kohn-Sham matrix evaluation into a Coulomb and an exchange contribution, the Fock/Kohn-Sham matrix may be computed in a linear-scaling manner.\textsuperscript{42-53} Since the response functions are expressed in the local AO basis, the solution of the response equations and the evaluation of the response functions and their residues may also be done within a linear-scaling framework using sparse matrix algebra. The evaluation of

<table>
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<th>Units and Frequency</th>
<th>Two-photon transition tensor $\Gamma$ ($10^{-3}$ a.u.)</th>
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</thead>
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<tr>
<td>Units</td>
<td>$\omega_1$ (a.u.)</td>
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<tr>
<td>1</td>
<td>0.255 556</td>
</tr>
<tr>
<td>7</td>
<td>0.236 087</td>
</tr>
<tr>
<td>19</td>
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</tr>
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<table>
<thead>
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</tr>
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<td>0.237 073</td>
</tr>
</tbody>
</table>
linear and higher-order response functions and their residues may therefore be carried out in a linear-scaling manner.

We have extended the linear-scaling implementation in Ref. 12 for calculating molecular properties obtained from the linear response function to include molecular properties that may be computed from the quadratic response function and its residues. Sample calculations have been presented for boron nitride sheets. The extension of the linear-scaling development to include molecular properties that may be related to the cubic response function and its residues is in progress.

ACKNOWLEDGMENTS

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APPENDIX A: THE DECOUPLING OF THE EXPECTATION VALUE OF A TWO-ELECTRON OPERATOR

Using induction, we shall prove here that the expectation value of a two-electron operator [Eq. (12)] decouples into products of expectation values of one-electron operators as

\[ \Gamma_{\mu \nu \rho \sigma} = \Delta_{\mu \nu} \Delta_{\rho \sigma} - \Delta_{\mu \rho} \Delta_{\nu \sigma}. \]  

(A1)

First, we show that Eq. (12) is valid for a two-electron state \( |a^\dagger a^\dagger a a \rangle \) \( |\text{vac} \rangle \). Second, we prove that if Eq. (12) is valid for a given \( n \)-electron state, \( |n\rangle = |a^\dagger \ldots a^\dagger a^\dagger \rangle \) \( |\text{vac} \rangle \), then it is also valid for the \((n+1)\)-electron state, \( |n+1\rangle = |a^\dagger a^\dagger \rangle \text{vac} \). We prove that it is then also fulfilled for state \( |n+1\rangle \) [Eq. (12)] decouples into products of expectation values of one-electron operators as

\[ \Gamma_{\mu \nu \rho \sigma} = \Delta_{\mu \nu} \Delta_{\rho \sigma} - \Delta_{\mu \rho} \Delta_{\nu \sigma}. \]  

(A1)

\[ \Gamma_{\mu \nu \rho \sigma} = \Delta_{\mu \nu} \Delta_{\rho \sigma} - \Delta_{\mu \rho} \Delta_{\nu \sigma}. \]  

(A1)

We prove that it is then also fulfilled for state \( |n+1\rangle \) [Eq. (12)] decouples into products of expectation values of one-electron operators as

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(A1)

We prove that it is then also fulfilled for state \( |n+1\rangle \) [Eq. (12)] decouples into products of expectation values of one-electron operators as

\[ \Gamma_{\mu \nu \rho \sigma} = \Delta_{\mu \nu} \Delta_{\rho \sigma} - \Delta_{\mu \rho} \Delta_{\nu \sigma}. \]  

(A1)
\[
\langle n|a_\mu^\dagger a_\nu^\dagger a_\alpha a_\beta|n\rangle = \sum_{k+i} \Delta_{\mu\nu}^{(k)} \Delta_{\alpha\beta}^{(k)} - \sum_{k+i} \Delta_{\mu\nu} \Delta_{\alpha\beta},
\]
(A13)

Since \(\langle n|a_\mu^\dagger a_\nu^\dagger a_\alpha a_\beta|n\rangle\) is assumed to fulfill Eq. (12), we have
\[
\langle n|a_\mu^\dagger a_\nu^\dagger a_\alpha a_\beta|n\rangle = \sum_{k+i} \Delta_{\mu\nu}^{(k)} \Delta_{\alpha\beta}^{(k)} - \sum_{k+i} \Delta_{\mu\nu} \Delta_{\alpha\beta},
\]
(A14)

Inserting Eq. (A14) into Eq. (A12), we straightforwardly obtain
\[
\langle n+1|a_\mu^\dagger a_\nu^\dagger a_\alpha a_\beta|n+1\rangle = \Delta_{\mu\nu} \Delta_{\alpha\beta} - \Delta_{\mu\nu} \Delta_{\alpha\beta},
\]
(A15)

thereby demonstrating that the expectation value \(\langle 0|a_\mu^\dagger a_\nu^\dagger a_\alpha a_\beta|0\rangle\) decouples in the same way as the two-electron density matrix.

**APPENDIX B: THE SYMMETRY, TRACE, AND IDEMPOTENCY RELATIONS OF \(\Delta\)**

We here prove that, if \(\Delta\) fulfills Eqs. (17)–(19), then so does \(\Delta\) of Eq. (26). The Hermiticity of \(\Delta\), Eq. (17), follows straightforwardly from the Hermiticity of \(S\) and \(\kappa\). The trace relation [Eq. (18)] is shown as follows:
\[
\text{Tr} \Delta (S^T)^{-1} = \text{Tr} \Delta \exp(i\kappa T^S) (S^T)^{-1}
\times \exp(-i S^T \kappa^T S^T) (S^T)^{-1}
= \text{Tr} \Delta \exp(i\kappa T^S) \exp(-i S^T \kappa^T S^T) (S^T)^{-1}
= \text{Tr} \Delta (S^T)^{-1},
\]
(B1)

where we have used the relation\(^{26}\)
\[
B^{-1} \exp(A) B = \exp(B^{-1} A B).
\]
(B2)

The same relation may be used to show the idempotency relation Eq. (19):
\[
\Delta (S^T)^{-1} \Delta = \exp(-i S^T \kappa^T) \Delta \exp(i\kappa T^S) (S^T)^{-1}
\times \exp(-i S^T \kappa^T) \Delta \exp(i\kappa T^S)
= \exp(-i S^T \kappa^T) \Delta \exp(i\kappa T^S)
\times \exp(-i\kappa T^S) (S^T)^{-1} \Delta \exp(i\kappa T^S)
= \exp(-i S^T \kappa^T) \Delta \exp(i\kappa T^S) = \Delta.
\]
(B3)

**APPENDIX C: THE TIME DERIVATIVE OF THE TRANSFORMED OPERATOR \(\tilde{\Lambda}\) TO SECOND ORDER**

We prove here the relation
\[
i(0) \left( \frac{\partial}{\partial t} \tilde{\Lambda} \right) |0\rangle = -\langle 0 | [\hbar \kappa, \Lambda] |0\rangle
- \frac{i}{2} \langle 0 | [\Lambda, [\hbar \kappa, \Lambda]] |0\rangle + O(\kappa^2),
\]
(C1)

where the transformed operator \(\tilde{\Lambda}\) is given by
\[
\tilde{\Lambda} = \exp(i\kappa t) \Lambda \exp(-i\kappa t).
\]
(C2)

We first derive a compact form of \(\partial / \partial t\). The operator \(\Lambda\) has no time dependence and the time derivative of \(\tilde{\Lambda}\) becomes
\[
\frac{\partial}{\partial t} \tilde{\Lambda} = -i \frac{\partial}{\partial t} \exp(i\kappa t) \Lambda \exp(-i\kappa t)
+ \exp(i\kappa t) \left( \frac{\partial}{\partial t} \exp(-i\kappa t) \right).
\]
(C3)

The time derivative of the exponential operator was derived in Ref. 2:
\[
\frac{\partial}{\partial t} \exp(i\kappa t) = \left( i\kappa - \frac{1}{2} [\kappa, \kappa] + \cdots \right) \exp(i\kappa t),
\]
(C4a)
\[
\frac{\partial}{\partial t} \exp(-i\kappa t) = -\exp(-i\kappa t) \left( i\kappa - \frac{1}{2} [\kappa, \kappa] + \cdots \right).
\]
(C4b)

Using Eqs. (C4a) and (C4b), we may express Eq. (C3) in the form
\[
\frac{\partial}{\partial t} \tilde{\Lambda} = \left[ i\kappa, \Lambda \right] - [\kappa, \Lambda] - \frac{1}{2} [\kappa, \kappa, \Lambda].
\]
(C5)

Expressing \(\tilde{\Lambda}\) as a Hausdorff expansion and collecting terms to second order, we obtain
\[
\frac{\partial}{\partial t} \tilde{\Lambda} = i [\kappa, \Lambda] - [\kappa, \Lambda] - \frac{1}{2} [\kappa, \kappa, \Lambda].
\]
(C6)

The time derivative of \(\tilde{\Lambda}\) has now been rewritten in a compact form that facilitates the evaluation of the expectation value in a transformed basis,
\[
i(0) \left( \frac{\partial}{\partial t} \tilde{\Lambda} \right) |0\rangle = i(0) \left( \frac{\partial}{\partial t} \tilde{\Lambda} \right) |0\rangle + \left( 0 \right) \left( \frac{\partial}{\partial t} \tilde{\Lambda} \right) |0\rangle + \cdots
\]
(C7)

we obtain
\[
-\langle 0 | [\kappa, \Lambda] |0\rangle - \langle 0 | [\kappa, [\kappa, \Lambda]] |0\rangle = 0.
\]
(C8)

Using the Jacobi identity\(^{26}\)
\[
[A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0,
\]
(C9)

we find
\[
-\langle 0 | [\kappa, \Lambda] |0\rangle - \langle 0 | [\kappa, [\kappa, \Lambda]] |0\rangle = 0.
\]
(C10)

Insertion of Eq. (C10) into Eq. (C8) then shows that Eq. (C1) is valid.

\(^{1}\) D. N. Zubarev, *Nonequilibrium Statistical Thermodynamics* (Consultants Bureau, New York, 1974).


Response theory in a formalism suitable for linear scaling


25. DALTON, an ab initio electronic structure program. Release 2.0, 2005; see http://www.kjemi.uio.no/software/dalton/dalton.html.