

Hierarchies of methods towards the exact Kohn-Sham correlation energy based on the adiabatic-connection fluctuation-dissipation theorem

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A formal procedure to construct the contributions to the frequency-dependent density-density (potential-density) response function in a series expansion with respect to the coupling constant of the electrons is presented. The required input quantities are obtained from static perturbation theory along the adiabatic connection. The contributions to the response function up to a given order are shown to determine the corresponding contributions in a coupling constant expansion of the frequency-dependent exchange-correlation kernel, the key quantity in time-dependent density-functional theory (TDDFT) in the linear response regime. Both the frequency-dependent response function as well as the exchange-correlation kernel thus are accessible in an order by order fashion. By exploiting the relations between the expansions of the response function and the exchange-correlation kernel, various methods are proposed to calculate the Kohn-Sham correlation energy via the adiabatic-connection fluctuation-dissipation (ACFD) theorem, including a hierarchy of ACFD methods towards the exact Kohn-Sham correlation energy. For a recently introduced ACFD method relying on a truncated power series approximation of the correlation kernel, a formal justification for the underlying ansatz is provided. The presented formal approach to construct the exchange-correlation kernel in an order by order fashion not only represents a basis for new ACFD methods for the Kohn-Sham correlation energy but additionally is of interest to devise new TDDFT methods in the linear response regime.

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I. INTRODUCTION

A longstanding goal of electronic structure theory is the development of methods that have a competitive ratio between accuracy and computational effort and, perhaps even more challenging, are universally applicable. Universal applicability here shall refer to various aspects. That is, an electronic structure method ideally should be applicable to finite, i.e., atomic and molecular, as well as infinite, i.e., periodic, systems, to metals as well as insulators and semiconductors, to electronic systems of single reference as well as multireference character. The label multireference character comprises very different electronic structures and situations. Important cases are the left-right or static correlation occurring upon breaking of chemical bonds. The simplest example is the dissociation of the hydrogen molecule which results in a two-determinant wave function corresponding to an antiferromagnetic coupling of the two electrons with the spin polarization on each nucleus fluctuating and being zero on average as required for a singlet state. Left-right correlation can occur in small molecular systems and, in larger molecules, often is restricted to a few electrons in a specific part, e.g., a bond, of the molecule. The other extreme is Wigner crystallization of the homogeneous electron gas an infinite system in which at low density all electrons of the system are strongly correlated. Correlation of electrons with different angular momentum, e.g., in the beryllium atom, again occurs locally for a few electrons and is not restricted to free atoms but frequently

occurs at specific sites in solids, typically in materials containing transition metals.

The holy grail in electronic structure theory is a method that is both efficient and applicable in all of the above situations with predictive power. By predictive power it is meant that the method by itself detects and treats a possible multireference character. That is, a system-dependent specification of active spaces or other parameters to treat correlation should not be necessary. The adiabatic-connection fluctuation-dissipation (ACFD) theorem [1,2] for the Kohn-Sham (KS) correlation energy provides a formal basis to develop electronic structure methods approaching the above sketched goals of general applicability, predictive power, accuracy, and efficiency for the ground states of electronic systems. ACFD methods [3–67] are density-functional methods falling in the class of DFT (density-functional theory) methods with orbital-dependent functionals [68]. This means the exchange and correlation energy is not given by an explicit functional of the electron density and its gradients but by expressions in terms of KS orbitals and eigenvalues. KS orbitals and eigenvalues implicitly are functionals of the ground-state electron density. Therefore orbital-dependent exchange and correlation functionals also are implicit functionals of the electron density and the realm of DFT is not left.

The KS exchange energy is known exactly in terms of the KS orbitals and therefore is calculated exactly in ACFD methods. All other parts of the ground-state energy except the correlation contribution are routinely treated exactly in KS methods. Thus the treatment of the correlation energy remains to be considered. Firstly, it shall be noted that a

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combination of an exact calculation of the exchange energy with a treatment of the correlation via one of the numerous conventional density functionals [69–71] within the local density approximation or the generalized gradient approximation does not work because the latter functionals rely on error cancellations between exchange and correlation.

The ACFD theorem provides an exact expression for the KS correlation energy in terms of dynamic, i.e., frequency-dependent, density-density (potential-density) response functions. In more detail, the quantities entering the ACFD theorem are the dynamic response function of the KS system and the dynamic response functions of corresponding interacting systems with the electron-electron interaction scaled by a coupling constant between zero and one. The response function for the case of full coupling, i.e., a coupling constant of one, is the response function of the physical electron system. The KS response function is known exactly in terms of the KS orbitals and eigenvalues. The interacting response functions, on the other hand, are not known exactly and typically are obtained approximately via time-dependent DFT (TDDFT) in the linear response regime [72–74]. TDDFT, in principle, yields the required response functions exactly but the exchange-correlation kernel, the frequency-dependent functional derivative of the exchange-correlation potential, which would be required to that end, is not known exactly and needs to be approximated. Thus the quantity to approximate in ACFD methods is the exchange-correlation kernel.

ACFD methods have been developed and investigated for about 20 years [3–67]. The vast majority of ACFD methods employ the direct random phase approximation (dRPA) which means the exchange-correlation kernel is simply neglected and only the remaining frequency-independent Hartree kernel, which, of course, is known, is taken into account. With respect to reaction energies dRPA methods can compete with standard DFT methods using hybrid functionals but in addition can take into account dispersion interactions. On the other hand, dRPA methods exhibit the serious fundamental shortcoming that they are not free of unphysical self-interaction. This shows up, amongst others, in the fact that the dRPA correlation energy for one electron systems like the hydrogen atom is nonzero. As a result of the unphysical self-interactions, dRPA total energies are much too low and dRPA atomization energies are very poor.

A step beyond the dRPA is to take into account the exact frequency-dependent exchange kernel in addition to the Hartree kernel. The exchange kernel itself is not known explicitly neither in terms of the electron density nor in terms of KS orbitals and eigenvalues. The exchange kernel, however, is accessible via an integral equation containing KS orbitals and eigenvalues [75–77]. ACFD methods using the Hartree plus the exact exchange kernel are rigorously free of unphysical self-interactions and yield more accurate energetic data than dRPA methods [46,55]. However, in certain cases, related to singlet-singlet instabilities of the exact-exchange-only energy unphysical singularities can occur [61]. Although these singularities are integrable in the integration over complex frequencies that is carried out in ACFD methods this is clearly unsatisfying. Indeed, the appearance of these instabilities goes

along with interacting response functions which are no longer negative semidefinite as required.

The only approximation in ACFD methods based on the Hartree plus the exact exchange kernel is the neglect of the correlation kernel. In Ref. [63], an approximation of the correlation kernel in terms of a power series of the Hartree plus exchange kernel was introduced. In the first approach, this power series was truncated after the fourth-order term and weights of the second- to fourth-order terms of the power series were treated as parameters which were optimized by minimizing errors of a set of reaction energies. This truncated power series approximation (PSA) leads to highly accurate reaction energies and energies of transition states. Reaction energies, e.g., were approaching the quality of CCSD(T) (coupled cluster singles doubles and perturbative triples) methods and energies of transition states were clearly more accurate than those from CCSD (coupled cluster singles doubles) methods. The computational effort of the ACFD method based on the truncated PSA is significantly lower than that of CCSD or CCSD(T) method. The method exhibits an N^5 scaling with N characterizing the system size compared to an N^6 or N^7 scaling behavior of canonical CCSD or CCSD(T) methods. Even more important, the ACFD approach employing the truncated PSA for the correlation kernel was shown to be applicable to multireference systems. For example, a highly accurate dissociation curve for the nitrogen molecules was obtained, which was superior to that from a multireference CISD (configuration interaction with singles and doubles) calculation, despite the fact that the reference KS state for all bond distances was a single non-spin-polarized Slater determinant [63]. While a treatment of multireference systems obviously is not possible in single-reference wave-function methods, it is a promise of the KS formalism that all systems independent of their electronic nature can be described on the basis of a single Slater determinant, the KS determinant, provided the ground state is nondegenerate as in the case of dissociating nitrogen. The ACFD method based on the truncated PSA was the first KS method to live up to this promise. The success of the PSA demonstrated that ACFD methods have the potential to become a new family of electronic structure methods that reach the above sketched goals of accuracy, general applicability, predictive power, and computational efficiency.

In Ref. [63], the PSA was introduced in an ad hoc fashion without further justification. Here expansions of the interacting response function as well as the exchange-correlation kernel with respect to the coupling constant, i.e., the strength of the electron-electron interaction, are introduced and analyzed in detail and the relations between the expansions for the response function and the kernel are uncovered. As part of this analysis integral equations for the exchange kernel and, in an order by order fashion, for the correlation kernel are presented. For the exchange kernel, this represents a rederivation of its known integral equation [75–77] in a different manner which sheds light on the meaning of the quantities occurring in this integral equation. The relation of expansions for the response function and the exchange-correlation kernel is then shown to provide a formal basis for the ansatz of a PSA for the correlation kernel. In a next step, various possible variants of employing truncated as well as infinite, renormalized PSAs in future ACFD methods are presented.

The expansions of exchange-correlation kernels considered here are different from those in conventional many-body perturbation theory because the kernels are functional derivatives of local multiplicative KS exchange-correlation potentials with respect to the electron density and thus depend on only two spatial coordinates, i.e., are two-point quantities in the language of many-body perturbation theory. Expansions within many-body perturbation theory, like, for instance, that of Ref. [53], typically are based on kernels from nonlocal potentials, e.g., the nonlocal exchange potential, and typically are four-point quantities.

Finally, a hierarchy of ACFD methods is introduced that represents as sequence of methods which go beyond the PSA based on the Hartree plus the exchange kernel or equivalently the first order term of the response function but which additionally take into account exact contributions to the correlation kernel up to some order in the coupling constant. The presented hierarchy of ACFD methods systematically becomes exact in higher and higher orders of the coupling constant and, in this way, systematically approaches the Kohn-Sham correlation energy.

The paper is organized as follows. In the proceeding section, the ACFD theorem is discussed. In Sec. III the adiabatic connection along the coupling constant in the static case and a corresponding perturbation theory with respect to the coupling constant for ground and excited electronic states and their energies [78–80] is briefly reviewed. The first and higher-order contributions to wave functions and energies are prerequisites to expand the frequency-dependent response function with respect to the coupling constant. Furthermore, the optimized effective potential method [68,81–86] is briefly reconsidered in Sec. III because it yields KS exchange and correlation potentials that are needed later on. In Sec. IV, expansions of the frequency-dependent response function and the exchange-correlation kernel with respect to the coupling constant are introduced and the relations between the expansions for response function and kernel are uncovered. Moreover, equations for the exchange kernel and for each order of the correlation kernel are derived and discussed. In Sec. V A, various methods that are based on the first order contribution to the response function or equivalently on the sum of Hartree and exchange kernel are presented and discussed including truncated as well as infinite, renormalized PSAs. In Sec. V B, a hierarchy of ACFD methods approaching the KS correlation energy is introduced. Finally, the last Section draws some conclusions, in particular concerning the scope of ACFD methods and possible further applications of the derived expansions of the frequency-dependent response function and the exchange-correlation kernel.

II. THE ADIABATIC-CONNECTION FLUCTUATION-DISSIPATION THEOREM

The adiabatic-connection fluctuation-dissipation theorem [1,2]

$$E_c = \frac{-1}{2\pi} \int_0^1 d\alpha \int d\mathbf{r}d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \times \int_0^\infty d\omega [\chi(\alpha, i\omega, \mathbf{r}, \mathbf{r}') - \chi_s(i\omega, \mathbf{r}, \mathbf{r}')] \quad (1)$$

provides an exact expression for the KS correlation energy E_c in terms of the frequency- and coupling-constant-dependent response function $\chi(\alpha, i\omega, \mathbf{r}, \mathbf{r}')$ and the KS response function $\chi_s(i\omega, \mathbf{r}, \mathbf{r}')$. Here α denotes the coupling-constant, i.e., a scaling of the electron-electron interaction, and $i\omega$ an imaginary frequency. For a coupling constant of $\alpha = 0$, the interacting response function χ turns into the KS response function χ_s , that is

$$\chi_s(i\omega, \mathbf{r}, \mathbf{r}') = \chi(\alpha = 0, i\omega, \mathbf{r}, \mathbf{r}'). \quad (2)$$

For a simple elementary derivation of the ACFD theorem see Ref. [40].

The KS response function χ_s is given by

$$\chi_s(i\omega, \mathbf{r}, \mathbf{r}') = \sum_i \sum_a \frac{\phi_i^\dagger(\mathbf{r})\phi_a(\mathbf{r})\phi_a^\dagger(\mathbf{r}')\phi_i(\mathbf{r}')}{\varepsilon_i - \varepsilon_a + i\omega} + \sum_i \sum_a \frac{\phi_a^\dagger(\mathbf{r})\phi_i(\mathbf{r})\phi_i^\dagger(\mathbf{r}')\phi_a(\mathbf{r}')}{\varepsilon_i - \varepsilon_a - i\omega} \quad (3)$$

in terms of the occupied and unoccupied KS orbitals ϕ_i and ϕ_a , respectively, and their eigenvalues ε_i and ε_a . Throughout this work, indices i, j , and k , refer to occupied orbitals, indices a, b , and c , to unoccupied ones, and indices s and t to orbitals that are occupied as well as unoccupied. Summations always run over all orbitals corresponding to the index, i.e., summation over i, j , or k run over all occupied and summations over a, b , or c run over all unoccupied orbitals unless indicated otherwise. Unless noted otherwise, the most general case of orbitals ϕ_s that are complex-valued two-dimensional spinors is considered.

The orbitals are eigenfunctions of the KS equation

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + v_x(\mathbf{r}) + v_c^{\text{ACFD}}(\mathbf{r}) \right] \phi_s = \varepsilon_s \phi_s, \quad (4)$$

which contains the external potential v_{ext} , typically given by the electrostatic potentials of the nuclei, the Hartree potential v_H , the local multiplicative KS exchange potential v_x , and the correlation potential v_c^{ACFD} which, in practice, is approximated in ACFD methods. In a self-consistent approximate ACFD method, the potential v_c^{ACFD} is obtained as functional derivative of the ACFD expression E_c^{ACFD} for the correlation energy with respect to the electron density. Because ACFD correlation energies are obtained from KS orbitals and eigenvalues and not directly from the electron density and its gradients this derivative has to be taken via the optimized effective potential (OEP) method, see Sec. III C. The same holds true for the exact exchange potential, the functional derivative of the exchange energy, which is exactly known only in terms of the KS orbitals. In practice, often non-self-consistent ACFD methods are carried out. In the simplest case, orbitals and eigenvalues are obtained by a conventional KS calculation relying, e.g., on semilocal exchange-correlation functionals. Alternatively, an exact-exchange-only KS calculation [68,81–86] is used for this purpose, which means to take into account the exact local KS exchange potential via the OEP method but to completely neglect the correlation potential in the calculation of the KS orbitals. Finally, the potential v_c^{ACFD} can be obtained via the OEP method from an ACFD correlation energy expression at a more approximate level

than the one used in the evaluation of the ground-state energy E_0 . The latter is given in ACFD methods by

$$E_0 = \langle \Phi_0 | \hat{T} + \hat{V}_{ee} + \hat{v}_{\text{ext}} | \Phi_0 \rangle + E_c^{\text{ACFD}} \quad (5)$$

with Φ_0 denoting the KS determinant constructed by the occupied KS orbitals ϕ_i . By \hat{T} the kinetic energy operator is denoted, by \hat{V}_{ee} the operator of the electron-electron interaction, and \hat{v}_{ext} is the operator generated by the external potential v_{ext} .

In practice, the response functions are typically represented in an auxiliary basis set [46] often called resolution-of-the-identity basis set. For notational simplicity, here the auxiliary basis set is assumed to be orthonormal although in practice nonorthonormal basis sets may be employed. The ACFD theorem (1) then reads as

$$E_c = \frac{-1}{2\pi} \int_0^1 d\alpha \int_0^\infty d\omega \text{Tr}\{[\mathbf{X}(\alpha, i\omega) - \mathbf{X}_s(i\omega)]\mathbf{F}_H\} \quad (6)$$

with \mathbf{X} and \mathbf{X}_s being the matrices representing the response functions χ and χ_s , respectively, and with the matrix \mathbf{F}_H representing the Coulomb interaction $1/|\mathbf{r} - \mathbf{r}'|$. The integration over the space variables \mathbf{r} and \mathbf{r}' in the ACFD theorem (1) turns into taking the trace between the response matrices and the matrix \mathbf{F}_H in the basis set representation (6) of the ACFD theorem.

III. STATIC PERTURBATION THEORY WITH RESPECT TO THE COUPLING CONSTANT

In this section, the adiabatic connection [1,87,88], perturbation theory with respect to the coupling constant [78–80], and the OEP method [68,81–86] are briefly reviewed because quantities from the perturbation theory are needed later on and in order to introduce concepts to be used later in the time- or frequency-dependent case.

A. Adiabatic connection and expansions with respect to coupling constant

The many-electron Schrödinger equation along the adiabatic connection for coupling constants $0 \leq \alpha \leq 1$ is given by

$$[\hat{T} + \alpha \hat{V}_{ee} + \hat{v}(\alpha)]\Psi_n(\alpha) = E_n(\alpha)\Psi_n(\alpha). \quad (7)$$

The potential $v(\alpha, \mathbf{r})$ generating the operator $\hat{v}(\alpha)$ is a local multiplicative potential that is uniquely determined up to an additive constant through the Hohenberg-Kohn theorem by the condition that the ground-state electron density $\rho_0(\alpha, \mathbf{r})$ for all values of the coupling constant equals the physical ground-state electron density $\rho_0(\mathbf{r})$, i.e., that

$$\begin{aligned} \rho_0(\alpha, \mathbf{r}) &= \langle \Psi_0(\alpha) | \hat{\rho}(\mathbf{r}) | \Psi_0(\alpha) \rangle \\ &= \rho_0(\alpha = 0, \mathbf{r}) \\ &= \rho_0(\mathbf{r}). \end{aligned} \quad (8)$$

The expansion

$$v(\alpha, \mathbf{r}) = v^{(0)}(\mathbf{r}) + \alpha v^{(1)}(\mathbf{r}) + \alpha^2 v^{(2)}(\mathbf{r}) + \dots \quad (9)$$

of $v(\alpha, \mathbf{r})$ with respect to the coupling constant, in zeroth order, contains the effective KS potential v_s , that is

$$v^{(0)}(\mathbf{r}) = v(\alpha = 0, \mathbf{r}) = v_s(\mathbf{r}). \quad (10)$$

The first-order contribution equals the negative of the sum of the Hartree potential v_H and the exchange potential v_x ,

$$v^{(1)}(\mathbf{r}) = -v_H(\mathbf{r}) - v_x(\mathbf{r}), \quad (11)$$

while the sum of all higher order constitute according to

$$\sum_{n=2}^{\infty} \alpha^n v^{(n)}(\mathbf{r}) = -v_c(\alpha, \mathbf{r}) \quad (12)$$

the negative of the correlation potential v_c . Equation (11) in conjunction with the expression

$$v_H(\mathbf{r}) = \int d\mathbf{r}' \frac{\rho_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (13)$$

for the Hartree potential represents a definition of the KS exchange potential. Later on in Sec. III C, an integral equation, the OEP equation, for the KS exchange potential is discussed. For a coupling constant of one $v(\alpha, \mathbf{r})$ turns into the external potential of the real physical electron system at full physical electron-electron interaction, i.e.,

$$v(\alpha = 1, \mathbf{r}) = v_{\text{ext}}(\mathbf{r}). \quad (14)$$

Next expansions

$$E_n(\alpha) = E_n^{(0)} + \alpha E_n^{(1)} + \alpha^2 E_n^{(2)} + \dots \quad (15)$$

and

$$\Psi_n(\alpha) = \Psi_n^{(0)} + \alpha \Psi_n^{(1)} + \alpha^2 \Psi_n^{(2)} + \dots \quad (16)$$

of the energy eigenvalues $E_n(\alpha)$ and the eigenstates $\Psi_n(\alpha)$ are considered. The zeroth-order eigenstates

$$\Psi_n^{(0)} = \Psi_n(\alpha = 0) = \Phi_n \quad (17)$$

are the KS eigenstates, the eigenstates of the many-electron KS equation

$$[\hat{T} + \hat{v}_s]\Phi_n = E_n^{(0)}\Phi_n, \quad (18)$$

i.e., Eq. (7) for $\alpha = 0$. The many-electron KS equation (18) decouples into one-electron KS equations

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right]\phi_s = \varepsilon_s \phi_s \quad (19)$$

for the KS eigenvalues ε_s and the KS orbitals ϕ_s , from which the KS determinants Φ_n are constructed. Here electronic systems with a nondegenerate ground state are considered. In this case, the KS wave functions can be chosen as single determinants. The energy eigenvalue $E_0^{(0)}$ of the KS ground state Φ_0 equals the sum of the occupied KS eigenvalues ε_i

$$E_0^{(0)} = \langle \Phi_0 | \hat{T} + \hat{v}_s | \Phi_0 \rangle = \sum_i \varepsilon_i. \quad (20)$$

Next excited KS determinants Φ_n with $n \neq 0$ are specified in more detail as singly, doubly, and triply excited KS determinants Φ_i^a , Φ_{ij}^{ab} , and Φ_{ijk}^{abc} , respectively. Higher excited KS determinant can specified analogously, however, are not needed here. The KS energy eigenvalue $E_n^{(0)}$ of a singly excited KS determinant Φ_i^a is denoted E_i^a and given by

$$E_i^a = \langle \Phi_i^a | \hat{T} + \hat{v}_s | \Phi_i^a \rangle = E_0^{(0)} + \varepsilon_a - \varepsilon_i. \quad (21)$$

The energy eigenvalues E_{ij}^{ab} and E_{ijk}^{abc} of higher excited KS determinants are given by analogous expressions. In the following, excited KS determinant will be either denoted by Φ_n or more specifically by Φ_i^a , Φ_{ij}^{ab} , and Φ_{ijk}^{abc} depending on what is more suitable. Similarly, for the energy eigenvalues, both notations will be used.

The described perturbation theory along the adiabatic connection has some peculiarities. (i) For a given physical system, the Hamiltonian operator of the unperturbed system, i.e., the KS Hamiltonian operator, is not known because the KS potential v_s corresponding to a given external potential is not known. Thus perturbation theory along the adiabatic connection can not be directly used for practical calculations but is rather a tool used to develop formalism. To that end, it is assumed that the KS potential v_s was known. Indeed, any local multiplicative potential can be considered as KS potential v_s for a system of noninteracting electrons. The potential of the corresponding interacting electron system then, however, is initially unknown, see point (iii) below. (ii) The perturbation is not linear in the coupling constant α but contains higher-order contributions $v^{(n)}$ with $n > 1$. (iii) Parts of the perturbation, the potentials $v^{(n)}$ with $n > 0$ are not known a priori but need to be constructed within the perturbation theory exploiting condition (8) that the ground-state density is independent of the coupling constant. For details see Refs. [78–80]. The potential v_{ext} of the fully interacting physical electron system and the potential v_s of the KS model system differ by the potentials $v^{(n)}$ with $n > 0$ which are part of the perturbation. In practice, v_{ext} is known and the potentials $v^{(n)}$ are needed to obtain v_s . In the development of formalism, it is the other way around, v_s is assumed to be known and for v_{ext} the potentials $v^{(n)}$ are needed.

B. First-order wave functions and energies

Next first-order wave functions and energies within perturbation theory along the adiabatic connection are considered. Those are needed later on for expansions of the response function and the exchange-correlation kernel. The contribution $\Psi_0^{(1)}$ of first order to the ground state $\Psi_0(\alpha)$ is given by

$$\begin{aligned} \Psi_0^{(1)} &= \sum_{\substack{n \\ n \neq 0}} \Phi_n \frac{\langle \Phi_n | \hat{V}_{ee} + \hat{v}^{(1)} | \Phi_0 \rangle}{E_0^0 - E_n^0} \\ &= \sum_i \sum_a \Phi_i^a \frac{\langle \Phi_i^a | \hat{V}_{ee} + \hat{v}^{(1)} | \Phi_0 \rangle}{\varepsilon_i - \varepsilon_a} \\ &\quad + \sum_{i < j} \sum_{a < b} \Phi_{ij}^{ab} \frac{\langle \Phi_{ij}^{ab} | \hat{V}_{ee} | \Phi_0 \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \end{aligned}$$

$$\begin{aligned} \Phi_i^{a(1)} &= \Phi_0 \frac{\langle \Phi_0 | \hat{V}_{ee} + \hat{v}^{(1)} | \Phi_i^a \rangle}{E_i^a - E_0^{(0)}} + \sum_{b \neq a} \Phi_i^b \frac{\langle \Phi_i^b | \hat{V}_{ee} + \hat{v}^{(1)} | \Phi_i^a \rangle}{E_i^a - E_i^b} + \sum_{j \neq i} \Phi_j^a \frac{\langle \Phi_j^a | \hat{V}_{ee} + \hat{v}^{(1)} | \Phi_i^a \rangle}{E_i^a - E_j^a} + \sum_{j \neq i} \sum_{b \neq a} \Phi_j^b \frac{\langle \Phi_j^b | \hat{V}_{ee} | \Phi_i^a \rangle}{E_i^a - E_j^b} \\ &\quad + \sum_{j \neq i} \sum_{b \neq a} \Phi_{ij}^{ab} \frac{\langle \Phi_{ij}^{ab} | \hat{V}_{ee} + \hat{v}^{(1)} | \Phi_i^a \rangle}{E_i^a - E_{ij}^{ab}} + \sum_{j \neq i} \sum_{b \neq a} \sum_{\substack{c \neq a \\ c > b}} \Phi_{ij}^{bc} \frac{\langle \Phi_{ij}^{bc} | \hat{V}_{ee} | \Phi_i^a \rangle}{E_i^a - E_{ij}^{bc}} + \sum_{j \neq i} \sum_{\substack{k \neq i \\ k > j}} \sum_{b \neq a} \Phi_{jk}^{ab} \frac{\langle \Phi_{jk}^{ab} | \hat{V}_{ee} | \Phi_i^a \rangle}{E_i^a - E_{jk}^{ab}} \\ &\quad + \sum_{j \neq i} \sum_{\substack{k \neq i \\ k > j}} \sum_{b \neq a} \sum_{\substack{c \neq a \\ c > b}} \Phi_{ijk}^{abc} \frac{\langle \Phi_{ijk}^{abc} | \hat{V}_{ee} | \Phi_i^a \rangle}{E_i^a - E_{ijk}^{abc}}. \end{aligned} \quad (25)$$

$$\begin{aligned} &= \sum_i \sum_a \Phi_i^a \frac{\langle \Phi_a | \hat{v}_x^{\text{NL}} - \hat{v}_x | \Phi_i \rangle}{\varepsilon_i - \varepsilon_a} \\ &\quad + \sum_{i < j} \sum_{a < b} \Phi_{ij}^{ab} \frac{\langle \Phi_a \Phi_b | \Phi_i \Phi_j \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \end{aligned} \quad (22)$$

with v_x^{NL} denoting a nonlocal exchange operator of the form of the Hartree-Fock exchange operator but constructed from the occupied KS orbitals and with v_x denoting the local multiplicative KS exchange operator defined by Eq. (11) in conjunction with (13). By $\langle \Phi_a \Phi_b | \Phi_i \Phi_j \rangle$ the difference $\int d\mathbf{r} d\mathbf{r}' \phi_a^\dagger(\mathbf{r}) \phi_i(\mathbf{r}) \phi_b^\dagger(\mathbf{r}') \phi_j(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'| - \int d\mathbf{r} d\mathbf{r}' \phi_a^\dagger(\mathbf{r}) \phi_j(\mathbf{r}) \phi_b^\dagger(\mathbf{r}') \phi_i(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|$ of two electron integrals is denoted.

The first-order contribution $E_0^{(1)}$ to the ground-state energy $E_0(\alpha)$ is given by

$$\begin{aligned} E_0^{(1)} &= \langle \Phi_0 | \hat{V}_{ee} + \hat{v}^{(1)} | \Phi_0 \rangle \\ &= \langle \Phi_0 | \hat{V}_{ee} - \hat{v}_H - \hat{v}_x | \Phi_0 \rangle \\ &= \frac{1}{2} \sum_{ij} \langle \Phi_i \Phi_j | \Phi_i \Phi_j \rangle - \sum_j \langle \Phi_j | \hat{v}_H + \hat{v}_x | \Phi_j \rangle. \end{aligned} \quad (23)$$

The sum of the zeroth and first-order energies yields

$$\begin{aligned} E_0^{(0)} + E_0^{(1)} &= \langle \Phi_0 | \hat{T} + \hat{V}_{ee} + \hat{v}^{(0)} + \hat{v}^{(1)} | \Phi_0 \rangle \\ &= \langle \Phi_0 | \hat{T} + \hat{V}_{ee} + \hat{v}_s - \hat{v}_H - \hat{v}_x | \Phi_0 \rangle \\ &= \langle \Phi_0 | \hat{T} + \hat{V}_{ee} + \hat{v}_{\text{ext}} | \Phi_0 \rangle + \langle \Phi_0 | \hat{v}_c(\alpha = 1) | \Phi_0 \rangle. \end{aligned} \quad (24)$$

Note that this sum is not equal to the expectation value of the ground-state KS determinant with the Hamiltonian operator of the physical electron system. The reason is that from the perspective of perturbation theory along the coupling constant, the external potential of the physical electron system contains terms of orders in the coupling constant that are higher than one, i.e., the terms summing up to the KS correlation potential.

Next the contribution $\Psi_n^{(1)}$ of first order to the excited state $\Psi_n(\alpha)$ is considered. Here we concentrate on states $\Psi_n(\alpha)$ that in zeroth order are single excited KS determinants Φ_i^a and denote the corresponding contribution of first order by $\Phi_i^{a(1)}$. First-order perturbation theory yields

Evaluation of the matrix elements and reduction of the energy denominators to KS eigenvalue differences leads to

$$\begin{aligned}
\Phi_i^{a(1)} = & \Phi_0 \frac{\langle \phi_i | \hat{v}_x^{\text{NL}} - \hat{v}_x | \phi_a \rangle}{\varepsilon_a - \varepsilon_i} + \sum_{b \neq a} \Phi_i^b \frac{[\langle \phi_b | \hat{v}_x^{\text{NL}} - \hat{v}_x | \phi_a \rangle - \langle \phi_b \phi_i | | \phi_a \phi_i \rangle]}{\varepsilon_a - \varepsilon_b} - \sum_{j \neq i} \Phi_j^a \frac{[\langle \phi_i | \hat{v}_x^{\text{NL}} - \hat{v}_x | \phi_j \rangle + \langle \phi_i \phi_a | | \phi_j \phi_a \rangle]}{\varepsilon_j - \varepsilon_i} \\
& + \sum_{j \neq i} \sum_{b \neq a} \Phi_j^b \frac{\langle \phi_b \phi_i | | \phi_j \phi_a \rangle}{\varepsilon_j + \varepsilon_a - \varepsilon_b - \varepsilon_i} + \sum_{j \neq i} \sum_{b \neq a} \Phi_{ij}^{ab} \frac{1}{\varepsilon_j - \varepsilon_b} [\langle \phi_b | \hat{v}_x^{\text{NL}} - \hat{v}_x | \phi_j \rangle - \langle \phi_b \phi_i | | \phi_j \phi_i \rangle + \langle \phi_b \phi_a | | \phi_j \phi_a \rangle] \\
& + \sum_{j \neq i} \sum_{b \neq a} \sum_{\substack{c \neq a \\ c > b}} \Phi_{ij}^{bc} \frac{\langle \phi_b \phi_c | | \phi_a \phi_j \rangle}{\varepsilon_j + \varepsilon_a - \varepsilon_b - \varepsilon_c} - \sum_{j \neq i} \sum_{\substack{k \neq i \\ k > j}} \sum_{b \neq a} \Phi_{jk}^{ab} \frac{\langle \phi_i \phi_b | | \phi_j \phi_k \rangle}{\varepsilon_j + \varepsilon_k - \varepsilon_i - \varepsilon_b} \\
& + \sum_{j \neq i} \sum_{\substack{k \neq i \\ k > j}} \sum_{b \neq a} \sum_{\substack{c \neq a \\ c > b}} \Phi_{ijk}^{abc} \frac{\langle \phi_b \phi_c | | \phi_j \phi_k \rangle}{\varepsilon_j + \varepsilon_k - \varepsilon_b - \varepsilon_c}. \tag{26}
\end{aligned}$$

Finally the contribution $E_n^{(1)}$ of first order to the energy $E_n(\alpha)$ is considered. Again only contributions $E_n^{(1)}$ are considered that correspond to zeroth-order states being singly excited KS determinants. In analogy to the first-order terms of the wave functions, such first-order energy terms are denoted by $E_i^{a(1)}$ and are given by

$$\begin{aligned}
E_i^{a(1)} = & \langle \Phi_i^a | \hat{V}_{ee} + \hat{v}^{(1)} | \Phi_i^a \rangle \\
= & \langle \Phi_i^a | \hat{V}_{ee} - \hat{v}_H - \hat{v}_x | \Phi_i^a \rangle \\
= & E_0^{(1)} + \langle \phi_a | \hat{v}_x^{\text{NL}} - \hat{v}_x | \phi_a \rangle - \langle \phi_i | \hat{v}_x^{\text{NL}} - \hat{v}_x | \phi_i \rangle \\
& - \langle \phi_a \phi_i | | \phi_a \phi_i \rangle. \tag{27}
\end{aligned}$$

The first-order terms given above in Eqs. (22), (23), (26), and (27) are all the terms that are needed for the first-order contributions to the frequency-dependent response function and the exchange kernel discussed below.

The second-order contribution $E_0^{(2)}$ to the ground-state energy is the KS analog to the second-order Møller-Plesset perturbation theory, which is based on the Hartree-Fock instead of KS orbitals and eigenvalues. The second-order contribution $E_0^{(2)}$ is typically not used directly but as part of more sophisticated correlation functionals [89–91].

C. Optimized effective potential method

In Sec. III A, it was discussed that the potentials $v^{(n)}$ of Eq. (9) for $n > 0$ need to be constructed within perturbation theory along the adiabatic connection. This is done via the optimized effective potential (OEP) method. The OEP equations can be derived in various ways [68,78,79,81,82]. Here condition (8) is used which requires the ground-state electron density to be independent of the coupling constant [68,78,79]. Expanding the ground-state density $\rho_0(\alpha, \mathbf{r})$ according to

$$\rho_0(\alpha, \mathbf{r}) = \rho_0^{(0)}(\mathbf{r}) + \alpha \rho_0^{(1)}(\mathbf{r}) + \alpha^2 \rho_0^{(2)}(\mathbf{r}) + \dots \tag{28}$$

with respect to the coupling constant α together with condition (8) yields

$$\rho_0^{(0)}(\mathbf{r}) = \rho_0(\mathbf{r}) \tag{29}$$

and

$$\rho_0^{(n)}(\mathbf{r}) = 0 \quad \text{for } n > 0. \tag{30}$$

Equation (30) for each order $n > 0$ constitutes a condition that represents an equation determining the potential $v^{(n)}$. In first order, the OEP equation

$$\begin{aligned}
0 = & \langle \Psi_0^{(0)} | \hat{\rho}(\mathbf{r}) | \Psi_0^{(1)} \rangle + \langle \Psi_0^{(1)} | \hat{\rho}(\mathbf{r}) | \Psi_0^{(0)} \rangle \\
= & \sum_i \sum_a \langle \Phi_0 | \hat{\rho}(\mathbf{r}) | \Phi_i^a \rangle \frac{\langle \phi_a | \hat{v}_x^{\text{NL}} - \hat{v}_x | \phi_i \rangle}{\varepsilon_i - \varepsilon_a} \\
& + \sum_i \sum_a \frac{\langle \phi_i | \hat{v}_x^{\text{NL}} - \hat{v}_x | \phi_a \rangle}{\varepsilon_i - \varepsilon_a} \langle \Phi_i^a | \hat{\rho}(\mathbf{r}) | \Phi_0 \rangle \\
= & \sum_i \sum_a \phi_i^\dagger(\mathbf{r}) \phi_a(\mathbf{r}) \frac{\langle \phi_a | \hat{v}_x^{\text{NL}} - \hat{v}_x | \phi_i \rangle}{\varepsilon_i - \varepsilon_a} + \text{c.c.} \tag{31}
\end{aligned}$$

for the exchange potential v_x is obtained with Eq. (22). Because the Hartree potential is given by Eq. (13) in terms of the ground-state density ρ_0 , Eq. (31) for v_x determines by Eq. (11) the first-order contribution $v^{(1)}(\mathbf{r})$ to the potential $v(\alpha, \mathbf{r})$ of Eqs. (7) and (9).

The OEP equation (31) for v_x can be rearranged in the form

$$\int d\mathbf{r}' \chi_0(\mathbf{r}, \mathbf{r}') v_x(\mathbf{r}') = t(\mathbf{r}) \tag{32}$$

with the static response function

$$\chi_0(\mathbf{r}, \mathbf{r}') = \sum_i \sum_a \frac{\phi_i^\dagger(\mathbf{r}) \phi_a(\mathbf{r}) \phi_a^\dagger(\mathbf{r}') \phi_i(\mathbf{r}')}{\varepsilon_i - \varepsilon_a} + \text{c.c.} \tag{33}$$

of the KS system and the right-hand side

$$t(\mathbf{r}) = \sum_i \sum_a \phi_i^\dagger(\mathbf{r}) \phi_a(\mathbf{r}) \frac{\langle \phi_a | \hat{v}_x^{\text{NL}} | \phi_i \rangle}{\varepsilon_i - \varepsilon_a} + \text{c.c.} \tag{34}$$

OEP equations for the higher-order potentials $v^{(n)}$ that are part of the correlation potential can be obtained analogously and have the same form as Eq. (32), however, with a different right-hand side. The OEP equation for the first-order potential $v^{(1)}$ is special only in so far as the Hartree potential drops out of the OEP equation (31) and thus does not occur in Eq. (32) that represents the form of the OEP equation used in practice. As usual in perturbation theory the expressions for the right-hand sides of the OEP equations become increasingly complicated with higher orders n .

IV. EXPANSIONS OF THE FREQUENCY-DEPENDENT RESPONSE FUNCTION AND THE EXCHANGE-CORRELATION KERNEL WITH RESPECT TO THE COUPLING CONSTANT

A. Direct expansion of the frequency-dependent response function

The frequency-dependent density-density (potential-density) response function yields the first-order change $\delta\rho$ of the ground-state electron density due to a perturbing frequency-dependent local multiplicative potential $\delta v(\alpha, \nu, \mathbf{r})$, which corresponds to the time-dependent perturbing potential

$$\delta v(\alpha, t, \mathbf{r}) = \delta v(\alpha, \nu, \mathbf{r})e^{-i\nu t} + \delta v^*(\alpha, \nu, \mathbf{r})e^{i\nu^* t} \quad (35)$$

with the frequency $\nu = \omega + i\eta$ containing an imaginary part that guarantees that the perturbation vanishes at very early times $t \rightarrow -\infty$. In the ACFD theorem, Eqs. (1) and (6), purely imaginary frequencies are considered and denoted $i\omega$ instead of $i\eta$.

The frequency-dependent response function $\chi(\alpha, \nu, \mathbf{r}, \mathbf{r}')$ is given by the sum-over-states expression

$$\begin{aligned} \chi(\alpha, \nu, \mathbf{r}, \mathbf{r}') &= \sum_n \frac{\langle \Psi_0(\alpha) | \hat{\rho}(\mathbf{r}) | \Psi_n(\alpha) \rangle \langle \Psi_n(\alpha) | \hat{\rho}(\mathbf{r}') | \Psi_0(\alpha) \rangle}{E_0(\alpha) - E_n(\alpha) + \nu} \\ &+ \sum_n \frac{\langle \Psi_n(\alpha) | \hat{\rho}(\mathbf{r}) | \Psi_0(\alpha) \rangle \langle \Psi_0(\alpha) | \hat{\rho}(\mathbf{r}') | \Psi_n(\alpha) \rangle}{E_0(\alpha) - E_n(\alpha) - \nu} \end{aligned} \quad (36)$$

$$\begin{aligned} \chi^{(1)}(\nu, \mathbf{r}, \mathbf{r}') &= \left[\sum_n \frac{\langle \Psi_0^{(0)} | \hat{\rho}(\mathbf{r}) | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{\rho}(\mathbf{r}') | \Psi_0^{(1)} \rangle}{E_0^{(0)} - E_n^{(0)} + \nu} + \sum_n \frac{\langle \Psi_0^{(0)} | \hat{\rho}(\mathbf{r}) | \Psi_n^{(0)} \rangle \langle \Psi_n^{(1)} | \hat{\rho}(\mathbf{r}') | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)} + \nu} \right. \\ &+ \sum_n \frac{\langle \Psi_0^{(0)} | \hat{\rho}(\mathbf{r}) | \Psi_n^{(1)} \rangle \langle \Psi_n^{(0)} | \hat{\rho}(\mathbf{r}') | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)} + \nu} + \sum_n \frac{\langle \Psi_0^{(1)} | \hat{\rho}(\mathbf{r}) | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{\rho}(\mathbf{r}') | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)} + \nu} \\ &\left. - \sum_n \frac{\langle \Psi_0^{(0)} | \hat{\rho}(\mathbf{r}) | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{\rho}(\mathbf{r}') | \Psi_0^{(0)} \rangle}{(E_0^{(0)} - E_n^{(0)} + \nu)^2} (E_0^{(1)} - E_n^{(1)}) \right] + \text{c.c.}(-\nu). \end{aligned} \quad (39)$$

By c.c. $(-\nu)$ a term is designated that is obtained by firstly replacing the frequency ν by $-\nu$ and by subsequently taking the complex conjugate of the term in the square brackets on the right-hand side of Eq. (39).

If $\Psi_0^{(0)}$, $E_0^{(0)}$, $\Psi_n^{(0)}$, and $E_n^{(0)}$ are expressed by Eqs. (22), (23), (26), and (27), respectively, in Eq. (39), then the first-order contribution $\chi^{(1)}(\nu, \mathbf{r}, \mathbf{r}')$ to the response function $\chi(\alpha, \nu, \mathbf{r}, \mathbf{r}')$ is obtained in terms of KS orbitals and their eigenvalues and the local KS exchange potential v_x , which is accessible by the OEP equation (32) from the KS orbitals and eigenvalues. In Appendix, the resulting, somewhat lengthy expression is listed. The detailed form of it, does not need to be discussed here. The crucial point is

for each value of the coupling constant α in terms of the eigenstates $\Psi_n(\alpha)$ and eigenvalues $E_n(\alpha)$ of the Schrödinger equation (7). Equation (36) corresponds to the case that at very early times, i.e., times $t \rightarrow -\infty$, the electronic system is in the ground state $\Psi_0(\alpha)$ of the coupling-strength-dependent Schrödinger equation (7). This implies that the electron density of the system at very early times equals ρ_0 independently of α because the ground states $\Psi_0(\alpha)$ by construction of the static adiabatic connection all have the same electron density.

The eigenstates $\Psi_n(\alpha)$ of the many-electron Schrödinger equation (7) along the adiabatic connection can be chosen as real-valued because the local multiplicative potential $v(\alpha)$ has to be real-valued in order to get an Hamiltonian operator that is Hermitian. From the sum-over-states expression (36) then follows that the response matrix $\mathbf{X}(\alpha)$ has to be negative semidefinite for purely imaginary frequencies $\nu = i\omega$, i.e., $\mathbf{X}(\alpha)$ cannot have positive eigenvalues.

Next the expansion

$$\chi(\alpha, \nu, \mathbf{r}, \mathbf{r}') = \sum_{n=0}^{\infty} \alpha^n \chi^{(n)}(\nu, \mathbf{r}, \mathbf{r}') \quad (37)$$

of the response function with respect to α is considered. The zeroth-order contribution $\chi^{(0)}(\nu, \mathbf{r}, \mathbf{r}')$ equals the frequency-dependent KS response function $\chi_s(\nu, \mathbf{r}, \mathbf{r}')$ given in Eq. (3) for $\nu = i\omega$, i.e.,

$$\chi^{(0)}(\nu, \mathbf{r}, \mathbf{r}') = \chi_s(\nu, \mathbf{r}, \mathbf{r}'). \quad (38)$$

In order to obtain the first-order contribution $\chi^{(1)}(\nu, \mathbf{r}, \mathbf{r}')$ to the response function $\chi(\alpha, \nu, \mathbf{r}, \mathbf{r}')$, the expansions of the eigenvalues $E_n(\alpha)$ and eigenstates $\Psi_n(\alpha)$ with respect to the coupling constant, Eqs. (15) and (16), are substituted into the sum-over-states expression (36). Collecting the first-order terms results in

that $\chi^{(1)}(\nu, \mathbf{r}, \mathbf{r}')$ can be constructed explicitly from products $\phi_s^\dagger(\mathbf{r})\phi_t(\mathbf{r})$ of KS orbitals, KS eigenvalue differences $\varepsilon_s - \varepsilon_t$, and matrix elements of the type $\langle \phi_s | \hat{v}_x^{\text{NL}} - \hat{v}_x | \phi_t \rangle$ and $\langle \phi_i \phi_a | \phi_j \phi_b \rangle$ or $\langle \phi_i \phi_j | \phi_a \phi_b \rangle$. Moreover, matrix representations $\mathbf{X}^{(1)}(\nu)$ of $\chi^{(1)}(\nu, \mathbf{r}, \mathbf{r}')$ in an auxiliary (resolution-of-the-identity) basis set, can be constructed. The step determining the computational effort for doing this is the calculation of matrix elements of the type $\langle \phi_i \phi_a | \phi_j \phi_b \rangle$ or $\langle \phi_i \phi_j | \phi_a \phi_b \rangle$, which are also needed in Møller-Plesset perturbation theory of second order (MP2). Thus the computational effort for constructing matrices $\mathbf{X}^{(1)}(\nu)$ scales with N^5 with the system size N like canonical MP2 methods.

B. Expansion of the exchange-correlation kernel

The response function $\chi(\alpha, \nu, \mathbf{r}, \mathbf{r}')$, for each value of the coupling constant α , gives the first order change of the electron density ρ_0 due to an arbitrary frequency-dependent (and thus time-dependent) local multiplicative perturbation $\delta v(\alpha, \nu, \mathbf{r}')$ of the static potential $v(\alpha, \mathbf{r}')$ in the Schrödinger equation (7) describing the electronic system at very early times before the perturbation is switched on. Up to now, it is only required that the static potentials $v(\alpha, \mathbf{r}')$ for different values of the coupling constant α yield the same ground-state electron density ρ_0 for all values of α , which defines the adiabatic connection between $\alpha = 0$ and $\alpha = 1$, i.e., between the KS model system and the real physical electron system. The frequency-dependent perturbations $\delta v(\alpha, \nu, \mathbf{r}')$ for different values of α were unrelated, so far.

Now it shall be required that the first-order change of the electron density due to the perturbation $\delta v(\alpha, \nu, \mathbf{r}')$ for all values of α is identical, that is the first-order change $\delta\rho(\nu, \mathbf{r})$ shall be frequency but not α dependent. According to the Runge-Gross theorem [92–94], the time-dependent analog of the Hohenberg-Kohn theorem, the density response $\delta\rho(\nu, \mathbf{r})$ together with the initial state $\Psi_0(\alpha)$, the ground state of the Schrödinger equation (7), completely defines $\delta v(\alpha, \nu, \mathbf{r}')$ up to an irrelevant time-dependent constant. [For finite systems the requirement that $\delta v(\alpha, \nu, \mathbf{r}')$ vanishes infinitely far from the system removes the ambiguity due to this time-dependent additive constant.] If a perturbation $\delta v(\alpha = 0, \nu, \mathbf{r}')$ is chosen for $\alpha = 0$, i.e., for the KS case, then this determines $\delta\rho(\nu, \mathbf{r})$ which subsequently determines $\delta v(\alpha, \nu, \mathbf{r}')$ for all values of α . Next the response of the electron density $\delta\rho$ is expanded with respect to the coupling constant according to

$$\delta\rho(\alpha, \nu, \mathbf{r}) = \delta\rho^{(0)}(\nu, \mathbf{r}) + \alpha\delta\rho^{(1)}(\nu, \mathbf{r}) + \alpha^2\delta\rho^{(2)}(\nu, \mathbf{r}) + \dots \quad (40)$$

Because the response $\delta\rho$ is independent of the coupling constant α all terms in this expansion except the one of zeroth order have to vanish, i.e.,

$$\delta\rho^{(0)}(\nu, \mathbf{r}) = \delta\rho(\nu, \mathbf{r}) \quad (41)$$

and

$$\delta\rho^{(n)}(\nu, \mathbf{r}) = 0 \quad \text{for } n > 0. \quad (42)$$

Equations (40), (41), and (42) represent the frequency-dependent analog of Eqs. (28), (29), and (30) of static perturbation theory with respect to the coupling constant.

At this point, we switch to the representation in an auxiliary (resolution-of-the-identity) basis set. That is the response function $\chi(\alpha, \nu, \mathbf{r}, \mathbf{r}')$ turns into a response matrix $\mathbf{X}(\alpha, \nu)$, the perturbing potentials $\delta v(\alpha, \nu, \mathbf{r}')$ into vectors $\delta\mathbf{v}(\alpha, \nu)$ and the first-order density response $\delta\rho(\nu, \mathbf{r})$ into the vector $\delta\rho(\nu)$. The response matrix $\mathbf{X}(\alpha, \nu)$ relates $\delta\rho(\nu)$ and $\delta\mathbf{v}(\alpha, \nu)$ by the equation

$$\delta\rho(\nu) = \mathbf{X}(\alpha, \nu)\delta\mathbf{v}(\alpha, \nu), \quad (43)$$

which is a first-order response equation with a coupling-constant-dependent response matrix and perturbation but a response of the density that is independent of the coupling constant α

Next the first-order response equation (43) is expanded with respect to the coupling constant α . The expansion of $\mathbf{X}(\alpha, \nu)$ is given by Eq. (37) and the perturbation $\delta\mathbf{v}(\alpha, \nu)$ is expanded according to

$$\delta\mathbf{v}(\alpha, \nu) = \sum_{n=0}^{\infty} \alpha^n \delta\mathbf{v}^{(n)}(\nu) \quad (44)$$

with the zeroth-order term giving the perturbation $\delta\mathbf{v}_s(\nu)$ of the KS potential, i.e.,

$$\delta\mathbf{v}^{(0)}(\nu) = \delta\mathbf{v}(\alpha = 0, \nu) = \delta\mathbf{v}_s(\nu). \quad (45)$$

The first-order contribution $\delta\mathbf{v}^{(1)}(\nu)$ represents the negative of the perturbation $\delta\mathbf{v}_{Hx}(\nu)$ of the sum of the Hartree and the exchange potential, i.e.,

$$\delta\mathbf{v}^{(1)}(\nu) = -\delta\mathbf{v}_{Hx}(\nu) \quad (46)$$

while all higher-order terms represent the negative of the perturbation $\delta\mathbf{v}_c(\alpha, \nu)$ of the correlation potential, that is

$$\sum_{n=2}^{\infty} \alpha^n \delta\mathbf{v}^{(n)}(\nu) = -\delta\mathbf{v}_c(\alpha, \nu). \quad (47)$$

Note that here linear response with respect to a frequency-dependent perturbation $\delta\mathbf{v}(\alpha, \nu)$ of the potential, i.e., perturbation theory of first order with respect to $\delta\mathbf{v}(\alpha, \nu)$, is combined with perturbation theory with respect to the coupling constant α to arbitrary orders. In Ref. [95], higher-order, nonlinear response with respect to $\delta\mathbf{v}(\alpha, \nu)$ is combined with perturbation theory along the adiabatic connection.

The zeroth order of the response equation (43) reads as

$$\delta\rho(\nu) = \mathbf{X}_s(\nu)\delta\mathbf{v}_s(\nu) \quad (48)$$

and determines the response $\delta\rho(\nu)$ of the electron density. The first order is given by

$$0 = \mathbf{X}^{(1)}(\nu)\delta\mathbf{v}_s(\nu) + \mathbf{X}_s(\nu)\delta\mathbf{v}^{(1)}(\nu). \quad (49)$$

The left-hand side of Eq. (49) equals zero because the response of the electron density is independent of α , see Eq. (43). Rearrangement of Eq. (49) and use of Eq. (48) leads to

$$\begin{aligned} \delta\mathbf{v}^{(1)}(\nu) &= -\mathbf{X}_s^{-1}(\nu)\mathbf{X}^{(1)}(\nu)\delta\mathbf{v}_s(\nu) \\ &= -\mathbf{X}_s^{-1}(\nu)\mathbf{X}^{(1)}(\nu)\mathbf{X}_s^{-1}(\nu)\delta\rho(\nu). \end{aligned} \quad (50)$$

With the definition

$$\mathbf{F}^{(1)}(\nu) = \mathbf{X}_s^{-1}(\nu)\mathbf{X}^{(1)}(\nu)\mathbf{X}_s^{-1}(\nu). \quad (51)$$

Equation (50) turns into

$$\delta\mathbf{v}^{(1)}(\nu) = -\mathbf{F}^{(1)}(\nu)\delta\rho(\nu), \quad (52)$$

which identifies $-\mathbf{F}^{(1)}(\nu)$ as a functional derivative relating $\delta\mathbf{v}^{(1)}(\nu)$ and $\delta\rho(\nu)$. Because $\delta\mathbf{v}^{(1)}(\nu)$ is the negative of the perturbation $\delta\mathbf{v}_{Hx}(\nu)$ of the Hartree plus the exchange potential, see Eq. (46), $\mathbf{F}^{(1)}(\nu)$ is the frequency-dependent functional derivative of the exchange-correlation potential. That is

$$\mathbf{F}^{(1)}(\nu) = \mathbf{F}_{Hx}(\nu). \quad (53)$$

Equation (51) for the Hartree plus the exchange kernel was derived earlier in a somewhat different way in Refs. [75–77].

The quantity $\mathbf{X}^{(1)}(\nu)$ was denoted $\mathbf{H}(\nu)$ and was not recognized as the contribution to the response matrix of first order in the coupling constant α . The insight that $\mathbf{F}^{(1)}(\nu)$ depends by Eq. (51) on the first-order contribution $\mathbf{X}^{(1)}(\nu)$ of the response matrix will be exploited later on. A further crucial point is that the higher orders of the response equation (43) lead to expressions for the higher-order contributions $\mathbf{F}^{(n)}(\nu)$ to the correlation kernel by exploiting for each order that the response of the electron density does not contain contributions of orders of α higher than zero because it is independent of the coupling constant α , see Eq. (42). This means there is a certain analogy to the adiabatic connection of the ground-state case. In the latter case, the ground-state electron density is independent of the coupling constant α , which leads in each order of α to an OEP equation for the potential $v^{(n)}$ of this order. Here the fact that the linear response of the electron density is independent of the coupling constant α , see Eqs. (42) and (43), leads in each order of α to equations for contributions $\mathbf{F}^{(n)}(\nu)$ to the Hartree, exchange and correlation kernel.

For each order $n \geq 1$, the kernel contribution $\mathbf{F}^{(n)}(\nu)$ determines the perturbation $\delta\mathbf{v}^n(\nu)$ of the corresponding order by

$$\delta\mathbf{v}^n(\nu) = -\mathbf{F}^{(n)}(\nu)\delta\rho(\nu). \quad (54)$$

Equations for the second- and third-order contributions $\mathbf{F}^{(2)}(\nu)$ and $\mathbf{F}^{(3)}(\nu)$ are given later on in Eqs. (68) and (69). They contain contribution $\mathbf{X}^{(n)}(\nu)$ up to second or third order, respectively. The latter are accessible from perturbation theory expansions of the eigenstates $\Psi_n(\alpha)$ and their energies $E_n(\alpha)$. The same holds true for orders of the kernel higher than 3. This means that explicit expressions for the $\mathbf{F}^{(n)}(\nu)$ in terms of KS orbitals and their eigenvalues can be obtained order by order. As usual in perturbation theory higher-order terms will become exceedingly complicated. Such higher orders will not be considered in detail here. What will be studied here, are the relations between expansions of the sum of the Hartree, the exchange, and the correlation kernel and expansions of the response function which will lead to a hierarchy of ACFD methods based on these relations.

Combining the contributions $\mathbf{F}^{(n)}(\nu)$ of all orders yields the complete coupling-constant-dependent kernel

$$\mathbf{F}(\alpha, \nu) = \sum_{n=1}^{\infty} \alpha^n \mathbf{F}^{(n)}(\nu). \quad (55)$$

Inserting Eqs. (54) into to Eq. (44) together with Eqs. (45) and (55) gives

$$\delta\mathbf{v}(\alpha, \nu) = \delta\mathbf{v}_s(\nu) - \mathbf{F}(\alpha, \nu)\delta\rho(\nu) \quad (56)$$

or

$$\delta\mathbf{v}_s(\nu) = \delta\mathbf{v}(\alpha, \nu) + \mathbf{F}(\alpha, \nu)\delta\rho(\nu). \quad (57)$$

Substituting Eq. (57) for $\delta\mathbf{v}_s(\nu)$ in the response equation (48) after some rearrangement leads to

$$\delta\rho(\nu) = [\mathbf{1} - \mathbf{X}_s(\nu)\mathbf{F}(\alpha, \nu)]^{-1}\mathbf{X}_s(\nu)\delta\mathbf{v}(\alpha, \nu). \quad (58)$$

Equation (58) yields the linear response of the electron density due to a perturbation $\delta\mathbf{v}(\alpha, \nu)$, which, by definition, is the action of the response function $\mathbf{X}(\alpha, \nu)$. Thus it follows

$$\mathbf{X}(\alpha, \nu) = [\mathbf{1} - \mathbf{X}_s(\nu)\mathbf{F}(\alpha, \nu)]^{-1}\mathbf{X}_s(\nu) \quad (59)$$

which is the basic equation of TDDFT in the linear response regime. Of course, Eq. (59) was derived in different ways earlier [72–74]. Here, Eq. (59) was obtained via the series expansion of $\delta\mathbf{v}(\alpha, \nu)$ from the members $\mathbf{X}^{(n)}(\nu)$ of the series expansion of the response matrix $\mathbf{X}(\alpha, \nu)$ by using the independence of the linear response $\delta\rho$ from the coupling strength α resulting in Eq. (42) for each order n . This made it possible to define contributions $\mathbf{F}^{(n)}(\nu)$ and via Eq. (55) the complete kernel $\mathbf{F}(\alpha, \nu)$. Note in passing, that the kernel and its contributions were not defined as but turned out to be functional derivatives. That the kernel represents a functional derivative follows from equations like (52) and (54) which are part of the above derivation of equations for the various orders $\mathbf{F}^{(n)}(\nu)$ of $\mathbf{F}(\alpha, \nu)$.

The close relation between the series expansions of the response matrix $\mathbf{X}(\alpha, \nu)$ and the kernel $\mathbf{F}(\alpha, \nu)$ with respect to α can not only be uncovered as discussed above. Indeed, the relations between the contributions $\mathbf{X}^{(n)}(\nu)$ and $\mathbf{F}^{(n)}(\nu)$, see Eq. (51) for the relation between $\mathbf{X}^{(1)}(\nu)$ and $\mathbf{X}^{(1)}(\nu)$, can alternatively be obtained by inserting the series expansion for $\mathbf{X}(\alpha, \nu)$ into the TDDFT equation (59). Before doing so, the notation shall be simplified for the rest of the paper by suppressing the frequency variable ν . For a start, the square root \mathbf{L} of the negative of the KS response matrix \mathbf{X}_s is constructed from the spectral representation

$$-\mathbf{X}_s = \mathbf{V}\boldsymbol{\sigma}\mathbf{V}^\dagger \quad (60)$$

of $-\mathbf{X}_s$ according to

$$\mathbf{L} = \mathbf{V}\boldsymbol{\sigma}^{1/2}\mathbf{V}^\dagger \quad (61)$$

and leading to

$$-\mathbf{X}_s = \mathbf{L}\mathbf{L}. \quad (62)$$

Because the KS response matrix \mathbf{X}_s , like generally the response matrix $\mathbf{X}(\alpha)$ for all values of α , is negative semidefinite the square root of $-\mathbf{X}_s$ is well defined.

With the matrix \mathbf{L} , the TDDFT equation (59) for the response matrix $\mathbf{X}(\alpha)$ can be expressed as

$$\mathbf{X}(\alpha) = -\mathbf{L}[\mathbf{1} + \mathbf{L}\mathbf{F}(\alpha)\mathbf{L}]^{-1}\mathbf{L}, \quad (63)$$

which can be rearranged into

$$\mathbf{L}\mathbf{F}(\alpha)\mathbf{L} = -\mathbf{1} - [\mathbf{L}^{-1}\mathbf{X}(\alpha)\mathbf{L}^{-1}]^{-1}. \quad (64)$$

Inserting the expansion of $\mathbf{X}(\alpha)$ with respect to the coupling constant, see Eq. (37), into Eq. (64) yields

$$\begin{aligned} \mathbf{L}\mathbf{F}(\alpha)\mathbf{L} &= -\mathbf{1} + [\mathbf{1} - (\alpha\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1} + \alpha^2\mathbf{L}^{-1}\mathbf{X}^{(2)}\mathbf{L}^{-1} \dots)]^{-1}. \end{aligned} \quad (65)$$

The inverse of the square brackets in Eq. (65) represents a resummed geometric series in a variable given by the series in the round brackets. Exploiting this Eq. (65) can be rewritten as

$$\mathbf{L}\mathbf{F}(\alpha)\mathbf{L} = \sum_{n=1}^{\infty} (\alpha\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1} + \alpha^2\mathbf{L}^{-1}\mathbf{X}^{(2)}\mathbf{L}^{-1} \dots)^n. \quad (66)$$

For the time being, it is assumed that all series in the coupling constant α converge. Later on in Sec. V, the question of convergence is considered. Next expansion (55) of $\mathbf{F}(\alpha)$ with respect to the coupling constant is inserted into Eq. (66) and the sum on the right-hand side is sorted according to orders in α . This yields for each order in α an equation for the corresponding contribution $\mathbf{F}^{(n)}$ to the kernel. In first order, Eq. (51) results, which turns into

$$\mathbf{F}^{(1)} = \mathbf{L}^{-2}\mathbf{X}^{(1)}\mathbf{L}^{-2} \quad (67)$$

if the KS response matrix \mathbf{X}_s is replaced by $-\mathbf{L}^2$. The equations for second and third order read as

$$\mathbf{F}^{(2)} = \mathbf{L}^{-2}\mathbf{X}^{(1)}\mathbf{L}^{-2}\mathbf{X}^{(1)}\mathbf{L}^{-2} + \mathbf{L}^{-2}\mathbf{X}^{(2)}\mathbf{L}^{-2} \quad (68)$$

and

$$\begin{aligned} \mathbf{F}^{(3)} = & \mathbf{L}^{-2}\mathbf{X}^{(1)}\mathbf{L}^{-2}\mathbf{X}^{(1)}\mathbf{L}^{-2}\mathbf{X}^{(1)}\mathbf{L}^{-2} + \mathbf{L}^{-2}\mathbf{X}^{(1)}\mathbf{L}^{-2}\mathbf{X}^{(2)}\mathbf{L}^{-2} \\ & + \mathbf{L}^{-2}\mathbf{X}^{(2)}\mathbf{L}^{-2}\mathbf{X}^{(1)}\mathbf{L}^{-2} + \mathbf{L}^{-2}\mathbf{X}^{(3)}\mathbf{L}^{-2}. \end{aligned} \quad (69)$$

C. Expansion of the frequency-dependent response function using the expansion of the exchange-correlation kernel

In the preceding Sec. IV B, the equations for the contributions $\mathbf{F}^{(n)}$ to the kernel $\mathbf{F}(\alpha)$ were derived, see Eqs. (67), (68), (69). The equations give the $\mathbf{F}^{(n)}$ in terms of the contributions $\mathbf{X}^{(n)}$ to the response function $\mathbf{X}(\alpha)$. Because the $\mathbf{X}^{(n)}$ can be obtained in terms of KS orbitals and eigenvalues, see Sec. IV A, these equations actually make the contributions $\mathbf{F}^{(n)}$ accessible. Now the opposite is considered, the contributions $\mathbf{X}^{(n)}$ are expressed in terms of the $\mathbf{F}^{(n)}$.

Rearrangement of Eqs. (67), (68), and (69) leads to equations

$$\mathbf{X}^{(1)} = \mathbf{L}^2\mathbf{F}^{(1)}\mathbf{L}^2, \quad (70)$$

$$\mathbf{X}^{(2)} = -\mathbf{L}^2\mathbf{F}^{(1)}\mathbf{L}^2\mathbf{F}^{(1)}\mathbf{L}^2 + \mathbf{L}^2\mathbf{F}^{(2)}\mathbf{L}^2, \quad (71)$$

and

$$\begin{aligned} \mathbf{X}^{(3)} = & \mathbf{L}^2\mathbf{F}^{(1)}\mathbf{L}^2\mathbf{F}^{(1)}\mathbf{L}^2\mathbf{F}^{(1)}\mathbf{L}^2 - \mathbf{L}^2\mathbf{F}^{(1)}\mathbf{L}^2\mathbf{F}^{(2)}\mathbf{L}^2 \\ & - \mathbf{L}^2\mathbf{F}^{(2)}\mathbf{L}^2\mathbf{F}^{(1)}\mathbf{L}^2 + \mathbf{L}^2\mathbf{F}^{(3)}\mathbf{L}^2 \end{aligned} \quad (72)$$

for the contributions $\mathbf{X}^{(n)}$ in terms of the kernel contributions $\mathbf{F}^{(n)}$ and the square root \mathbf{L} of the negative of the KS response functions. Because the kernel contributions $\mathbf{F}^{(n)}$ are not accessible except through the contributions $\mathbf{X}^{(n)}$ these equations do not give access to the $\mathbf{X}^{(n)}$. However, they give some formal insight that will be used later on.

Equations (70), (71), and (72) can alternatively be derived directly from the basic TDDFT equations (59) or (63) that can be rearranged into

$$\begin{aligned} \mathbf{L}^{-1}\mathbf{X}(\alpha)\mathbf{L}^{-1} &= -[\mathbf{1} + \mathbf{L}\mathbf{F}(\alpha)\mathbf{L}]^{-1} \\ &= -\mathbf{1} - \sum_{n=1}^{\infty} (-)^n [\mathbf{L}\mathbf{F}(\alpha)\mathbf{L}]^n \\ &= -\mathbf{1} - \sum_{n=1}^{\infty} (-)^n (\alpha\mathbf{L}\mathbf{F}^{(1)}\mathbf{L} + \alpha^2\mathbf{L}\mathbf{F}^{(2)}\mathbf{L} \dots)^n. \end{aligned} \quad (73)$$

In the step to the second right-hand side of Eq. (73) it is used that the first right-hand side represents a geometric series in $-\mathbf{L}\mathbf{F}(\alpha)\mathbf{L}$. Inserting expansion (55) for $\mathbf{F}(\alpha)$ results in the final right-hand side of Eq. (73). Via reordering of the final sum in Eq. (73) equations for the $\mathbf{X}^{(n)}$ in each order $n \geq 0$ are obtained. The equations for the orders one to three are given above by Eqs. (70)–(72).

D. Expansions of finite order in either the frequency-dependent response function or the exchange-correlation kernel

1. Expansions starting from the zeroth- and first-order term of the frequency-dependent response function

So far, infinite series expansions in the coupling constant α were considered. Now the expansion of the response matrix $\mathbf{X}(\alpha)$, see Eq. (37), is truncated after the first-order term, i.e.,

$$\begin{aligned} \mathbf{X}(\alpha) &\approx \mathbf{X}^{(0)} + \alpha\mathbf{X}^{(1)} \\ &= \mathbf{X}_s + \alpha\mathbf{X}^{(1)}. \end{aligned} \quad (74)$$

Such a truncation of the expansion of response matrix $\mathbf{X}(\alpha)$ implies a change in the series expansion of the kernel $\mathbf{F}(\alpha)$. If all terms $\mathbf{X}^{(n)}$ with $n > 1$ are omitted in the equation for the contributions $\mathbf{F}^{(n)}$, Eqs. (67), (68), (69), and corresponding equations for orders higher than 3, then these equations reduce to

$$\mathbf{F}^{(n)} \approx \mathbf{L}^{-1}[\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1}]^n\mathbf{L}^{-1} \quad (75)$$

and the complete kernel $\mathbf{F}(\alpha)$ is given by the series

$$\mathbf{F}(\alpha) \approx \mathbf{L}^{-1} \left[\sum_{n=1}^{\infty} \alpha^n (\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1})^n \right] \mathbf{L}^{-1}. \quad (76)$$

With Eq. (70) for $\mathbf{X}^{(1)}$ Eq. (75) turns into

$$\mathbf{F}^{(n)} \approx \mathbf{L}^{-1}[\mathbf{L}\mathbf{F}^{(1)}\mathbf{L}]^n\mathbf{L}^{-1} \quad (77)$$

and Eq. (76) into

$$\mathbf{F}(\alpha) \approx \mathbf{L}^{-1} \left[\sum_{n=1}^{\infty} \alpha^n (\mathbf{L}\mathbf{F}^{(1)}\mathbf{L})^n \right] \mathbf{L}^{-1}. \quad (78)$$

This means a truncation of the series expansion of the response function $\mathbf{X}(\alpha)$ after the first-order term implies that the kernel $\mathbf{F}(\alpha)$ is approximated by a geometric series (without the leading constant) in $\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1}$ or equivalently in $\mathbf{L}\mathbf{F}^{(1)}\mathbf{L}$. Because $\mathbf{F}^{(1)}$ equals the sum of the Hartree plus the exchange kernel, Eq. (53), this means that the correlation kernel is approximated by a series in $\mathbf{L}\mathbf{F}_{Hx}\mathbf{L}$.

2. Expansions starting from the first-order term of the exchange-correlation kernel

In the previous Sec. IV D 1, a truncation of the series expansion of the response matrix $\mathbf{X}(\alpha)$ was considered. Here a truncation

$$\mathbf{F}(\alpha) \approx \alpha\mathbf{F}^{(1)} = \mathbf{F}_{Hx} \quad (79)$$

of the coupling constant expansion of the kernel $\mathbf{F}(\alpha)$ after the first order is considered. Inserting Eq. (79) into Eq. (63), a representation of the basic equation of TDDFT in the linear

response regime, yields

$$\begin{aligned}\mathbf{X}(\alpha) &\approx -\mathbf{L}[\mathbf{1} + \alpha\mathbf{L}\mathbf{F}^{(1)}\mathbf{L}]^{-1}\mathbf{L} \\ &= [\mathbf{1} - \alpha\mathbf{X}_s\mathbf{F}^{(1)}]^{-1}\mathbf{X}_s \\ &= [\mathbf{1} - \alpha\mathbf{X}_s\mathbf{F}_{Hx}]^{-1}\mathbf{X}_s.\end{aligned}\quad (80)$$

If all terms $\mathbf{F}^{(n)}$ with $n > 1$ are omitted in Eqs. (70)–(72) for the contributions $\mathbf{X}^{(n)}$ to the response function $\mathbf{X}(\alpha)$ then these contributions are approximately given by

$$\mathbf{X}^{(n)} \approx (-)^{n+1}\mathbf{L}[\mathbf{L}\mathbf{F}^{(1)}\mathbf{L}]^n\mathbf{L} \quad (81)$$

and the complete response matrix by

$$\mathbf{X}(\alpha) \approx -\mathbf{L}\left[\sum_{n=0}^{\infty}(-)^n(\alpha\mathbf{L}\mathbf{F}^{(1)}\mathbf{L})^n\right]\mathbf{L}. \quad (82)$$

Summing up the geometric series in Eq. (82) gives back the first line of Eq. (80).

With Eq. (67) for $\mathbf{F}^{(1)}$ Eq. (79) turns into

$$\mathbf{F}(\alpha) \approx \alpha\mathbf{L}^{-2}\mathbf{X}^{(1)}\mathbf{L}^{-2}, \quad (83)$$

Eq. (80) into

$$\mathbf{X}(\alpha) = -\mathbf{L}[\mathbf{1} + \alpha\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1}]^{-1}\mathbf{L}, \quad (84)$$

Eq. (81) into

$$\mathbf{X}^{(n)} \approx (-)^{n+1}\mathbf{L}[\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1}]^n\mathbf{L}, \quad (85)$$

and Eq. (82) into

$$\mathbf{X}(\alpha) \approx -\mathbf{L}\left[\sum_{n=0}^{\infty}(-)^n(\alpha\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1})^n\right]\mathbf{L}. \quad (86)$$

Equation (84) is the basis of the EXXRPA or ACFD[Hx] method of Ref. [46], see later on Sec. V A 2.

A truncation of the kernel $\mathbf{F}(\alpha)$ after the linear term, i.e., the neglect of the correlation contribution to the kernel, implies that the response function is approximated by a geometric series in $\mathbf{L}\mathbf{F}^{(1)}\mathbf{L}$. Because $\mathbf{L}\mathbf{F}^{(1)}\mathbf{L}$ equals $\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1}$ this means that the response matrix is approximated by a geometric series in its linear term which is exactly known in terms of KS orbitals and eigenvalues, see Sec. IV A and Appendix. Thus there exist two very different approximations for the response matrix $\mathbf{X}(\alpha)$ that are both based on the first-order term $\mathbf{X}^{(1)}$: (i) the straightforward first-order expansion (74) and (ii) the geometric series (86) or, in summed up form, (84).

3. Expansions starting from terms of the frequency-dependent response function up to second or higher order

If the coupling constant expansion of the response function $\mathbf{X}(\alpha)$ is truncated after the second-order term, i.e., is approximated by

$$\mathbf{X}(\alpha) \approx \mathbf{X}^{(0)} + \alpha\mathbf{X}^{(1)} + \alpha^2\mathbf{X}^{(2)}, \quad (87)$$

then this implies an expansion

$$\mathbf{F}(\alpha) \approx \mathbf{L}^{-1}\left[\sum_{n=1}^{\infty}(\alpha\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1} + \alpha^2\mathbf{L}^{-1}\mathbf{X}^{(2)}\mathbf{L}^{-1})^n\right]\mathbf{L}^{-1} \quad (88)$$

for the kernel $\mathbf{F}(\alpha)$. With Eqs. (70) and (71) the above expansion turns into

$$\mathbf{F}(\alpha) \approx \mathbf{L}^{-1}\left[\sum_{n=1}^{\infty}(\alpha\mathbf{L}\mathbf{F}^{(1)}\mathbf{L} - \alpha^2\mathbf{L}\mathbf{F}^{(1)}\mathbf{L}\mathbf{F}^{(1)}\mathbf{L} + \alpha^2\mathbf{L}\mathbf{F}^{(2)}\mathbf{L})^n\right]\mathbf{L}^{-1}. \quad (89)$$

A truncation of the coupling constant expansion of the response function $\mathbf{X}(\alpha)$ after the second-order term thus implies an expansion of the kernel $\mathbf{F}(\alpha)$ containing the terms $\mathbf{X}^{(1)}$ and $\mathbf{X}^{(2)}$ of $\mathbf{X}(\alpha)$. The contributions in each order are given by Eqs. (67), (68), (69), and corresponding equations for higher orders by neglecting all terms $\mathbf{X}^{(n)}$ with $n > 2$. Moreover, with Eq. (89) a coupling constant expansion of $\mathbf{F}(\alpha)$ containing only the leading terms $\mathbf{F}^{(1)}$ and $\mathbf{F}^{(2)}$ is implied from a truncation of the expansion of $\mathbf{X}(\alpha)$ after second order.

Similarly, truncations of the coupling constant expansion of the response matrix $\mathbf{X}(\alpha)$ after a higher-order n_{\max} imply corresponding expansions of the kernel $\mathbf{F}(\alpha)$ in terms $\mathbf{X}^{(n)}$ up to the order n_{\max} or in terms $\mathbf{F}^{(n)}$ up to the order n_{\max} .

4. Expansions starting from terms of the exchange-correlation kernel up to second or higher order

Now expansion (55) of the kernel $\mathbf{F}(\alpha)$ is truncated after the second-order term giving

$$\mathbf{F}(\alpha) \approx \alpha\mathbf{F}^{(1)} + \alpha^2\mathbf{F}^{(2)}. \quad (90)$$

Substitution of Eq. (90) into Eq. (73) yields

$$\begin{aligned}\mathbf{X}(\alpha) &\approx -\mathbf{L}[\mathbf{1} + \mathbf{L}(\alpha\mathbf{F}^{(1)} + \alpha^2\mathbf{F}^{(2)})\mathbf{L}]^{-1}\mathbf{L} \\ &= -\mathbf{L}\left[\mathbf{1} + \sum_{n=1}^{\infty}(-)^n(\alpha\mathbf{L}\mathbf{F}^{(1)}\mathbf{L} + \alpha^2\mathbf{L}\mathbf{F}^{(2)}\mathbf{L})^n\right]\mathbf{L}.\end{aligned}\quad (91)$$

With Eqs. (62), (67), and (68) the above equation for $\mathbf{X}(\alpha)$ turns into

$$\begin{aligned}\mathbf{X}(\alpha) &\approx \mathbf{X}_s - \mathbf{L}\sum_{n=1}^{\infty}(-)^n(\alpha\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1} \\ &\quad + \alpha^2\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-2}\mathbf{X}^{(1)}\mathbf{L}^{-1} + \alpha^2\mathbf{L}^{-1}\mathbf{X}^{(2)}\mathbf{L}^{-1})^n\mathbf{L} \\ &= -\mathbf{L}[\mathbf{1} + (\alpha\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1} + \alpha^2\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-2}\mathbf{X}^{(1)}\mathbf{L}^{-1} \\ &\quad + \alpha^2\mathbf{L}^{-1}\mathbf{X}^{(2)}\mathbf{L}^{-1})]\mathbf{L}.\end{aligned}\quad (92)$$

This means a truncation of the coupling constant expansion of the kernel $\mathbf{F}(\alpha)$ after the second-order term implies the expansion (92) of the response matrix $\mathbf{X}(\alpha)$ in terms of $\mathbf{X}^{(1)}$ and $\mathbf{X}^{(2)}$, which is very different from the straightforward second order expansion (87), similarly as the geometric series (86) or, in summed up form, (84) is very different from the first-order expansion (74).

Again a generalization of Eqs. (90)–(92) to orders higher than two is straightforward.

V. ACFD METHODS FOR THE KOHN-SHAM CORRELATION ENERGY BASED ON THE ADIABATIC-CONNECTION FLUCTUATION-DISSIPATION THEOREM

In this section, various ACFD methods are considered. This includes existing methods like the ACFD method of Ref. [46] that treats the Hartree and exchange kernel exactly and neglects the correlation kernel or the ACFD method of Ref. [63] that additionally takes into account the correlations kernel via the PSA but also new ACFD approaches proposed here. The existing methods are related to the expansions of the response matrix and the kernel derived in the previous section and in case of the PSA a formal justification is provided. In Sec. V A, methods based on the KS response matrix and the first-order contribution $\mathbf{X}^{(1)}$ of the response matrix are discussed and proposed. These methods all have a formal N^5 scaling with the system size N and, if not already implemented, can be easily implemented starting from existing ACFD implementations that use $\mathbf{X}^{(1)}$.

In Sec. V B, methods based on contributions $\mathbf{X}^{(n)}$ with $n > 1$ are briefly sketched. By considering terms $\mathbf{X}^{(n)}$ of higher orders a hierarchy of methods is obtained that approaches the full KS correlation energy. The $\mathbf{X}^{(n)}$ are accessible in any order by perturbation theory in terms of KS orbitals and their eigenvalues, however, like in other hierarchies of methods approaching the full correlation energy, e.g., the coupled cluster hierarchy, the resulting expressions are getting increasingly complicated and the scaling of the methods becomes increasingly unfavourable.

A. ACFD methods based on the first-order term of the frequency-dependent response function

All ACFD methods that are based on the first-order term $\mathbf{X}^{(1)}$ of the response matrix $\mathbf{X}(\alpha)$ approximate $\mathbf{X}(\alpha)$ by expressions containing $\mathbf{X}^{(1)}$. These expressions and the related series expansions are quite different. Starting point are two ACFD methods: (i) a method relying on the direct expansion of $\mathbf{X}(\alpha)$ up to first order, Eq. (74), and (ii) a method approximating $\mathbf{X}(\alpha)$ by a geometric series in $\mathbf{X}^{(1)}$, Eq. (84), which results if the correlation kernel is neglected but the Hartree and exchange kernel are treated exactly. Method (i) is presented in the following Sec. V A 1 and has not yet been implemented. Method (ii) has already been introduced earlier, was denoted EXXRPA (exact-exchange RPA) in Ref. [46] and ACFD[Hx] in Ref. [63], and is discussed in Sec. V A 2. In certain cases, methods (i) and (ii) both can yield unphysical response matrices $\mathbf{X}(\alpha)$ that are no longer negative semidefinite. Interestingly, each unphysical positive eigenvalue of the response matrix in one of the methods corresponds to a physically reasonable negative eigenvalue in the other method. This suggests to combine the two methods, leading to an approach presented in Sec. V A 3. The occurrence of unphysical response matrices turns out to be related to the convergence radius of the involved coupling constant expansions, a point discussed further below.

In method (i), the response matrix $\mathbf{X}(\alpha)$ is approximated according to Eq. (74) by its zeroth and first-order terms, $\mathbf{X}^{(0)} = \mathbf{X}_s$ and $\mathbf{X}^{(1)}$, respectively, which implies to approximate the kernel $\mathbf{F}(\alpha)$ by a geometric series in terms of $\mathbf{X}^{(1)}$,

Eq. (75). In method (ii), on the other hand, $\mathbf{X}(\alpha)$ turns out to be approximated by a geometric series in $\mathbf{X}^{(1)}$, Eq. (86), and the kernel $\mathbf{F}(\alpha)$ is approximated by its leading component $\mathbf{F}^{(1)} = \mathbf{L}^{-2}\mathbf{X}^{(1)}\mathbf{L}^{-2}$, Eq. (67), which is tantamount to neglecting the correlation kernel and taking into account the Hartree plus the exchange kernel exactly. By renormalizing the coefficients in the geometric series for $\mathbf{F}(\alpha)$ in method (i) or for $\mathbf{X}(\alpha)$ in method (ii) the two methods can be combined in one, because the renormalized coefficients of $\mathbf{F}(\alpha)$ determine the renormalized coefficients of $\mathbf{X}(\alpha)$ and vice versa. The resulting approximation introduced in detail in Sec. V A 4 is called the power series approximation (PSA). By a suitable choice of the renormalized coefficients physical response matrices $\mathbf{X}(\alpha)$ can be obtained that are always correctly negative definite and that do not suffer from unphysical singularities in the response matrix that are encountered in certain cases in methods (i) and (ii). If the renormalized series for $\mathbf{F}(\alpha)$ is truncated then the PSA of Ref. [63] is obtained, which is discussed in Sec. V A 5.

In all the ACFD methods considered in this section, the basic quantity $\mathbf{X}^{(1)}$ occurs pre- and post-multiplied by the inverse of the square root \mathbf{L} of the KS response function. That is, the matrix $\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1}$ or more precisely its spectral representation

$$\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1} = \mathbf{U}\boldsymbol{\tau}\mathbf{U}^\dagger \quad (93)$$

containing a diagonal matrix $\boldsymbol{\tau}$ with the eigenvalues and a matrix \mathbf{U} collecting the eigenvectors is the quantity that is actually entering the methods of this section. Within all the methods the KS correlation energy is calculated from the ACFD theorem in the form

$$E_c = \frac{-1}{2\pi} \int_0^1 d\alpha \int_0^\infty d\omega \text{Tr}\{\mathbf{L}[\mathbf{L}^{-1}\mathbf{X}(\alpha)\mathbf{L}^{-1} + \mathbf{1}]\mathbf{L}\mathbf{F}_H\}, \quad (94)$$

which follows with Eq. (62) from the ACFD theorem in the form given by Eq. (6). The dimensionless quantity $\mathbf{L}^{-1}\mathbf{X}(\alpha)\mathbf{L}^{-1}$, i.e., the response matrix $\mathbf{X}(\alpha)$ pre- and post-multiplied by \mathbf{L}^{-1} is approximated by expressions $\mathbf{U}g(\alpha\boldsymbol{\tau})\mathbf{U}^\dagger$ that contain functions $g(\alpha\boldsymbol{\tau})$ of the diagonal matrix $\boldsymbol{\tau}$ of the spectral representation (93) of $\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1}$. Equation (94) for the correlation energy then turns into

$$E_c = \frac{-1}{2\pi} \int_0^1 d\alpha \int_0^\infty d\omega \text{Tr}\{\mathbf{L}\mathbf{U}g(\alpha\boldsymbol{\tau})\mathbf{U}^\dagger\mathbf{L}\mathbf{F}_H\}. \quad (95)$$

If the coupling strength integration in Eq. (95) can be carried out analytically, the KS correlation energy is given by

$$E_c = \frac{-1}{2\pi} \int_0^\infty d\omega \text{Tr}\{\mathbf{L}\mathbf{U}G(\boldsymbol{\tau})\mathbf{U}^\dagger\mathbf{L}\mathbf{F}_H\} \quad (96)$$

with the function $G(\boldsymbol{\tau}) = \int_0^1 d\alpha g(\alpha\boldsymbol{\tau})$.

This means all methods discussed in this section require the same computational steps which include the construction of the matrix $\mathbf{X}^{(1)}$, the computationally most demanding step, the construction of the KS response matrix and the determination of the square root \mathbf{L} of its negative, and the diagonalization of $\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1}$. The methods only differ in the evaluation of the functions $g(\alpha\boldsymbol{\tau})$ or $G(\boldsymbol{\tau})$ a step requiring only negligible

computational effort. Moreover, this means that implementations for the different methods of this section differ only by one routine, the one evaluating the functions $g(\alpha\tau)$ or $G(\tau)$. Thus, if one of the methods has been implemented, then the others can be obtained with minimal programming effort.

1. ACFD methods using directly the zeroth- and first-order terms of the frequency-dependent response function

The direct coupling constant expansion (74) of the response function $\mathbf{X}(\alpha)$ up to first order with Eq. (62) for $\mathbf{X}^{(0)} = \mathbf{X}_s$ assumes the form

$$\begin{aligned}\mathbf{X}(\alpha) &\approx -\mathbf{L}\mathbf{L} + \alpha\mathbf{X}^{(1)} \\ &= \mathbf{L}[-\mathbf{1} + \alpha\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1}]\mathbf{L} \\ &= \mathbf{L}\mathbf{U}[-\mathbf{1} + \alpha\boldsymbol{\tau}]\mathbf{U}^\dagger\mathbf{L}\end{aligned}\quad (97)$$

with the spectral representation (93) of $\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1}$. Inserting the truncated expansion (97) into the ACFD theorem (94) yields equation

$$\begin{aligned}E_c &= \frac{-1}{2\pi} \int_0^1 d\alpha \int_0^\infty d\omega \text{Tr}\{\mathbf{L}[\alpha\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1}]\mathbf{L}\mathbf{F}_H\} \\ &= \frac{-1}{2\pi} \int_0^1 d\alpha \int_0^\infty d\omega \text{Tr}\{\mathbf{L}\mathbf{U}\alpha\boldsymbol{\tau}\mathbf{U}^\dagger\mathbf{L}\mathbf{F}_H\} \\ &= \frac{-1}{2\pi} \int_0^\infty d\omega \text{Tr}\left\{\mathbf{L}\mathbf{U}\frac{1}{2}\boldsymbol{\tau}\mathbf{U}^\dagger\mathbf{L}\mathbf{F}_H\right\},\end{aligned}\quad (98)$$

which equals Eqs. (95) and (96) for the KS correlation energy with the functions

$$g(\alpha\boldsymbol{\tau}) = \alpha\boldsymbol{\tau} \quad (99)$$

and

$$G(\boldsymbol{\tau}) = \frac{1}{2}\boldsymbol{\tau}.\quad (100)$$

Approximation (97) for $\mathbf{X}(\alpha)$ only would be negative semidefinite and thus would not have positive eigenvalues if $\alpha\tau_{\mu\mu} \leq 1$ held true for all diagonal values $\tau_{\mu\mu}$ of the diagonal matrix $\boldsymbol{\tau}$. Usually this is not the case, however, and the response matrix (97) exhibits unphysical positive eigenvalues.

In Sec. IV D 1, it was shown that a truncation of the coupling constant expansion of the response matrix $\mathbf{X}(\alpha)$ after the linear term implies to approximate the kernel $\mathbf{F}(\alpha)$ by a geometric series in $\alpha\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1}$, see Eq. (76). If the spectral representation (93) for $\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1}$ is inserted in this geometric series, then it assumes the form

$$\mathbf{F}(\alpha) \approx \mathbf{L}^{-1}\mathbf{U}\left[\sum_{n=1}^{\infty} \alpha^n \boldsymbol{\tau}^n\right]\mathbf{U}^\dagger\mathbf{L}^{-1}.\quad (101)$$

Inserting the above expansion (101) for $\mathbf{F}(\alpha)$ in the basic equation of TDDFT in the form given by Eq. (63) leads to

$$\begin{aligned}\mathbf{X}(\alpha) &\approx -\mathbf{L}\mathbf{U}[\mathbf{1} + \alpha\boldsymbol{\tau} + \alpha^2\boldsymbol{\tau}^2 + \dots]^{-1}\mathbf{U}^\dagger\mathbf{L} \\ &= -\mathbf{L}\mathbf{U}[(\alpha\boldsymbol{\tau} - \mathbf{1})^{-1}]^{-1}\mathbf{U}^\dagger\mathbf{L} \\ &= \mathbf{L}\mathbf{U}[-\mathbf{1} + \alpha\boldsymbol{\tau}]\mathbf{U}^\dagger\mathbf{L}.\end{aligned}\quad (102)$$

With the last line of Eq. (102) expression (97) was obtained again. This is not surprising because as discussed in Sec. IV D 1 a truncation of the coupling constant expansion of

$\mathbf{X}(\alpha)$ after the linear term $\mathbf{X}^{(1)}$ is equivalent to approximating $\mathbf{F}(\alpha)$ by a geometric series in terms of $\mathbf{X}^{(1)}$. The crucial point is that this equivalence holds true only within the convergence radius of the geometric series $\mathbf{F}(\alpha)$. If the diagonal matrix $\boldsymbol{\tau}$ contains elements $\tau_{\mu\mu}$ with $|\alpha\tau_{\mu\mu}| \geq 1$ this is no longer the case. For $\alpha\tau_{\mu\mu} \geq 1$, all elements of the series in the first line of Eq. (102) are positive which means that the geometric series approaches infinity and the response function $\mathbf{X}(\alpha)$ approaches zero because the inverse of the series appears in Eq. (102). This suggests to set $\alpha\tau_{\mu\mu}$ to one and thus $\mathbf{X}(\alpha)$ to zero if its original value is larger, i.e., if originally $\alpha\tau_{\mu\mu} > 1$. In this way it is guaranteed that the response matrix does not exhibit unphysical positive eigenvalues. For $\alpha\tau_{\mu\mu} \leq -1$, the series in the first line Eq. (102) no longer converges but has elements of alternating sign. In this case, it seems reasonable to use the function $[\alpha\boldsymbol{\tau} - \mathbf{1}]^{-1}$ beyond the range of convergence of the series, which does not lead to unphysical positive eigenvalues of the response matrix.

The above described modification of the response matrix of Eq. (97) is reflected in the evaluation of the correlation energy via Eq. (95) by a modification of the function $g(\alpha\boldsymbol{\tau})$. The function $g(\alpha\boldsymbol{\tau})$ yields a diagonal matrix \mathbf{g} with matrix elements $g_{\mu\mu}$ obtained by evaluating the function g for the matrix elements $\tau_{\mu\mu}$ of $\boldsymbol{\tau}$ after having multiplied them by α , i.e., $g_{\mu\mu} = g(\alpha\tau_{\mu\mu})$. The modified function g for the argument $\alpha\tau$ (suppressing the superscripts $\mu\mu$ for notational simplicity) is given by

$$g(\alpha\tau) = \alpha\tau \quad \text{for } \alpha\tau < 1 \quad (103)$$

and

$$g(\alpha\tau) = 1 \quad \text{for } \alpha\tau \geq 1.\quad (104)$$

The modified function g can be integrated analytically which leads to a modified function G to be used in Eq. (96) for the KS correlation energy. The function $G(\boldsymbol{\tau})$ yields a diagonal matrix \mathbf{G} with matrix elements $G_{\mu\mu}$ obtained by evaluating the function G for the matrix elements $\tau_{\mu\mu}$ of $\boldsymbol{\tau}$, i.e., $G_{\mu\mu} = G(\tau_{\mu\mu})$. The modified function G for the argument τ (suppressing the superscripts $\mu\mu$ for notational simplicity) is given by

$$G(\tau) = \frac{1}{2}\tau \quad \text{for } \alpha\tau < 1 \quad (105)$$

and

$$G(\tau) = 1 - \frac{1}{2\tau} \quad \text{for } \alpha\tau \geq 1,\quad (106)$$

respectively.

2. ACFD methods approximating the exchange-correlation kernel by its first-order term

If the kernel $\mathbf{F}(\alpha)$ is approximated according to Eq. (79) by its first-order contribution $\alpha\mathbf{F}^{(1)}$ equaling the sum of the Hartree plus the exchange kernel then the response matrix $\mathbf{X}(\alpha)$ is given by Eq. (84) if $\mathbf{F}^{(1)}$ is expressed according to Eq. (67) by $\mathbf{X}^{(1)}$ as shown in Sec. IV D 2. With the spectral representation (93) of $\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1}$, Eq. (84) for the response matrix $\mathbf{X}(\alpha)$ reads as

$$\mathbf{X}(\alpha) \approx -\mathbf{L}\mathbf{U}[\mathbf{1} + \alpha\boldsymbol{\tau}]^{-1}\mathbf{U}^\dagger\mathbf{L}.\quad (107)$$

Inserting Eq. (107) into the ACFD equation (94) yields

$$\begin{aligned} E_c &= \frac{-1}{2\pi} \int_0^1 d\alpha \int_0^\infty d\omega \text{Tr}\{\mathbf{L}\mathbf{U}[-(\mathbf{1} + \alpha\boldsymbol{\tau})^{-1} + \mathbf{1}]\mathbf{U}^\dagger\mathbf{L}\mathbf{F}_H\} \\ &= \frac{-1}{2\pi} \int_0^\infty d\omega \text{Tr}\{\mathbf{L}\mathbf{U}[-\boldsymbol{\tau}^{-1} \ln(|\mathbf{1} + \boldsymbol{\tau}| + \mathbf{1})]\mathbf{U}^\dagger\mathbf{L}\mathbf{F}_H\}, \end{aligned} \quad (108)$$

which equals Eqs. (95) and (96) for the KS correlation energy with the functions

$$g(\alpha\boldsymbol{\tau}) = -(1 + \alpha\boldsymbol{\tau})^{-1} + 1 \quad (109)$$

and

$$G(\boldsymbol{\tau}) = -\boldsymbol{\tau}^{-1} \ln(|\mathbf{1} + \boldsymbol{\tau}|) + 1, \quad (110)$$

respectively.

If elements in the diagonal matrix $\boldsymbol{\tau}$ assume values of -1 then the response function $\mathbf{X}(\alpha)$ in Eq. (107) becomes singular, for elements of $\boldsymbol{\tau}$ being smaller than 1 the response function exhibits unphysical positive eigenvalues. In practice such cases typically are encountered in electronic structures that exhibit a singlet-singlet instability in an exact-exchange-only KS treatment [61] or that are characterized by static correlation. From a technical point of view such singularities can be handled because they turn out to be integrable singularities in the frequency integration. To avoid numerical problems in the frequency integration, a regularization can be employed. To that end, the function $G(\boldsymbol{\tau})$ of Eq. (110) is replaced by

$$\begin{aligned} G(\boldsymbol{\tau}) &= -\boldsymbol{\tau}^{-1} \ln(|\mathbf{1} + \boldsymbol{\tau}|) + 1 \\ &\text{for } \boldsymbol{\tau} \leq -1 - \epsilon_\tau \text{ and } -1 + \epsilon_\tau \leq \boldsymbol{\tau} \end{aligned} \quad (111)$$

and by

$$\begin{aligned} G(\boldsymbol{\tau}) &= -\boldsymbol{\tau}^{-1} \ln(\epsilon_\tau) + 1 \\ &\text{for } -1 - \epsilon_\tau < \boldsymbol{\tau} < -1 + \epsilon_\tau. \end{aligned} \quad (112)$$

While this enables to treat the singularity at $\boldsymbol{\tau}$ values of minus one from a technical point of view, the formal problem that the response function $\mathbf{X}(\alpha)$ has unphysical positive eigenvalues for $\boldsymbol{\tau}$ values smaller than minus one remains.

3. ACFD method using the first-order term of the frequency-dependent response function directly and via the exchange-correlation kernel

In the previous two Secs. VA1 and VA2, two ACFD methods were discussed that both rely on the first-order contribution $\mathbf{X}^{(1)}$ of the response matrix $\mathbf{X}(\alpha)$. In one case, $\mathbf{X}^{(1)}$ enters via the direct expansion of $\mathbf{X}(\alpha)$ up to first order in the coupling constant α , in the other case, the leading contribution $\mathbf{F}^{(1)}$ of the kernel $\mathbf{F}(\alpha)$ is expressed by $\mathbf{X}^{(1)}$. Within both ACFD methods unphysical response matrices can emerge for certain eigenvalues of $\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1}$. Interestingly, however, the first method suffers from unphysical response functions if the eigenvalues of $\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1}$ are larger than one, while the second methods becomes problematic if the eigenvalues are equal or smaller than minus one. This suggests to combine both methods. Within both methods, the eigenvalues of $\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1}$ enter via a function $g(\alpha\boldsymbol{\tau})$ of the diagonal matrix $\boldsymbol{\tau}$, see spectral representation (93) of $\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1}$ and

expression (95) for the ACFD correlation energy in terms of $g(\alpha\boldsymbol{\tau})$.

Now the functions $g(\alpha\boldsymbol{\tau})$ of the two methods are simply combined such that the function $g(\alpha\boldsymbol{\tau})$ of the first method is employed for $\boldsymbol{\tau}$ values smaller or equal than zero and the function $g(\alpha\boldsymbol{\tau})$ of the second method applies for $\boldsymbol{\tau}$ values greater than zero. That is the function g is given by

$$g(\alpha\boldsymbol{\tau}) = \alpha\boldsymbol{\tau} \quad \text{for } \alpha\boldsymbol{\tau} \leq 0 \quad (113)$$

and

$$g(\alpha\boldsymbol{\tau}) = 1 - (1 + \alpha\boldsymbol{\tau})^{-1} \quad \text{for } 0 < \alpha\boldsymbol{\tau}_{\mu\mu}. \quad (114)$$

Because both value and derivative of the two branches of the function g approach the same value at $\boldsymbol{\tau} = 0$ the function g is continuous and differentiable everywhere.

The integration over the coupling constant α in expression (95) for the correlation energy can be carried out analytically such that the latter is given by Eq. (96) with the function $G(\boldsymbol{\tau})$ given by

$$G(\boldsymbol{\tau}) = \frac{1}{2}\boldsymbol{\tau} \quad \text{for } \boldsymbol{\tau} \leq 0 \quad (115)$$

and

$$G(\boldsymbol{\tau}) = 1 - \boldsymbol{\tau}^{-1} \ln(1 + \boldsymbol{\tau}) \quad \text{for } 0 < \boldsymbol{\tau}_{\mu\mu}. \quad (116)$$

This combined method is free of parameters but nevertheless does not suffer from unphysical response matrices and can be implemented with minimal programming effort starting from an implementation of the EXXRP or ACFD[Hx] method of Sec. VA2 that is described in Ref. [46].

4. ACFD methods with renormalized power series approximation in the variable $\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1}$ for frequency-dependent response function and exchange-correlation kernel

In Secs. IVD1 and IVD2, it was shown that a truncation of the coupling constant expansion of the response matrix $\mathbf{X}(\alpha)$ after the first-order term $\mathbf{X}^{(1)}$ implies a geometric series (without zeroth-order term) for the kernel $\mathbf{F}(\alpha)$ in the variable $\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1}$, Eqs. (74) to (76), and that a truncation of the coupling constant expansion of the kernel $\mathbf{F}(\alpha)$ after the leading first-order term $\mathbf{F}^{(1)} = \mathbf{L}^{-2}\mathbf{X}^{(1)}\mathbf{L}^{-2}$ implies a geometric series for $\mathbf{X}(\alpha)$ in the variable $\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1}$, Eqs. (79) to (86). The geometric series have a finite convergence radius. Moreover, both series can lead to unphysical response functions. In one case, if the eigenvalues of $\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1}$ are larger than one, in the other case, if they are smaller than minus one. One way to handle this problem was presented in the previous Sec. VA3 by using piecewise the one or the other series. Another way to relate the two series is to renormalize the coefficients of all terms of an order higher than one. This leads for the response function to the series

$$\begin{aligned} \mathbf{X}(\alpha) &\approx -\mathbf{L} \left[\mathbf{1} - \mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1} + \sum_{n=2}^{\infty} \gamma_n (-)^n (\alpha\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1})^n \right] \mathbf{L} \\ &= -\mathbf{L}\mathbf{U} \left[\mathbf{1} - \alpha\boldsymbol{\tau} + \sum_{n=2}^{\infty} \gamma_n (-)^n (\alpha\boldsymbol{\tau})^n \right] \mathbf{U}^\dagger \mathbf{L} \\ &= \mathbf{L}\mathbf{U}[g(\alpha\boldsymbol{\tau}) - 1]\mathbf{U}^\dagger \mathbf{L} \end{aligned} \quad (117)$$

instead of the original series (86) with

$$g(\alpha\tau) = \left(\alpha\tau + \sum_{n=2}^{\infty} (-)^{n+1} \gamma_n \alpha^n \tau^n \right) \quad (118)$$

and with the renormalized coefficients γ_n . The leading coefficient γ_1 has to equal one, i.e., $\gamma_1 = 1$, in order to guarantee that the exact first-order term of the coupling constant expansion of $\mathbf{X}(\alpha)$ is retained. The function $g(\alpha\tau)$ is defined such that $g(\alpha\tau) - 1$ leads to the series expansion of $\mathbf{X}(\alpha)$ because $g(\alpha\tau)$ then corresponds to the previously defined function g that can be directly used in Eq. (95) for the KS correlation energy.

For the kernel the series

$$\begin{aligned} \mathbf{F}(\alpha) &\approx \mathbf{L}^{-1} \left[\sum_{n=1}^{\infty} \beta_n (\alpha \mathbf{L}^{-1} \mathbf{X}^{(1)} \mathbf{L}^{-1})^n \right] \mathbf{L}^{-1} \\ &= \mathbf{L}^{-1} \mathbf{U} \left[\sum_{n=1}^{\infty} \beta_n (\alpha \boldsymbol{\tau})^n \right] \mathbf{U}^\dagger \mathbf{L}^{-1} \\ &= \mathbf{L}^{-1} \mathbf{U} f(\alpha \boldsymbol{\tau}) \mathbf{U}^\dagger \mathbf{L}^{-1} \end{aligned} \quad (119)$$

is obtained instead of the original series (76) with

$$f(\alpha\tau) = \alpha\tau + \sum_{n=2}^{\infty} \beta_n \alpha^n \tau^n \quad (120)$$

and with the renormalized coefficients β_n . Again the leading coefficient β_1 has to equal one, i.e., $\beta_1 = 1$, in order to guarantee that the exact first-order term of the coupling constant expansion of $\mathbf{F}(\alpha)$ is preserved.

If the renormalized expansion (119) for the kernel $\mathbf{F}(\alpha)$ is inserted into the basic equation (63) of TDDFT in the linear response regime then the response matrix assumes the form

$$\mathbf{X}(\alpha) = -\mathbf{L}\mathbf{U}[\mathbf{1} + f(\alpha\boldsymbol{\tau})]^{-1}\mathbf{U}^\dagger\mathbf{L}. \quad (121)$$

Comparison of Eqs. (117) and (121) shows that

$$g(\alpha\tau) = -\frac{1}{1 + f(\alpha\tau)} + 1 \quad (122)$$

For $f(\alpha\tau) = \alpha\tau$, the EXXRP or ACFD[Hx] method [46] described in Sec. V A 2 is recovered. Eq. (122) shows that the expansions (118) and (120) are not independent of each other but that one determines the other. Expansions (118) in conjunction with Eq. (117) represents the PSA for the response matrix $\mathbf{X}(\alpha)$ while expansion (120) in conjunction with Eq. (119) represents the PSA for the kernel $\mathbf{F}(\alpha)$.

The integration

$$G(\tau) = \int_0^1 d\alpha g(\alpha\tau) = \int_0^\infty d\alpha \left(-\frac{1}{1 + f(\alpha\tau)} + 1 \right) \quad (123)$$

yields a function $G(\tau)$ that can be used in the ACFD theorem in form of Eq. (96).

ACFD methods that evaluate the KS correlation energy according to Eq. (95) or (96) require functions $g(\alpha\tau)$, $f(\alpha\tau)$, or $G(\tau)$. In order to go beyond the simple first-order approximations discussed in the previous Secs. V A 1–V A 3 an ansatz for one of the three functions is required. Ongoing first attempts to represent the function $g(\alpha\tau)$ by a linear combination of Gaussian type functions have been

highly promising. Optimization of the coefficients of such linear combinations using as reference the correlation energy of the homogeneous electron gas and potential energy curves of simple two-electron systems like the hydrogen molecule have lead to first preliminary ACFD approaches that seem to approach the goal of high accuracy and universal applicability [96].

5. ACFD methods with truncated power series approximation in the variable $\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1}$ for the exchange-correlation kernel

If the renormalized expansion (120) for the function $f(\alpha\tau)$ determining via Eq. (119) the kernel $\mathbf{F}(\alpha)$ is truncated after the N th-order term then with Eq. (122) a function $g(\alpha\tau)$ of the form

$$g(\alpha\tau) = -\left(1 + \alpha\tau + \sum_{n=2}^N \beta_n \alpha^n \tau^n \right)^{-1} + 1 \quad (124)$$

is obtained which can be used to evaluate the KS correlation energy by Eq. (95). In Ref. [63], an ACFD method based on such a function $g(\alpha\tau)$ truncated after the forth order was presented and applied to various molecules and molecular aggregates. Furthermore, the name PSA was introduced in Ref. [63] for expansions of the response matrix and the kernel in terms of the dimensionless quantity $\mathbf{L}^{-1}\mathbf{X}^{(1)}\mathbf{L}^{-1}$ or the matrix $\boldsymbol{\tau}$ of its eigenvalues. In Ref. [63], the PSA was introduced in an *ad hoc* fashion. The discussion of the series expansions of the response matrix $\mathbf{X}(\alpha)$ and the kernel $\mathbf{F}(\alpha)$ in this work provides a formal justification of the PSA, however, without supplying values for the coefficients β_n . The coefficients $\beta_2, \beta_3, \beta_4$ required in the forth-order PSA of Ref. [63] were obtained by optimizing a set of reaction energies. The resulting ACFD approach showed excellent results for various molecular systems, including transition states and dimers bound by dispersion interactions. Moreover, bond dissociation, e.g., dissociation of the nitrogen molecule, that requires a correct treatment of strong static correlation could be described highly accurately, despite the fact that the underlying KS wave function is a single non-spin-polarized KS determinant. The ability to correctly describe electronic structures with multireference character on the basis of a single Slater determinant is a promise of the KS formalism, to which all previous KS methods cannot live up.

B. Hierarchies of methods towards the exact Kohn-Sham correlation energy

All ACFD methods in the previous Sec. V A require besides the KS response matrix $\mathbf{X}_s = \mathbf{X}^{(0)}$ only the first order contribution $\mathbf{X}^{(1)}$ to the response matrix $\mathbf{X}(\alpha)$. In this section, ACFD methods employing in addition higher-order contributions $\mathbf{X}^{(n)}$ are briefly sketched. Explicit formulas for $n = 2$ are presented, however, a generalization to higher orders is straightforward. A contribution of order $n \geq 2$ can be explicitly constructed in terms of KS orbitals and eigenvalues, the KS exchange potential, and contributions $v^{(m)}$ to the correlation potential with $m \leq n$ along the lines discussed in Secs. III and IV. The required potentials are accessible via the OEP approach, see Sec. III C, which yields the potentials for given KS orbitals and eigenvalues. Thus, for a given set of KS

orbitals and eigenvalues, the contributions $\mathbf{X}^{(n)}$ to the response matrix, in principle, can be evaluated to any order.

1. ACFD methods based on a direct expansion of the frequency-dependent response function

Inserting the coupling strength expansion (87) of the response matrix $\mathbf{X}(\alpha)$ up to second order in the ACFD expression (94) for the KS correlation energy yields

$$\begin{aligned} E_c &= \frac{-1}{2\pi} \int_0^1 d\alpha \int_0^\infty d\omega \text{Tr}\{[\alpha\mathbf{X}^{(1)} + \alpha^2\mathbf{X}^{(2)}]\mathbf{F}_H\} \\ &= \frac{-1}{2\pi} \int_0^\infty d\omega \text{Tr}\left\{\left[\frac{1}{2}\mathbf{X}^{(1)} + \frac{1}{3}\mathbf{X}^{(2)}\right]\mathbf{F}_H\right\}. \end{aligned} \quad (125)$$

With the spectral representation

$$\mathbf{L}^{-1}[\alpha\mathbf{X}^{(1)} + \alpha^2\mathbf{X}^{(2)}]\mathbf{L}^{-1} = \mathbf{U}(\alpha)\boldsymbol{\tau}(\alpha)\mathbf{U}^\dagger(\alpha). \quad (126)$$

Equation (125) assumes the form

$$E_c = \frac{-1}{2\pi} \int_0^1 d\alpha \int_0^\infty d\omega \text{Tr}\{\mathbf{L}\mathbf{U}(\alpha)\boldsymbol{\tau}(\alpha)\mathbf{U}^\dagger(\alpha)\mathbf{L}\mathbf{F}_H\}, \quad (127)$$

which differs from Eq. (98) by the coupling strength dependence of the matrices $\mathbf{U}(\alpha)$ and $\boldsymbol{\tau}(\alpha)$. Like in the first-order case, the eigenvalues collected in the diagonal matrix $\boldsymbol{\tau}(\alpha)$ must be smaller or equal to one to avoid that the corresponding response matrix $\mathbf{X}(\alpha)$ has unphysical positive eigenvalues. Again this can be enforced by defining a function $g[\boldsymbol{\tau}(\alpha)]$ according to

$$g[\boldsymbol{\tau}(\alpha)] = \alpha\boldsymbol{\tau} \quad \text{for } \boldsymbol{\tau}(\alpha) \leq 1 \quad (128)$$

and

$$g(\alpha\boldsymbol{\tau}) = 1 \quad \text{for } \boldsymbol{\tau}(\alpha) > 1 \quad (129)$$

and by evaluating the KS correlation energy by the equation

$$E_c = \frac{-1}{2\pi} \int_0^1 d\alpha \int_0^\infty d\omega \text{Tr}\{\mathbf{L}\mathbf{U}(\alpha)g[\boldsymbol{\tau}(\alpha)]\mathbf{U}^\dagger(\alpha)\mathbf{L}\mathbf{F}_H\}, \quad (130)$$

which differs from Eq. (95) again by the coupling strength dependence of the matrices $\mathbf{U}(\alpha)$ and $\boldsymbol{\tau}(\alpha)$.

2. ACFD methods based on expansions of the exchange-correlation kernel

In the previous section, ACFD methods based on direct expansions of the response matrix $\mathbf{X}(\alpha)$ to higher orders than one in the coupling constant are considered, in this section, ACFD methods relying on expansion of the kernel $\mathbf{F}(\alpha)$ to orders higher than one are briefly considered. Taking into account terms of first- and second-order term in the expansion of the kernel $\mathbf{F}(\alpha)$, see Eq. (90), together with Eqs. (63) and (94) leads to the KS correlation energy

$$\begin{aligned} E_c &= \frac{-1}{2\pi} \int_0^1 d\alpha \int_0^\infty d\omega \\ &\quad \times \text{Tr}\{\mathbf{L}[-(\mathbf{1} + \mathbf{L}[\alpha\mathbf{F}^{(1)} + \alpha^2\mathbf{F}^{(2)}]\mathbf{L})^{-1} + \mathbf{1}]\mathbf{L}\mathbf{F}_H\}. \end{aligned} \quad (131)$$

Expressing the $\mathbf{F}^{(1)}$ and $\mathbf{F}^{(2)}$ by the accessible quantities $\mathbf{X}^{(1)}$ and $\mathbf{X}^{(2)}$ with the help of Eqs. (67) and (68) suggests the

spectral representation

$$\begin{aligned} &\mathbf{L}[\alpha\mathbf{F}^{(1)} + \alpha^2\mathbf{F}^{(2)}]\mathbf{L} \\ &= \mathbf{L}^{-1}[\alpha\mathbf{X}^{(1)} + \alpha^2\mathbf{X}^{(1)}\mathbf{L}^{-2}\mathbf{X}^{(1)} + \alpha^2\mathbf{X}^{(2)}]\mathbf{L}^{-1} \\ &= \mathbf{U}(\alpha)\boldsymbol{\tau}(\alpha)\mathbf{U}^\dagger(\alpha) \end{aligned} \quad (132)$$

and equation

$$\begin{aligned} E_c &= \frac{-1}{2\pi} \int_0^1 d\alpha \int_0^\infty d\omega \\ &\quad \times \text{Tr}\{\mathbf{L}\mathbf{U}(\alpha)[-(\mathbf{1} + \boldsymbol{\tau}(\alpha))^{-1} + \mathbf{1}]\mathbf{U}^\dagger(\alpha)\mathbf{L}\mathbf{F}_H\} \end{aligned} \quad (133)$$

for the KS correlation energy. Equation (133) equals Eq. (130) with

$$g[\boldsymbol{\tau}(\alpha)] = -(\mathbf{1} + \boldsymbol{\tau}(\alpha))^{-1} + \mathbf{1}. \quad (134)$$

In contrast to Eqs. (108) and (109) again the matrices $\boldsymbol{\tau}$ and \mathbf{U} and thus the variable τ of the function g depend on the coupling constant α .

For τ values equal minus one, like in the lower-order case, the response matrix $\mathbf{X}(\alpha)$ becomes singular and for τ values smaller than minus one it has unphysical positive eigenvalues. One way to deal with the problem of unphysical response matrices is to combine the methods of this Sec. VB 2 with the one of the previous Section. VB 1 as it is described in Sec. VA 3 for the methods using only the first-order contribution $\mathbf{X}^{(1)}$. That is to use for the function $g[\boldsymbol{\tau}(\alpha)]$ expression (134) for $\boldsymbol{\tau}(\alpha) > 0$ and expression (128) for $\boldsymbol{\tau}(\alpha) \leq 0$.

3. ACFD methods with renormalized power series approximations for frequency-dependent response function and exchange-correlation kernel using variables of higher order in the coupling constant

Finally it is possible to generalize the concept of a PSA described in Secs. VA 4 and VA 5 to cases that use contributions $\mathbf{X}^{(n)}$ of an order n higher than one. The functions g and f corresponding to those of Eqs. (118) and (120) are given by

$$g[\boldsymbol{\tau}(\alpha)] = -\left(1 + \boldsymbol{\tau}(\alpha) + \sum_{n=2}^N \gamma_n[\boldsymbol{\tau}(\alpha)]^n\right)^{-1} + 1 \quad (135)$$

and

$$f[\boldsymbol{\tau}(\alpha)] = \boldsymbol{\tau}(\alpha) + \sum_{n=2}^{\infty} \beta_n[\boldsymbol{\tau}(\alpha)]^n. \quad (136)$$

VI. CONCLUDING REMARKS

The approach presented in Sec. IV A to derive contributions $\mathbf{X}^{(n)}$ to the response matrix $\mathbf{X}(\alpha)$ in any order in the coupling constant α not only gives access to the contributions $\mathbf{X}^{(n)}$ in a straightforward way using quantities accessible in static perturbation theory along the adiabatic connection. In addition, Sec. IV B shows how the $\mathbf{X}^{(n)}$ determine the contributions $\mathbf{F}^{(n)}$ to the frequency-dependent exchange-correlation kernel $\mathbf{F}(\alpha)$ in the corresponding order of the coupling constant. The presented relations between the coupling constant expansions of the response matrix $\mathbf{X}(\alpha)$ and the kernel $\mathbf{F}(\alpha)$ suggest a manifold of mostly new ACFD methods

including hierarchies of methods towards the exact KS correlation energy.

From the various ACFD methods based on the first-order contribution $\mathbf{X}^{(1)}$ of the response function that are considered in Sec. VA only the EXXRPA or ACFD[Hx] method described in Sec. VA2 and the truncated PSA described in Sec. VA5 have been implemented and tested so far [46,62,63]. Because all the methods based on $\mathbf{X}^{(1)}$ differ only in the employed function $g(\alpha\tau)$ all the methods can easily be implemented once one of the methods is available. The computational effort of handling of the function $g(\alpha\tau)$ including the integration over the coupling strength α is completely negligible thus all methods of Sec. VA require almost the same computational resources determined by the construction of the first-order contribution $\mathbf{X}^{(1)}$ to the response matrix that scales with N^5 with the system size N . The new ACFD methods presented in Sec. VA thus can be tested quite easily. A challenge is the optimization of the functions g , f or G in the renormalized PSA of Sec. VA4, which, on the other hand, offers many opportunities. One obvious strategy is to optimize one of these functions using reference data like molecular reaction energies or potential energy surfaces of simple molecules. First attempts in this direction turned out to be promising [96]. There remain, however, many possible ways to pursue such a strategy that are largely unexplored. In addition, it is desirable to investigate whether properties, e.g., the asymptotic behavior, of the functions g , f , and G can be deduced from formal considerations.

ACFD methods taking into account contributions $\mathbf{X}^{(n)}$ to the response matrix of an order higher than one, prior to this work, have not been proposed. An implementation of such methods, which are sketched in Sec. VB, clearly requires considerable programming effort and will lead to ACFD methods with higher computational demands than the methods based on the first-order contribution $\mathbf{X}^{(1)}$. Because the latter ACFD methods already can compete with high-level wave-function methods with respect to accuracy and wide applicability it seems reasonable to firstly explore and exploit the potential of these first-order methods. If the better ratio of computational effort to performance seen for first-order ACFD methods compared to wave-function methods holds true also for the higher-order ACFD methods suggested in Sec. VB then, however, it seems worth to explore these methods in practice.

ACFD methods are amenable to Laplace transform techniques [97], which can reduce the scaling of the computational effort with the system size up to linear scaling. First successful

attempts along these lines have already been made for dRPA methods [58,98–100]. In a similar way the scaling of the more advanced ACFD methods considered here should be improvable.

Here the formal considerations of Secs. III and IV are used to analyze existing and to suggest new ACFD methods for the KS correlation energy. To that end, in Sec. IV, response matrices and exchange-correlation kernels for complex valued frequencies are considered. All formulas in Sec. IV, however, are equally valid for frequencies $\nu = \omega + i\eta$ with a real valued frequency ω and a complex contribution $i\eta$ approaching zero. This is the situation usually considered in TDDFT in the response regime for calculating excitation energies or response properties like frequency-dependent polarizations. Most present TDDFT methods [72–74] rely on crude frequency-independent approximations for the exchange-correlation kernel that are obtained as simple functional derivatives of conventional exchange-correlation potentials, with respect to the electron density. Typically, functional derivatives are taken of exchange-correlation potentials from local or semilocal functionals or from hybrid or meta GGA functionals. The resulting kernels not only lead to substantial errors in excitation energies or other quantities but suffer from basic limitations, they are, e.g., not able to describe charge transfer processes or excitations that correspond to double excitations in a one electron picture. Already some time ago, it has been shown that taking into account the exact frequency-dependent exchange kernel enables a treatment of charge transfer excitations [101–103]. By including only the exact exchange kernel in addition to the Hartree kernel, however, results similar to time-dependent Hartree-Fock are obtained, which is not sufficient for practical purposes. How approximations that have been discussed here, such as the PSA for the correlation kernel, perform in the calculation of response properties and excitation energies is an highly interesting open question to be explored in the future.

An objection raised against both DFT as well as TDDFT methods is that they were not systematically improvable towards the correct answer as it is possible by hierarchies of wave-function methods like the coupled cluster hierarchy. Here hierarchies of ACFD methods approaching the KS correlation energy have been sketched that address this objection for DFT. With the presented approach to systematically improving the exchange-correlation kernel additionally a path towards a systematic improvement of TDDFT in the response regime is opened up.

APPENDIX: CONTRIBUTION TO THE FREQUENCY-DEPENDENT RESPONSE FUNCTION OF FIRST ORDER IN THE COUPLING CONSTANT

The contribution $\chi^{(1)}(\nu, \mathbf{r}, \mathbf{r}')$ of first order in the coupling constant α to the response function $\chi(\alpha, \nu, \mathbf{r}, \mathbf{r}')$ is given by

$$\chi^{(1)}(\nu, \mathbf{r}, \mathbf{r}') = \chi_{\text{I}}^{(1)}(\nu, \mathbf{r}, \mathbf{r}') + \chi_{\text{II}}^{(1)}(\nu, \mathbf{r}, \mathbf{r}') + \chi_{\text{III}}^{(1)}(\nu, \mathbf{r}, \mathbf{r}') + \chi_{\text{IV}}^{(1)}(\nu, \mathbf{r}, \mathbf{r}') \quad (\text{A1})$$

with

$$\chi_{\text{I}}^{(1)}(\nu, \mathbf{r}, \mathbf{r}') = \sum_{i,j} \sum_{a,b} \frac{\langle \phi_i | \hat{\rho}(\mathbf{r}) | \phi_a \rangle \langle \phi_a \phi_j | | \phi_i \phi_b \rangle \langle \phi_b | \hat{\rho}(\mathbf{r}') | \phi_j \rangle}{(\varepsilon_i - \varepsilon_a + \nu)(\varepsilon_j - \varepsilon_b + \nu)} + \sum_{i,j} \sum_{a,b} \frac{\langle \phi_a | \hat{\rho}(\mathbf{r}) | \phi_i \rangle \langle \phi_i \phi_b | | \phi_a \phi_j \rangle \langle \phi_j | \hat{\rho}(\mathbf{r}') | \phi_b \rangle}{(\varepsilon_i - \varepsilon_a - \nu)(\varepsilon_j - \varepsilon_b - \nu)}, \quad (\text{A2})$$

$$\chi_{\text{II}}^{(1)}(\nu, \mathbf{r}, \mathbf{r}') = \sum_{i,j} \sum_{a,b} \frac{\langle \phi_i | \hat{\rho}(\mathbf{r}) | \phi_a \rangle \langle \phi_a \phi_b | | \phi_i \phi_j \rangle \langle \phi_j | \hat{\rho}(\mathbf{r}') | \phi_b \rangle}{(\varepsilon_i - \varepsilon_a + \nu)(\varepsilon_j - \varepsilon_b - \nu)} + \sum_{i,j} \sum_{a,b} \frac{\langle \phi_b | \hat{\rho}(\mathbf{r}) | \phi_j \rangle \langle \phi_i \phi_j | | \phi_a \phi_b \rangle \langle \phi_a | \hat{\rho}(\mathbf{r}') | \phi_i \rangle}{(\varepsilon_i - \varepsilon_a + \nu)(\varepsilon_j - \varepsilon_b - \nu)}, \quad (\text{A3})$$

$$\begin{aligned} \chi_{\text{III}}^{(1)}(\nu, \mathbf{r}, \mathbf{r}') = & \sum_i \sum_{a,b} \frac{\langle \phi_i | \hat{\rho}(\mathbf{r}) | \phi_a \rangle \langle \phi_a | \hat{v}_x^{\text{NL}} - \hat{v}_x | \phi_b \rangle \langle \phi_b | \hat{\rho}(\mathbf{r}') | \phi_i \rangle}{(\varepsilon_i - \varepsilon_a + \nu)(\varepsilon_i - \varepsilon_b + \nu)} + \sum_i \sum_{a,b} \frac{\langle \phi_a | \hat{\rho}(\mathbf{r}) | \phi_i \rangle \langle \phi_b | \hat{v}_x^{\text{NL}} - \hat{v}_x | \phi_a \rangle \langle \phi_i | \hat{\rho}(\mathbf{r}') | \phi_b \rangle}{(\varepsilon_i - \varepsilon_a - \nu)(\varepsilon_i - \varepsilon_b - \nu)} \\ & - \sum_{i,j} \sum_a \frac{\langle \phi_i | \hat{\rho}(\mathbf{r}) | \phi_a \rangle \langle \phi_j | \hat{v}_x^{\text{NL}} - \hat{v}_x | \phi_i \rangle \langle \phi_a | \hat{\rho}(\mathbf{r}') | \phi_j \rangle}{(\varepsilon_i - \varepsilon_a + \nu)(\varepsilon_j - \varepsilon_a + \nu)} - \sum_{i,j} \sum_a \frac{\langle \phi_a | \hat{\rho}(\mathbf{r}) | \phi_i \rangle \langle \phi_i | \hat{v}_x^{\text{NL}} - \hat{v}_x | \phi_j \rangle \langle \phi_j | \hat{\rho}(\mathbf{r}') | \phi_a \rangle}{(\varepsilon_i - \varepsilon_a - \nu)(\varepsilon_j - \varepsilon_a - \nu)}, \end{aligned} \quad (\text{A4})$$

and

$$\begin{aligned} \chi_{\text{IV}}^{(1)}(\nu, \mathbf{r}, \mathbf{r}') = & \sum_i \sum_{a,b} \frac{\langle \phi_i | \hat{\rho}(\mathbf{r}) | \phi_a \rangle \langle \phi_b | \hat{v}_x^{\text{NL}} - \hat{v}_x | \phi_i \rangle \langle \phi_a | \hat{\rho}(\mathbf{r}') | \phi_b \rangle}{(\varepsilon_i - \varepsilon_a + \nu)(\varepsilon_i - \varepsilon_b)} + \sum_i \sum_{a,b} \frac{\langle \phi_b | \hat{\rho}(\mathbf{r}) | \phi_a \rangle \langle \phi_i | \hat{v}_x^{\text{NL}} - \hat{v}_x | \phi_b \rangle \langle \phi_a | \hat{\rho}(\mathbf{r}') | \phi_i \rangle}{(\varepsilon_i - \varepsilon_a + \nu)(\varepsilon_i - \varepsilon_b)} \\ & + \sum_i \sum_{a,b} \frac{\langle \phi_a | \hat{\rho}(\mathbf{r}) | \phi_i \rangle \langle \phi_i | \hat{v}_x^{\text{NL}} - \hat{v}_x | \phi_b \rangle \langle \phi_b | \hat{\rho}(\mathbf{r}') | \phi_a \rangle}{(\varepsilon_i - \varepsilon_a - \nu)(\varepsilon_i - \varepsilon_b)} + \sum_i \sum_{a,b} \frac{\langle \phi_a | \hat{\rho}(\mathbf{r}) | \phi_b \rangle \langle \phi_b | \hat{v}_x^{\text{NL}} - \hat{v}_x | \phi_i \rangle \langle \phi_i | \hat{\rho}(\mathbf{r}') | \phi_a \rangle}{(\varepsilon_i - \varepsilon_a - \nu)(\varepsilon_i - \varepsilon_b)} \\ & - \sum_{i,j} \sum_a \frac{\langle \phi_i | \hat{\rho}(\mathbf{r}) | \phi_a \rangle \langle \phi_a | \hat{v}_x^{\text{NL}} - \hat{v}_x | \phi_j \rangle \langle \phi_j | \hat{\rho}(\mathbf{r}') | \phi_i \rangle}{(\varepsilon_i - \varepsilon_a + \nu)(\varepsilon_j - \varepsilon_a)} - \sum_{i,j} \sum_a \frac{\langle \phi_i | \hat{\rho}(\mathbf{r}) | \phi_j \rangle \langle \phi_j | \hat{v}_x^{\text{NL}} - \hat{v}_x | \phi_a \rangle \langle \phi_a | \hat{\rho}(\mathbf{r}') | \phi_i \rangle}{(\varepsilon_i - \varepsilon_a + \nu)(\varepsilon_j - \varepsilon_a)} \\ & - \sum_{i,j} \sum_a \frac{\langle \phi_a | \hat{\rho}(\mathbf{r}) | \phi_i \rangle \langle \phi_j | \hat{v}_x^{\text{NL}} - \hat{v}_x | \phi_a \rangle \langle \phi_i | \hat{\rho}(\mathbf{r}') | \phi_j \rangle}{(\varepsilon_i - \varepsilon_a - \nu)(\varepsilon_j - \varepsilon_a)} - \sum_{i,j} \sum_a \frac{\langle \phi_j | \hat{\rho}(\mathbf{r}) | \phi_i \rangle \langle \phi_a | \hat{v}_x^{\text{NL}} - \hat{v}_x | \phi_j \rangle \langle \phi_i | \hat{\rho}(\mathbf{r}') | \phi_a \rangle}{(\varepsilon_i - \varepsilon_a - \nu)(\varepsilon_j - \varepsilon_a)}. \end{aligned} \quad (\text{A5})$$

With the help of the first-order contribution $\chi^{(1)}(\nu, \mathbf{r}, \mathbf{r}')$ of the response function an equation for the sum of the Hartree and the frequency-dependent exchange kernel can be derived, see Eqs. (51) and (67) of the main text. This equation was derived earlier in Refs. [75–77]. The contribution $\chi^{(1)}(\nu, \mathbf{r}, \mathbf{r}')$ was designated as function $h^{(1)}(\nu, \mathbf{r}, \mathbf{r}')$ in Refs. [75–77] because it was not identified as the contribution to the response matrix of first order in the coupling constant α .

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