

Exchange-correlation potentials in the adiabatic connection fluctuation-dissipation framework

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We provide the expression of the exchange-correlation potential in the adiabatic connection fluctuation-dissipation (ACFD) framework, for arbitrary time-dependent (TD) kernels. We investigate the asymptotic behavior of the ACFD potential in three relevant approximations: the random-phase approximation, the exact-exchange kernel in two-electron systems, and the adiabatic local-density approximation. We show that these potentials have the expected $-1/r + Q/r^3 - \alpha/(2r^4)$ tail (in closed-shell systems with spherical symmetry), where Q and α depend on the TD kernel and reflect the physics included in each approximation. We also discuss approximate ACFD potentials that are much simpler to compute than the exact ones while being likely of reasonable accuracy.

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I. INTRODUCTION

The Kohn-Sham density-functional theory (DFT) [1–3] has now become a standard and convenient method for the calculation of the ground-state properties of solid-state and molecular systems. The total energy $E[n]$, a functional of the electron density $n(\mathbf{r})$, includes an exchange-correlation part $E_{xc}[n]$ that accounts for all many-body effects beyond the Hartree level. However, the exact expression of $E_{xc}[n]$ remains unknown, so that approximations have to be made for practical purposes. The widely used local-density approximation [2] (LDA) and semilocal generalized gradient approximations (GGA's) [4] usually yield a good description of the atomic equilibrium structure and vibrational properties of molecules and solids. However, they notably fail to predict molecular dissociation energies within chemical accuracy (50 meV), and do not properly include van der Waals interactions between distant subsystems. The exact-exchange scheme [5], or the hybrid functionals [6], also fail to include these interactions.

These shortcomings arise from the truly nonlocal nature of the exchange-correlation functional $E_{xc}[n]$, which cannot be accounted for by local or semilocal approximations such as the LDA or GGA's. In particular, the van der Waals forces are due to long-range correlations, and as such are beyond the scope of these approximations. Their description requires a fully nonlocal exchange-correlation functional as provided, for example, by the adiabatic connection fluctuation-dissipation (ACFD) theorem [7]. In this formalism, $E_{xc}[n]$ is computed (via an integration over the coupling constant λ) from the dynamical susceptibility χ_λ of the system, calculated for a scaled Coulomb interaction $\lambda/|\mathbf{r}-\mathbf{r}'|$ between electrons. The time-dependent density-functional theory [8–10] (TDDFT) provides various approximations to χ_λ , depending on the choice for the dynamical exchange and correlation kernel f_{xc} . Even the random-phase approximation (RPA), the simplest approximation to χ_λ ($f_{xc}=0$), al-

ready yields a long-range van der Waals tail. The basics of the ACFD formalism will be briefly reviewed in Sec. II of this paper.

The ACFD formalism has first been applied to jellium [11], jellium slabs [12,13], and to the asymptotic atom-atom van der Waals interaction [14]. The calculation of the full potential-energy curve of simple diatomic molecules, which is much more demanding, has been achieved only recently by Furche [15], and by Fuchs and Gonze [16]. Their results proved to be rather accurate in the vicinity of the bonding region, even for difficult cases such as Be_2 . However, the dissociation curves calculated for N_2 [16], H_2 [17], and Be_2 [18] all show an unphysical bump at intermediate separations. This bump may arise because the TDDFT kernels f_{xc} used in these works are not accurate enough, and/or because of the lack of self-consistency. Indeed, all calculations were performed using LDA, GGA, or exchange-only optimized effective potential (x-OEP) [5,19,20] orbitals as input for the ACFD exchange and correlation energy. In this paper, we investigate the possibility of doing self-consistent ACFD calculations. We derive the integral equation that determines the exchange-correlation potential as the functional derivative of the ACFD exchange-correlation energy $E_{xc}[n]$, for an arbitrary TDDFT kernel f_{xc} . This expression can be understood (and analyzed) as the ACFD counterpart of the Sham-Schlüter equation [21,22] for $v_{xc}(\mathbf{r})$, established in the framework of many-body perturbation theory [23,24] (MBPT). Although its numerical solution seems rather involved, this equation lends itself as a starting point to discuss general properties of the ACFD exchange-correlation potential. Here we discuss the asymptotic behavior of the ACFD potentials in some of the state of the art approximations (RPA, etc.). We show that these potentials have the expected [25] $-1/r + Q/r^3 - \alpha/(2r^4)$ tail (in closed-shell systems with spherical symmetry), where Q and α depend on the TDDFT kernel f_{xc} used to calculate χ_λ . We also discuss approximate ACFD potentials that are much simpler to compute than the exact ones while being likely of reasonable accuracy.

This paper is organized as follows: in Sec. II, we briefly review the basics of the ACFD formalism and highlight some links with many-body perturbation theory. We then derive

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the expression of the ACFD exchange-correlation potential $v_{xc}(\mathbf{r})$ for an arbitrary TDDFT kernel f_{xc} in Sec. III. We show that this potential is the sum of two terms, one of which has the structure of the linear-response Sham-Schlüter equation [21,22]. Last, we discuss the asymptotic behavior of the ACFD potential in Sec. IV, and propose approximate ACFD potentials in Sec. V.

II. THE ACFD FORMALISM

In this section, we briefly review the basics of the ACFD formalism and recall the main practical approximations (RPA, etc.). We then discuss actual calculations in model systems and diatomic molecules, as well as the problem of self-consistency. Finally, we highlight some links with many-body perturbation theory.

A. Basic equations

We consider an interacting electron gas with ground-state density $n(\mathbf{r})$ in an external (ionic) potential $v_{ext}(\mathbf{r})$. We restrict ourselves to spin-compensated systems, the extension to spin densities being straightforward. The basic idea of the ACFD formalism [7] is to establish an adiabatic connection between the Hamiltonian H of this interacting electron gas and the corresponding Kohn-Sham (KS) Hamiltonian H_{KS} . To that end, we introduce the set of Hamiltonians $H(\lambda)$ that describe electrons repelling each other with a scaled Coulomb interaction $\lambda/|\mathbf{r}-\mathbf{r}'|$ and moving in an external potential $v_\lambda(\mathbf{r})$ such that the ground-state density of $H(\lambda)$ equals $n(\mathbf{r})$. $H(1)$ is the physical many-body Hamiltonian with $v_{\lambda=1}(\mathbf{r})=v_{ext}(\mathbf{r})$, and $H(0)$ is the KS Hamiltonian with $v_{\lambda=0}(\mathbf{r})=v_{KS}(\mathbf{r})=v_{ext}(\mathbf{r})+v_h(\mathbf{r})+v_{xc}(\mathbf{r})$, where $v_h(\mathbf{r})$ and $v_{xc}(\mathbf{r})$ are, respectively, the Hartree and exchange-correlation potentials. Calling $|\Psi(\lambda)\rangle$ and $E(\lambda)=\langle\Psi(\lambda)|H(\lambda)|\Psi(\lambda)\rangle$ the ground-state and ground-state energy of $H(\lambda)$, we get from the usual Hellmann-Feynman trick

$$\frac{dE(\lambda)}{d\lambda}=\langle\Psi(\lambda)|V_{ee}|\Psi(\lambda)\rangle+\int d^3\mathbf{r}\frac{\partial v_\lambda}{\partial\lambda}(\mathbf{r})n(\mathbf{r}), \quad (1)$$

$V_{ee}=\sum_{i<j}1/|\mathbf{r}_i-\mathbf{r}_j|$ being the Coulomb interaction between electrons. Integrating Eq. (1) over the coupling constant λ between 0 and 1 thus yields

$$E_{hxc}=\int_0^1 d\lambda\langle\Psi(\lambda)|V_{ee}|\Psi(\lambda)\rangle, \quad (2)$$

where E_{hxc} is the sum of the Hartree (E_h), exchange, and correlation energies. Moreover, the ground-state expectation value of V_{ee} can be calculated from the imaginary frequency density-density response function $\chi_\lambda(\mathbf{r},\mathbf{r}';iu)$ of the interacting electron gas, thanks to the fluctuation-dissipation theorem:

$$\begin{aligned} &\langle\Psi(\lambda)|V_{ee}|\Psi(\lambda)\rangle \\ &= E_h - \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \\ &\quad \times \left\{ \left[\int \frac{du}{2\pi} \chi_\lambda(\mathbf{r},\mathbf{r}';iu) \right] + n(\mathbf{r}) \delta(\mathbf{r}-\mathbf{r}') \right\}, \end{aligned} \quad (3)$$

where the integral over u runs over the whole imaginary frequency axis. This relation can be straightforwardly inferred from the usual ‘‘sum-over-states’’ expression for $\chi_\lambda(\mathbf{r},\mathbf{r}';iu)$. Since $|\Psi(0)\rangle$ is the Slater determinant built from the occupied KS orbitals, $\langle\Psi(0)|V_{ee}|\Psi(0)\rangle$ is the sum of the Hartree and exchange energies. The correlation energy E_c thus reads, in matrix form:

$$E_c[n] = -\frac{1}{2} \int_0^1 d\lambda \int \frac{du}{2\pi} \text{Tr}\{v[\chi_\lambda(iu) - \chi_0(iu)]\}, \quad (4)$$

where we have defined

$$\text{Tr}\{A(iu)B(iu)\} = \int d^3\mathbf{r} \int d^3\mathbf{r}' A(\mathbf{r},\mathbf{r}';iu)B(\mathbf{r}',\mathbf{r};iu). \quad (5)$$

In Eq. (4), $v(\mathbf{r},\mathbf{r}')=1/|\mathbf{r}-\mathbf{r}'|$ and $\chi_0(\mathbf{r},\mathbf{r}';iu)$ is the KS density-density response function, whose expression as a function of the KS orbitals $\varphi_i(\mathbf{r})$ and KS energies ε_i is:

$$\chi_0(\mathbf{r},\mathbf{r}';iu) = \sum_j \sum_k \frac{n_j - n_k}{iu + \varepsilon_j - \varepsilon_k} \varphi_j^*(\mathbf{r})\varphi_k(\mathbf{r})\varphi_k^*(\mathbf{r}')\varphi_j(\mathbf{r}'), \quad (6)$$

where the sum runs over all doubly occupied ($n_i=2$) and unoccupied ($n_i=0$) KS orbitals. Additionally, the exchange energy E_x can be calculated from $\chi_0(\mathbf{r},\mathbf{r}';iu)$ using Eq. (3), which reduces to the well-known Fock expression. Finally, the interacting and KS density-density response functions are related in the framework of the TDDFT [8–10] by a Dyson-like equation:

$$\begin{aligned} \chi_\lambda(\mathbf{r},\mathbf{r}';iu) &= \chi_0(\mathbf{r},\mathbf{r}';iu) + \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \chi_0(\mathbf{r},\mathbf{r}_1;iu) \\ &\quad \times K_{hxc}^\lambda(\mathbf{r}_1,\mathbf{r}_2;iu)\chi_\lambda(\mathbf{r}_2,\mathbf{r}';iu), \end{aligned} \quad (7)$$

where $K_{hxc}^\lambda(\mathbf{r},\mathbf{r}';iu) = \lambda v(\mathbf{r},\mathbf{r}') + f_{xc}^\lambda[n](\mathbf{r},\mathbf{r}';iu)$ and $f_{xc}^\lambda[n](\mathbf{r},\mathbf{r}';iu)$ is the dynamical exchange-correlation kernel at coupling constant λ (scaling relations between $f_{xc}^\lambda[n]$ and $f_{xc}^{\lambda=1}[n]$ are given in Refs. [11,26]). The set of ACFD equations (4)–(7) formally yields the exact correlation energy $E_c[n]$, which is an implicit functional of the density through the KS orbitals and energies and through the TDDFT kernel $f_{xc}^\lambda[n]$. In principle, the ACFD total energy $E[n]$ should be minimized [2] with respect to the density (the number of electrons being kept fixed). The stationarity of $E[n]$ requires the KS orbitals and energies to be the self-consistent solu-

tions of the KS equations, $H_{\text{KS}}\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r})$, with $v_{\text{xc}}(\mathbf{r}) = \delta E_{\text{xc}}[n]/\delta n(\mathbf{r})$. The expression of the ACFD $v_{\text{xc}}(\mathbf{r})$ will be derived later in Sec. III.

B. Practical approximations

In practice, the set of equations (4)–(7) is the starting point for fully nonlocal approximations to the correlation energy $E_c[n]$ through (i) the use of an approximate TDDFT kernel f_{xc} and (ii) the use of non-self-consistent KS orbitals and energies.

The simplest approximation [27] to χ_λ , known as the random-phase approximation, is to set $f_{\text{xc}}^\lambda[n](\mathbf{r}, \mathbf{r}'; iu) = 0$. The RPA already accounts for van der Waals interactions but poorly describes short-range (SR) correlations. Indeed, the on-top correlation hole is too deep [28,29], making the RPA total energies too negative (though isoelectronic energy differences are expected to be quite accurate [30]). To improve the description of short-range effects, the RPA can combine with a local-density correction $E_{\text{c,sr}}^{\text{LDA}}[n] = E_{\text{c}}^{\text{LDA}}[n] - E_{\text{c}}^{\text{LDA-RPA}}[n]$, $E_{\text{c}}^{\text{LDA-RPA}}[n]$ being the local density approximation based on the RPA correlation energy for the homogeneous electron gas [30,31]. This defines the so-called RPA + approximation $E_{\text{c}}^{\text{RPA+}}[n] = E_{\text{c}}^{\text{RPA}}[n] + E_{\text{c,sr}}^{\text{LDA}}[n]$. Alternatively, short-range exchange effects can be included using the frequency-independent approximate exchange kernel of Petersilka, Gossmann, and Gross [32] (PGG):

$$f_{\text{xc}}^\lambda[n](\mathbf{r}, \mathbf{r}'; iu) = -2\lambda \frac{\left| \sum_{j=1}^{N/2} \varphi_j^*(\mathbf{r}) \varphi_j(\mathbf{r}') \right|^2}{n(\mathbf{r})n(\mathbf{r}')|\mathbf{r} - \mathbf{r}'|}, \quad (8)$$

where N is the number of electrons. The PGG kernel is the exact-exchange kernel in one-electron systems (where it yields zero correlation energy, unlike RPA and RPA+) and in two-electron systems. The exact-exchange kernel for arbitrary systems, though known [33], is still too demanding to apply. Short-range effects can also be included using the adiabatic local-density approximation [34] (ALDA), which is based on the LDA exchange-correlation energy $E_{\text{xc}}^{\text{LDA}}[n]$:

$$f_{\text{xc}}^\lambda[n](\mathbf{r}, \mathbf{r}'; iu) = \lambda^2 \frac{\delta^2 E_{\text{xc}}^{\text{LDA}}[n_{1/\lambda}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')}, \quad (9)$$

where $n_\lambda(\mathbf{r}) = \lambda^3 n(\lambda\mathbf{r})$. The total energy of the homogeneous electron gas [11,35,36] and of jellium slabs [12,13,31] has been calculated in the RPA, RPA+, and ALDA approximations. The atomization energies, equilibrium bond lengths, and vibrational properties of a dozen of molecules have been calculated by Furche [15] using RPA and RPA+, and by Fuchs and Gonze [16] (H_2 and Be_2) using RPA, RPA+, and PGG. Although these approximations have an overall accuracy comparable to GGA, they clearly perform better in difficult cases such as Be_2 , which has a very small binding energy. However, the full dissociation curves of N_2 [15], H_2 [17], and Be_2 [18] all show an unphysical bump at intermediate distances, which may reflect some deficiencies of these kernels or the lack of self-consistency (see below). Other

approximations remain to be tested on molecules, such as the ALDA, the BPG kernel of Burke, Petersilka, and Gross [37] (PGG for parallel spins and ALDA for antiparallel spins), or the energy-optimized kernels of Dobson and Wang [38]. Thus progress can be expected from future improvements of the TDDFT kernels, in view of the only rather recent interest in the ACFD functionals.

The other approximation made in actual ACFD calculations is the use of non-self-consistent KS orbitals and energies as input for Eqs. (4)–(7). Indeed, the expression of the ACFD exchange-correlation potential $v_{\text{xc}}(\mathbf{r})$ is still missing. In practice, the ACFD energies are thus computed with orbitals $\varphi_i(\mathbf{r})$ and energies ε_i that come from a former LDA, GGA, or x-OEP run. Although a self-consistent ACFD calculation can be expected quite tricky, ACFD potentials may be used to discuss general properties or design approximate v_{xc} 's that include long-range effects. In Secs. III, IV, and V, we will investigate the possibility of performing self-consistent ACFD calculations and provide the ACFD exchange-correlation potential for an arbitrary TDDFT kernel f_{xc} . Before that, we would like to stress the links between ACFD functionals and other recent works in the framework of MBPT.

C. Links with MBPT

In the past few years, there has been a renewal of interest in the calculation of total energies from many-body perturbation theory. For example, the total energy of the homogeneous electron gas has been calculated by Holm and von Barth [39] and by García-González and Godby [40] in the self-consistent GW approximation [28], using the well-known Galitskii-Midgal (GM) formula [23,41]. The results proved to be very accurate over a wide range of densities. Almladh *et al.* [42] also calculated the total energy of the homogeneous electron gas using another scheme based on the Luttinger-Ward (LW) formula [43], again in the GW approximation for the self-energy. The LW total energy is a functional of the Green function, which is equal to the GM total energy if the self-consistent Green function G is plugged into both formulas [44]. However, the LW total energy is variational with respect to the Green function, unlike GM. Hence, it is much more robust than GM with respect to errors in the Green function. Indeed rather accurate total energies were obtained by Almladh *et al.* evaluating the LW functional at the noninteracting KS Green function.

Moreover, the Nozières functional [45] in the GW approximation for the self-energy has been used by Aryasetiawan *et al.* [46] to compute the dissociation curve of H_2 (see also Ref. [17]), and by Miyake *et al.* [47] to compute the total energy of bulk silicon and sodium. The Nozières functional is also a variational functional of the Green function, which however differs from the original LW formula. In the same spirit as Almladh *et al.*, they evaluated this functional at the LDA Green function G_{LDA} . Their correlation energy reads [Eq. (6) of Ref. [46] has been symmetrized for convenience and their $P(iu)$ is our $\chi_0(iu)$]

$$E_c[n] = \Phi_c = \frac{1}{2} \int \frac{du}{2\pi} \text{Tr} \{ \ln[1 - \chi_0(iu)\nu] + \chi_0(iu)\nu \}. \quad (10)$$

This is just the ACFD-RPA correlation energy. Indeed, the integration over the coupling constant λ can be carried out analytically in the ACFD-RPA, because

$$\text{Tr} \{ \nu \chi_\lambda^{\text{RPA}}(iu) \} = - \frac{\partial}{\partial \lambda} \text{Tr} \{ \ln[1 - \lambda \chi_0(iu)\nu] \}, \quad (11)$$

where $\chi_\lambda^{\text{RPA}}(iu) = [1 - \lambda \chi_0(iu)\nu]^{-1} \chi_0(iu)$. This then directly yields Eq. (10). Thus the scheme of Refs. [46,47] is equivalent [17] to the ACFD-RPA calculation of Refs. [15,16]. In the homogeneous electron gas, the RPA however performs much worse than LW, which shows that the variational properties of the Nozières functional are not as good as those of the LW functional [42].

The link with MBPT is almost completely lost beyond RPA, because most TDDFT kernels have no obvious diagrammatic structure. There is still, however, a connection between the ACFD-ALDA (and ACFG-PGG in two-electron systems) and the so-called $G\Gamma$ approximation [48] for the self-energy, which includes vertex corrections from the DFT. Indeed, taking the chemical potential $\mu=0$ as the reference of energies, one can write

$$\chi_0(\mathbf{r}, \mathbf{r}'; iu) = 2 \int \frac{dv}{2\pi} G_0(\mathbf{r}, \mathbf{r}'; iu + iv) G_0(\mathbf{r}', \mathbf{r}; iv), \quad (12)$$

where

$$G_0(\mathbf{r}, \mathbf{r}'; iu) = \sum_j \frac{\varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}')}{iu - \varepsilon_j} \quad (13)$$

is the imaginary frequency KS Green function (when $\mu=0$, the poles of G_0 corresponding to the occupied KS states are on the left of the imaginary axis, whereas those corresponding to the empty KS states are on the right). In the same way, the exchange energy E_x can be cast in the form (the limits $\delta \rightarrow 0^+$, $\delta' \rightarrow 0^+$ are implied)

$$E_x = - \int \frac{du}{2\pi} e^{iu\delta} \int \frac{dv}{2\pi} e^{iv\delta'} \int d^3\mathbf{r} \int d^3\mathbf{r}' G_0(\mathbf{r}, \mathbf{r}'; iu + iv) \times G_0(\mathbf{r}', \mathbf{r}; iv) \nu(\mathbf{r}, \mathbf{r}'). \quad (14)$$

Inserting Eq. (12) into Eq. (4), and adding Eq. (14), we get after straightforward manipulation

$$E_{xc}[n] = \int_0^1 \frac{d\lambda}{\lambda} \int \frac{du}{2\pi} e^{iu\delta} \text{Tr} \{ \Sigma_{xc}^\lambda(iu) G_0(iu) \}, \quad (15)$$

where the effective self-energy $\Sigma_{xc}^\lambda(iu)$ reads

$$\Sigma_{xc}^\lambda(\mathbf{r}, \mathbf{r}'; iu) = - \int \frac{dv}{2\pi} e^{iv\delta} G_0(\mathbf{r}, \mathbf{r}'; iu + iv) W_\lambda(\mathbf{r}, \mathbf{r}'; iv), \quad (16)$$

with

$$W_\lambda(iu) = \lambda \varepsilon_\lambda^{-1}(iu) \nu, \quad (17)$$

$$\varepsilon_\lambda(iu) = 1 - K_{\text{hxc}}^\lambda(iu) \chi_0(iu).$$

$\varepsilon_\lambda(iu)$ and $W_\lambda(iu)$ are the electron-test charge dielectric function and screened Coulomb interaction, respectively. $W_\lambda(iu)$ indeed yields the total potential (including exchange and correlation) felt by an electron in response to a test charge [49]. In the RPA approximation, Σ_{xc}^λ is just the imaginary frequency GW self-energy (calculated from the KS Green function G_0) at coupling constant λ [Eqs. (15) and (16) can also be written with integrals along the real frequency axis [50], multiplying each integral by $-i$, in which case Σ_{xc}^λ appears in the form familiar to quasiparticle calculations]. In the ALDA approximation, f_{xc}^λ can be written as

$$f_{xc}^\lambda[n](\mathbf{r}, \mathbf{r}'; iu) = \frac{\delta v_{xc}^\lambda[n](\mathbf{r})}{\delta n(\mathbf{r}')}, \quad (18)$$

where $v_{xc}^\lambda[n](\mathbf{r})$ is the LDA exchange-correlation potential at coupling constant λ . Therefore, the ALDA Σ_{xc}^λ is the $G\Gamma$ self-energy that includes vertex corrections from the LDA [48]. In the same way, the PGG f_{xc}^λ is the functional derivative of the x-OEP potential [5,19,20] in two-electron systems [$v_x(\mathbf{r}) = -v_h(\mathbf{r})/2$ in that case]. Hence, the PGG Σ_{xc}^λ is again the $G\Gamma$ self-energy that includes vertex corrections from the x-OEP (in two-electron systems). Equation (15) thus allows to calculate and compare total energies from various $G\Gamma$ approximations.

III. ACFD POTENTIALS

In this section, we derive the ACFD exchange-correlation potential $v_{xc}(\mathbf{r})$ for an arbitrary TDDFT kernel f_{xc} . As usual, we split $v_{xc}(\mathbf{r}) = v_x(\mathbf{r}) + v_c(\mathbf{r})$ into an exchange potential $v_x(\mathbf{r})$ and a correlation potential $v_c(\mathbf{r})$, which are defined by

$$v_{x/c}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}. \quad (19)$$

We shall take care of $v_x(\mathbf{r})$ later in this section and now focus on $v_c(\mathbf{r})$. We will notably show that $v_c(\mathbf{r})$ can be split in two terms, one of which has the same structure as the linear-response Sham-Schlüter equation [21,22]. To proceed, we first substitute ${}^t\varepsilon_\lambda^{-1}(iu)\chi_0(iu)$ for $\chi_\lambda(iu)$ in Eq. (4), where $\varepsilon_\lambda(iu) = 1 - K_{\text{hxc}}^\lambda(iu)\chi_0(iu)$ is the electron-test charge dielectric function introduced in the preceding section and ${}^t\varepsilon_\lambda^{-1}(\mathbf{r}, \mathbf{r}'; iu) = \varepsilon_\lambda^{-1}(\mathbf{r}', \mathbf{r}; iu)$. This yields

$$E_c[n] = - \frac{1}{2} \int_0^1 d\lambda \int \frac{du}{2\pi} \text{Tr} \{ \nu [{}^t\varepsilon_\lambda^{-1}(iu) - 1] \chi_0(iu) \}. \quad (20)$$

The correlation potential thus reads

$$v_c[n](\mathbf{r}) = -\frac{1}{2} \int_0^1 d\lambda \int \frac{du}{2\pi} \text{Tr} \left\{ \nu \frac{\delta[{}^t \varepsilon_\lambda^{-1}(iu)]}{\delta n(\mathbf{r})} \chi_0(iu) \right\} \\ - \frac{1}{2} \int_0^1 d\lambda \int \frac{du}{2\pi} \text{Tr} \left\{ \nu [{}^t \varepsilon_\lambda^{-1}(iu) - 1] \frac{\delta \chi_0(iu)}{\delta n(\mathbf{r})} \right\}. \quad (21)$$

Moreover, the functional derivative of ${}^t \varepsilon_\lambda^{-1}(iu)$ follows from the relation

$$\frac{\delta[{}^t \varepsilon_\lambda^{-1}(iu) {}^t \varepsilon_\lambda(iu)]}{\delta n(\mathbf{r})} = 0 \Rightarrow \frac{\delta[{}^t \varepsilon_\lambda^{-1}(iu)]}{\delta n(\mathbf{r})} \\ = -{}^t \varepsilon_\lambda^{-1}(iu) \frac{\delta[{}^t \varepsilon_\lambda(iu)]}{\delta n(\mathbf{r})} {}^t \varepsilon_\lambda^{-1}(iu). \quad (22)$$

Hence,

$$\frac{\delta[{}^t \varepsilon_\lambda^{-1}(iu)]}{\delta n(\mathbf{r})} = {}^t \varepsilon_\lambda^{-1}(iu) \frac{\delta \chi_0(iu)}{\delta n(\mathbf{r})} K_{\text{hxc}}^\lambda(iu) {}^t \varepsilon_\lambda^{-1}(iu) \\ + {}^t \varepsilon_\lambda^{-1}(iu) \chi_0(iu) \frac{\delta f_{\text{xc}}^\lambda(iu)}{\delta n(\mathbf{r})} {}^t \varepsilon_\lambda^{-1}(iu). \quad (23)$$

At this stage, Eqs. (21) and (23) provide an expression for $v_c(\mathbf{r})$ in terms of the functional derivatives of $\chi_0(iu)$ and $f_{\text{xc}}^\lambda(iu)$. We first gather the functional derivatives of $\chi_0(iu)$ in $v_c^{\text{ss}}(\mathbf{r})$ (“ss” stands for Sham-Schlüter, see below) and those of $f_{\text{xc}}^\lambda(iu)$ in $v_c^{\text{dk}}(\mathbf{r})$ (“dk” stands for derivatives of the kernel). We then simplify $v_c^{\text{ss}}(\mathbf{r})$ using the relation

$$1 + K_{\text{hxc}}^\lambda(iu) {}^t \varepsilon_\lambda^{-1}(iu) \chi_0(iu) = \varepsilon_\lambda^{-1}(iu), \quad (24)$$

which follows from the definition of $\varepsilon_\lambda(iu)$ by straightforward algebra. This finally yields

$$v_c[n](\mathbf{r}) = v_c^{\text{ss}}[n](\mathbf{r}) + v_c^{\text{dk}}[n](\mathbf{r}), \quad (25)$$

where

$$v_c^{\text{ss}}[n](\mathbf{r}) = -\frac{1}{2} \int_0^1 d\lambda \int \frac{du}{2\pi} \text{Tr} \left\{ [\varepsilon_\lambda^{-1}(iu) \nu {}^t \varepsilon_\lambda^{-1}(iu) - \nu] \frac{\delta \chi_0(iu)}{\delta n(\mathbf{r})} \right\} \quad (26)$$

and

$$v_c^{\text{dk}}[n](\mathbf{r}) = -\frac{1}{2} \int_0^1 d\lambda \int \frac{du}{2\pi} \text{Tr} \left\{ \chi_\lambda(iu) \nu \chi_\lambda(iu) \frac{\delta f_{\text{xc}}^\lambda(iu)}{\delta n(\mathbf{r})} \right\}. \quad (27)$$

$v_c^{\text{dk}}(\mathbf{r})$ (which is zero in the RPA) involves the third derivative of the TDDFT action, $\delta f_{\text{xc}}^\lambda(iu)/\delta n(\mathbf{r})$. We will not further elaborate on this term until Sec. IV C and now show that $v_c^{\text{ss}}(\mathbf{r})$ satisfies a linear-response Sham-Schlüter-like equation. Indeed, using the chain rule, the functional derivative of $\chi_0(iu)$ can be written as

$$\frac{\delta \chi_0(iu)}{\delta n(\mathbf{r})} = \int d^3 \mathbf{r}' \frac{\delta \chi_0(iu)}{\delta v_{\text{KS}}(\mathbf{r}')} \frac{\delta v_{\text{KS}}(\mathbf{r}')}{\delta n(\mathbf{r})} \\ = \int d^3 \mathbf{r}' \chi_0^{-1}(\mathbf{r}', \mathbf{r}; iu=0) \frac{\delta \chi_0(iu)}{\delta v_{\text{KS}}(\mathbf{r}')}, \quad (28)$$

since by definition $\delta n(\mathbf{r})/\delta v_{\text{KS}}(\mathbf{r}') = \chi_0(\mathbf{r}, \mathbf{r}'; iu=0)$. Furthermore, we get from Eq. (12),

$$\frac{\delta \chi_0(\mathbf{r}_1, \mathbf{r}_2; iu)}{\delta v_{\text{KS}}(\mathbf{r})} = 2 \int \frac{dv}{2\pi} \frac{\delta G_0(\mathbf{r}_1, \mathbf{r}_2; iu+iv)}{\delta v_{\text{KS}}(\mathbf{r})} G_0(\mathbf{r}_2, \mathbf{r}_1; iv) \\ + 2 \int \frac{dv}{2\pi} G_0(\mathbf{r}_1, \mathbf{r}_2; iu+iv) \\ \times \frac{\delta G_0(\mathbf{r}_2, \mathbf{r}_1; iv)}{\delta v_{\text{KS}}(\mathbf{r})}. \quad (29)$$

The functional derivative of $G_0(iu)$ is then given by [see Eq. (22)]

$$\frac{\delta G_0(iu)}{\delta v_{\text{KS}}(\mathbf{r})} = -G_0(iu) \frac{\delta G_0^{-1}(iu)}{\delta v_{\text{KS}}(\mathbf{r})} G_0(iu), \quad (30)$$

where, because $G_0^{-1}(iu) = iu - H_{\text{KS}} = iu - T - v_{\text{KS}}$ (T being the kinetic-energy operator):

$$\frac{\delta G_0^{-1}(\mathbf{r}_1, \mathbf{r}_2; iu)}{\delta v_{\text{KS}}(\mathbf{r})} = -\delta(\mathbf{r} - \mathbf{r}_1) \delta(\mathbf{r} - \mathbf{r}_2). \quad (31)$$

Insertion of Eqs. (28)–(31) into Eq. (26) thus finally yields

$$v_c^{\text{ss}}[n](\mathbf{r}) = 2 \int d^3 \mathbf{r}_1 \chi_0^{-1}(\mathbf{r}, \mathbf{r}_1; iu=0) \int \frac{du}{2\pi} \int d^3 \mathbf{r}_2 \\ \times \int d^3 \mathbf{r}_3 G_0(\mathbf{r}_1, \mathbf{r}_2; iu) \tilde{\Sigma}_c(\mathbf{r}_2, \mathbf{r}_3; iu) \\ \times G_0(\mathbf{r}_3, \mathbf{r}_1; iu), \quad (32)$$

where we have defined an effective self-energy $\tilde{\Sigma}_c(iu)$,

$$\begin{aligned} \tilde{\Sigma}_c(\mathbf{r}, \mathbf{r}'; iu) = & - \int \frac{dv}{2\pi} G_0(\mathbf{r}, \mathbf{r}'; iu + iv) \\ & \times [\tilde{W}(\mathbf{r}, \mathbf{r}'; iv) - v(\mathbf{r}, \mathbf{r}')], \end{aligned} \quad (33)$$

and an effective screened Coulomb interaction $\tilde{W}(iu)$,

$$\tilde{W}(iu) = \int_0^1 d\lambda \varepsilon_\lambda^{-1}(iu) v' \varepsilon_\lambda^{-1}(iu). \quad (34)$$

Note that $\tilde{W}(iu)$ is symmetric [$\tilde{W}(\mathbf{r}, \mathbf{r}'; iu) = \tilde{W}(\mathbf{r}', \mathbf{r}; iu)$]. Using Eq. (12), Eq. (32) can also be cast in the form

$$\begin{aligned} 0 = & \int \frac{du}{2\pi} \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 G_0(\mathbf{r}, \mathbf{r}_1; iu) \{ \tilde{\Sigma}_c(\mathbf{r}_1, \mathbf{r}_2; iu) \\ & - v_c^{\text{ss}}[n](\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2) \} G_0(\mathbf{r}_2, \mathbf{r}; iu). \end{aligned} \quad (35)$$

Equation (35) has the same structure as the linear-response Sham-Schlüter equation for the correlation potential [21,22], with a GW -like effective self-energy involving a modified screened Coulomb interaction $\tilde{W}(iu)$ defined by Eq. (34) [if needed, Eqs. (33)–(35) can also be written with integrals along the real frequency axis [50], multiplying each integral by $-i$]. This formal similarity with the linear-response Sham-Schlüter equation will prove helpful later to analyze the asymptotic behavior of the potential.

We now turn to the exchange potential $v_x(\mathbf{r})$, which is the functional derivative of the exchange energy [Eq. (14)] with respect to the density. Taking this functional derivative [51] yields the x-OEP equation [5,19,20,51] or equivalently the linear-response Sham-Schlüter equation in the exchange-only approximation for the self-energy [21]:

$$\Sigma_x(\mathbf{r}, \mathbf{r}') = - \int \frac{dv}{2\pi} e^{iv\delta} G_0(\mathbf{r}, \mathbf{r}'; iv) v(\mathbf{r}, \mathbf{r}') \quad (36a)$$

$$= - \sum_{j=1}^{N/2} \varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}') v(\mathbf{r}, \mathbf{r}'), \quad (36b)$$

where the limit $\delta \rightarrow 0^+$ is implied. Note that $v_x(\mathbf{r})$ explicitly depends on the KS orbitals, and thus depends on the treatment of correlation. In the exchange-only case [setting $E_c = 0$ hence $v_c(\mathbf{r}) = 0$], $v_x(\mathbf{r})$ is precisely the x-OEP potential, i.e., the solution of the x-OEP equation with the respective self-consistent KS orbitals. If correlation is included (as is the case in the ACFD framework), the self-consistent KS orbitals will be different from their exchange-only counterparts, so that $v_x(\mathbf{r})$ will be different from the exchange-only OEP. Finally, the exchange-correlation potential $v_{xc}(\mathbf{r})$ can be written as

$$v_{xc}[n](\mathbf{r}) = v_{xc}^{\text{ss}}[n](\mathbf{r}) + v_c^{\text{dk}}[n](\mathbf{r}), \quad (37)$$

where $v_c^{\text{dk}}(\mathbf{r})$ is given by Eq. (27) and $v_{xc}^{\text{ss}}(\mathbf{r})$ is given by Eq. (32) using the effective self-energy

$$\tilde{\Sigma}_{xc}(\mathbf{r}, \mathbf{r}'; iu) = - \int \frac{dv}{2\pi} e^{iv\delta} G_0(\mathbf{r}, \mathbf{r}'; iu + iv) \tilde{W}(\mathbf{r}, \mathbf{r}'; iv). \quad (38)$$

Note that $v_{xc}^{\text{ss}}(\mathbf{r})$ is defined by Eq. (32) only up to an additive constant [since $\int d^3\mathbf{r}' \chi_0(\mathbf{r}, \mathbf{r}'; iu=0) = 0$]. For the sake of simplicity, we choose this constant such that $v_{xc}^{\text{ss}}(\mathbf{r}) \rightarrow 0$ when $r \rightarrow \infty$ [provided $v_{xc}^{\text{ss}}(\mathbf{r})$ has a finite limit]. However, the resulting KS spectrum must be shifted to be used as input for the next self-consistent iteration, because Eq. (32) requires [52] $\mu = 0$. Also, in the RPA+ approximation, the potential that derives from $E_{c,\text{sr}}^{\text{LDA}}[n]$ (see Sec. II B) must be added to Eq. (37). Since $E_{c,\text{sr}}^{\text{LDA}}[n]$ is a LDA-like correction, the calculation of this potential is straightforward. In the following section, we discuss the asymptotic behavior of the ACFD-RPA(+), ACFD-PGG, and ACFD-ALDA potentials.

IV. ASYMPTOTIC BEHAVIOR OF THE ACFD POTENTIALS

The asymptotic behavior of the ACFD potentials gives further insight into the physics included in each approximation. It is a key criterion to compare various ACFD functionals, that reveals their relative merits and drawbacks. We consider here the case of a system with spherical symmetry and a nondegenerate N -electron ground state. We note $\hat{\varphi}_m(\mathbf{r})$ ($-l \leq m \leq l$) the highest occupied, $(2l+1)$ -fold degenerate KS orbitals, which are all doubly occupied. Let us first recall the asymptotic behavior of the exact-exchange and correlation potentials. On one hand, the exchange potential $v_x(\mathbf{r})$ is the solution of the linear-response Sham-Schlüter equation [Eq. (35)] in the exchange-only approximation for the self-energy [Eq. (36)]. It behaves asymptotically like [5]

$$v_x(\mathbf{r}) \sim \frac{1}{2\hat{n}(\mathbf{r})} \sum_m \hat{u}_{xm}(\mathbf{r}) |\hat{\varphi}_m(\mathbf{r})|^2 + \text{c.c.}, \quad (39)$$

where $\hat{n}(\mathbf{r}) = \sum_m |\hat{\varphi}_m(\mathbf{r})|^2$ and

$$\hat{u}_{xm}(\mathbf{r}) = \frac{1}{\hat{\varphi}_m^*(\mathbf{r})} \int d^3\mathbf{r}' \Sigma_x(\mathbf{r}', \mathbf{r}) \hat{\varphi}_m^*(\mathbf{r}'). \quad (40)$$

$\hat{u}_{xm}(\mathbf{r})$ is the local potential that has the same action on the orbital $\hat{\varphi}_m^*(\mathbf{r})$ as the exchange-only self-energy $\Sigma_x(\mathbf{r}, \mathbf{r}')$. Since $\varphi_j^*(\mathbf{r}) \hat{\varphi}_m(\mathbf{r}) / \hat{n}(\mathbf{r})$ ($j \leq N/2$) decays exponentially if φ_j does not belong to the set of $\hat{\varphi}_m$'s, we get from Eq. (36b):

$$\begin{aligned} v_x(\mathbf{r}) \sim & - \frac{1}{\hat{n}(\mathbf{r})} \sum_m \sum_{m'} \hat{\varphi}_m^*(\mathbf{r}) \hat{\varphi}_{m'}(\mathbf{r}) \\ & \times \int d^3\mathbf{r}' \hat{\varphi}_{m'}^*(\mathbf{r}') v(\mathbf{r}, \mathbf{r}') \hat{\varphi}_m(\mathbf{r}'). \end{aligned} \quad (41)$$

Expanding $v(\mathbf{r}, \mathbf{r}')$ in powers of $1/r$ then yields

$$v_x(\mathbf{r}) = -\frac{1}{r} + \frac{Q_{N-1}^0}{r^3} + O\left(\frac{1}{r^5}\right), \quad (42)$$

where Q_{N-1}^0 is the axial quadrupole moment of the $(N-1)$ -electron state obtained by removing one electron from the highest occupied orbital(s) (all other orbitals being frozen). Q_{N-1}^0 is zero if the highest occupied orbital is s -like, and reads in the general case:

$$Q_{N-1}^0 = -\frac{1}{2} \int d^3\mathbf{r} [3z^2 - r^2] |\hat{\varphi}_0(\mathbf{r})|^2, \quad (43)$$

where $\hat{\varphi}_0(\mathbf{r})$ is the orbital with zero angular momentum along z .

On the other hand, the exact exchange-correlation potential is expected to behave as [25]

$$v_{xc}(\mathbf{r}) = -\frac{1}{r} + \frac{Q_{N-1}}{r^3} - \frac{\alpha_{N-1}}{2r^4} + O\left(\frac{1}{r^5}\right), \quad (44)$$

where Q_{N-1} and α_{N-1} are the axial quadrupole moment and static polarizability of the $(N-1)$ -electron system in its ground state, respectively (see Appendix A of Ref. [25]; Q_{N-1} is zero if the $(N-1)$ -electron ground state is nondegenerate). These lowest-order terms can be classically understood as the potential acting on an electron dragged away from the system. Subtracting Eq. (42) from Eq. (44), we thus get

$$v_c(\mathbf{r}) = \frac{Q_{N-1} - Q_{N-1}^0}{r^3} - \frac{\alpha_{N-1}}{2r^4} + O\left(\frac{1}{r^5}\right). \quad (45)$$

Note that the simple LDA or GGA potentials decay exponentially in the vacuum [53], at variance with the expected behavior. The empty KS spectrum is thus qualitatively wrong in the LDA and GGA (they do not bind a Rydberg series for example), which is not a good starting point for TDDFT [54,55]. On the contrary, ACFD functionals all include exact exchange. They hence yield the exact-exchange potential $v_x(\mathbf{r})$, which decays like $-1/r$ [Eq. (42)]. This is a great improvement over LDA and GGA, provided the correlation potential has a sound behavior.

As for $v_{xc}^{ss}(\mathbf{r})$, we have carefully investigated the asymptotic behavior of the solutions of the linear-response Sham-Schlüter equation in Ref. [56]. We only recall our main results here. We can formally split $\tilde{\Sigma}_{xc}(iu)$ into a ‘‘screened exchange’’ part $\tilde{\Sigma}_{sex}(iu)$ and a ‘‘Coulomb hole’’ part $\tilde{\Sigma}_{coh}(iu)$ (these names are borrowed from the usual GW self-energy nomenclature [28], also see Sec. V B). $\tilde{\Sigma}_{sex}(iu)$ is the contribution from the poles of $G_0(iu)$ in Eq. (38):

$$\tilde{\Sigma}_{sex}(\mathbf{r}, \mathbf{r}'; iu) = -\sum_{j=1}^{N/2} \varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}') \tilde{W}(\mathbf{r}, \mathbf{r}'; \varepsilon_j - iu). \quad (46)$$

It has the same functional form as the exchange-only self-energy [Eq. (36b)] with $\nu(\mathbf{r}, \mathbf{r}')$ replaced by $W(\mathbf{r}, \mathbf{r}'; \varepsilon_j - iu)$, hence its name. $\tilde{\Sigma}_{coh}(iu) = \tilde{\Sigma}_{xc}(iu) - \tilde{\Sigma}_{sex}(iu)$ is the remainder. In the same way, we can split $v_{xc}^{ss}(\mathbf{r}) = v_{xc}^{ss}(\mathbf{r}) + v_{coh}^{ss}(\mathbf{r})$ into a screened exchange and a Coulomb hole part, which are the solutions of the linear-response Sham-Schlüter equation with $\tilde{\Sigma}_{sex}(iu)$ and $\tilde{\Sigma}_{coh}(iu)$ as the self-energy, respectively. Following the lines of Ref. [56], one can show that, when $r \rightarrow \infty$,

$$v_{sex}^{ss}(\mathbf{r}) \sim \frac{1}{2\hat{n}(\mathbf{r})} \sum_m \hat{u}_{sexm}(\mathbf{r}) |\hat{\varphi}_m(\mathbf{r})|^2 + \text{c.c.}, \quad (47a)$$

$$v_{coh}^{ss}(\mathbf{r}) \sim \frac{1}{2} \tilde{W}_s(\mathbf{r}, \mathbf{r}; iu=0), \quad (47b)$$

where

$$\hat{u}_{sexm}(\mathbf{r}) = \frac{1}{\hat{\varphi}_m^*(\mathbf{r})} \int d^3\mathbf{r}' \tilde{\Sigma}_{sex}(\mathbf{r}', \mathbf{r}; \varepsilon_{N/2}) \hat{\varphi}_m^*(\mathbf{r}'). \quad (48)$$

$\varepsilon_{N/2}$ is the energy of the highest occupied orbital(s), and $\tilde{W}_s(\mathbf{r}, \mathbf{r}'; iu) = \tilde{W}(\mathbf{r}, \mathbf{r}'; iu) - \nu(\mathbf{r}, \mathbf{r}')$ is the response part of the screened Coulomb interaction $\tilde{W}(\mathbf{r}, \mathbf{r}'; iu)$. Using the same trick as for the exchange-only potential, we further get

$$v_{sex}^{ss}(\mathbf{r}) \sim -\frac{1}{\hat{n}(\mathbf{r})} \sum_m \sum_{m'} \hat{\varphi}_m^*(\mathbf{r}) \hat{\varphi}_{m'}(\mathbf{r}) \times \int d^3\mathbf{r}' \hat{\varphi}_{m'}^*(\mathbf{r}') \tilde{W}(\mathbf{r}, \mathbf{r}'; iu=0) \hat{\varphi}_m(\mathbf{r}'). \quad (49)$$

We will make use of these results in the ACFD-RPA, ACFD-PGG, and ACFD-ALDA approximations below. The asymptotic behavior of $v_c^{\text{dk}}(\mathbf{r})$ will be discussed later in Sec. IV C in the case of the ACFD-ALDA potential.

A. The ACFD-RPA potential

We first discuss the RPA approximation ($f_{xc}=0$). In the RPA, $v_c^{\text{dk}}(\mathbf{r})$ is zero, leaving $v_{xc}(\mathbf{r}) = v_{xc}^{ss}(\mathbf{r})$ [Eq. (32)]. Furthermore, we get from Eq. (34) with $\varepsilon_\lambda(iu) = 1 - \lambda \nu \chi_0(iu)$:

$$\tilde{W}(iu) = \int_0^1 d\lambda \frac{d}{d\lambda} \{ \lambda [1 - \lambda \nu \chi_0(iu)]^{-1} \nu \} = W^{\text{RPA}}(iu), \quad (50)$$

where $W^{\text{RPA}}(iu) = [1 - \nu \chi_0(iu)]^{-1} \nu$ is the RPA screened Coulomb interaction. Hence, $\tilde{\Sigma}_{xc}(iu)$ [Eq. (38)] is just the usual GW self-energy, so that the ACFD-RPA potential is the solution of the linear-response Sham-Schlüter equation in the GW approximation for the self-energy. This could be expected from Sec. II C. Indeed, Casida [22] has shown that the exchange-correlation potential that derives from the Nozières functional [57] (evaluated at the KS Green function in

a given approximation for the self-energy) satisfies the linear-response Sham-Schlüter equation in that approximation for the self-energy. This directly yields the aforementioned result for the RPA, which amounts to the Nozières functional (evaluated at the KS Green function) in the GW approximation for the self-energy.

We now investigate the asymptotic behavior of the ACFD-RPA potential. To proceed with Eq. (49), we write $W^{\text{RPA}}(iu) = \nu' \varepsilon_{\text{RPA}}^{-1}(iu)$, where $\varepsilon_{\text{RPA}}(iu) = 1 - \nu \chi_0(iu)$. Expanding $\nu(\mathbf{r}, \mathbf{r}')$ in powers of $1/r$ in $W^{\text{RPA}}(iu)$, we then find

$$v_{\text{sex}}^{\text{ss}}(\mathbf{r}) = -\frac{1}{r} + \frac{Q_{N-1}^{\text{RPA}}}{r^3} + O\left(\frac{1}{r^5}\right), \quad (51)$$

where Q_{N-1}^{RPA} is a “screened” quadrupole moment. As usual, it is zero if the highest occupied orbital is s -like, and reads in the general case

$$Q_{N-1}^{\text{RPA}} = -\frac{1}{2} \int d^3\mathbf{r} [3z^2 - r^2] \int d^3\mathbf{r}' \varepsilon_{\text{RPA}}^{-1}(\mathbf{r}', \mathbf{r}; iu=0) \times |\hat{\varphi}_0(\mathbf{r}')|^2. \quad (52)$$

As for $v_{\text{coh}}^{\text{ss}}(\mathbf{r})$, we cast $W_s^{\text{RPA}}(\mathbf{r}, \mathbf{r}'; iu) = W^{\text{RPA}}(\mathbf{r}, \mathbf{r}'; iu) - \nu(\mathbf{r}, \mathbf{r}')$ in the form

$$W_s^{\text{RPA}}(iu) = \nu \chi^{\text{RPA}}(iu) \nu, \quad (53)$$

where $\chi^{\text{RPA}}(iu) = [1 - \chi_0(iu)\nu]^{-1} \chi_0(iu)$ is the RPA density-density response function. Expanding both $\nu(\mathbf{r}, \mathbf{r}')$'s in powers of $1/r$ in Eq. (53) then yields

$$v_{\text{coh}}^{\text{ss}}(\mathbf{r}) = -\frac{\alpha_N^{\text{RPA}}}{2r^4} + O\left(\frac{1}{r^5}\right), \quad (54)$$

where α_N^{RPA} is the static RPA polarizability of the N -electron system:

$$\alpha_N^{\text{RPA}} = - \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 z_1 z_2 \chi^{\text{RPA}}(\mathbf{r}_1, \mathbf{r}_2; iu=0). \quad (55)$$

Hence, we finally get

$$v_{\text{xc}}(\mathbf{r}) = -\frac{1}{r} + \frac{Q_{N-1}^{\text{RPA}}}{r^3} - \frac{\alpha_N^{\text{RPA}}}{2r^4} + O\left(\frac{1}{r^5}\right). \quad (56)$$

This result is consistent with the physics of the GW (or RPA) approximation. Equation (56) is to be compared with the behavior of the exact-exchange [Eq. (42)] and exact-exchange-correlation potentials [Eq. (44)]. In the exact-exchange potential, the $1/r^3$ term is proportional to the axial quadrupole moment Q_{N-1}^0 of the *unrelaxed* [frozen orbitals] $(N-1)$ -electron state obtained by removing one electron from the highest occupied orbital(s), instead of the quadrupole moment of the true $(N-1)$ -electron ground state. This bare quadrupole moment Q_{N-1}^0 is now screened in the ACFD-RPA potential by the static RPA dielectric function $\varepsilon_{\text{RPA}}^{-1}(iu=0)$. This partly accounts for orbital relaxation, al-

though $\varepsilon_{\text{RPA}}^{-1}(iu=0)$ describes the response of a N - instead of $(N-1)$ -electron system. Indeed, one would rather expect in Eq. (52) some kernel describing the relaxation of the remaining occupied orbitals. In the same way, the $1/r^4$ term is found proportional to the N -electron RPA polarizability instead of some $(N-1)$ -electron-like polarizability. These deficiencies can be traced back to the fact that W^{RPA} is a “test charge-test charge” screened Coulomb interaction [49]. Thus $W_s^{\text{RPA}}(\mathbf{r}, \mathbf{r}; iu=0)$ is the potential acting on a test charge, which does not account for the fact that an electron dragged away from the highest occupied orbital(s) only interacts with $N-1$ particles (compare with the ACFD-PGG potential in the following paragraph). This is reminiscent of the “self-interaction” problem in the RPA response, as each electron interacts with itself in the screening charge (this is partly why the on-top correlation hole is so deep in the RPA [28,29], yielding too negative correlation energies). Despite these limitations, Eq. (56) is clearly a real improvement on the LDA, GGA, and exchange-only potentials.

Note that ACFD-RPA and ACFD-RPA+ correlation potentials have the same asymptotic behaviors, since the potential that derives from the local correction $E_{\text{c, sr}}^{\text{LDA}}[n]$ (see Sec. II B) decays exponentially in the vacuum (like any LDA).

The linear-response Sham-Schlüter equation has been solved in the GW approximation by Eguluz *et al.* [58], for a jellium surface. The RPA potential was shown to have the $-1/(4z)$ behavior expected for surface systems [25]. It has also been solved by Godby *et al.* [59] in bulk silicon (although not up to full self-consistency). There the RPA potential was found close to the LDA one, which may explain the success of the LDA in solids. The band-gap energy of silicon is, however, not improved by the RPA potential, which suggests that the discontinuity in the exact-exchange-correlation potential upon addition or removal of an electron is large (see, however, Ref. [60]). Unfortunately, the calculation of the RPA potential in arbitrary systems remains beyond present computational capabilities. Nonetheless, we can design approximate RPA potentials for practical use. These approximate RPA potentials will be discussed in Sec. V.

B. The ACFD-PGG potential in two-electron systems

In this paragraph, we discuss the ACFD-PGG potential in the He atom, where the PGG kernel is the exact-exchange kernel [32]. The PGG kernel reads in two-electron systems:

$$f_{\text{xc}}^\lambda(\mathbf{r}, \mathbf{r}'; iu) = -\frac{\lambda}{2} \frac{1}{|\mathbf{r} - \mathbf{r}'|} = -\frac{\lambda}{2} \nu(\mathbf{r}, \mathbf{r}'). \quad (57)$$

Therefore, $K_{\text{hxc}}^\lambda(\mathbf{r}, \mathbf{r}'; iu) = (\lambda/2) \nu(\mathbf{r}, \mathbf{r}')$. Again, $v_{\text{c}}^{\text{dk}}(\mathbf{r})$ is zero, leaving $v_{\text{xc}}(\mathbf{r}) = v_{\text{xc}}^{\text{ss}}(\mathbf{r})$. Furthermore,

$$\tilde{W}(iu) = \int_0^1 d\lambda \frac{d}{d\lambda} \left\{ \lambda \left[1 - \frac{\lambda}{2} \nu \chi_0(iu) \right]^{-1} \nu \right\} = W^{\text{PGG}}(iu), \quad (58)$$

where $W^{\text{PGG}}(iu) = [1 - \frac{1}{2} \nu \chi_0(iu)]^{-1} \nu$. At variance with the RPA, $W^{\text{PGG}}(iu)$ is an electron-test charge [49] screened Coulomb interaction that only accounts for the effect of one elec-

tron on the other. Indeed, we can build $W^{\text{PGG}}(\omega)$ in the following way: let us consider a two-electron system and a test charge at \mathbf{r} oscillating with frequency $\omega/(2\pi)$. This test charge induces variations $\delta n_{\uparrow}(\mathbf{r}';\omega)$ and $\delta n_{\downarrow}(\mathbf{r}';\omega)$ in the spin-up and spin-down electron densities, respectively. We now assume that each electron responds to the bare Coulomb potential $v_b(\omega) \equiv \nu$ created by the test charge plus the average potential $\nu \delta n_{\uparrow}(\omega)$ or $\nu \delta n_{\downarrow}(\omega)$ created by the other electron. We get

$$\delta n_{\uparrow}(\omega) = \delta n_{\downarrow}(\omega) = \delta n_s(\omega) = \frac{1}{2} \chi_0(\omega) [\nu + \nu \delta n_s(\omega)]. \quad (59)$$

Hence,

$$\delta n_s(\omega) = \frac{1}{2} \left[1 - \frac{1}{2} \chi_0(\omega) \nu \right]^{-1} \chi_0(\omega) \nu = \frac{1}{2} \chi^{\text{PGG}}(\omega) \nu, \quad (60)$$

where $\chi^{\text{PGG}}(\omega) = [1 - \frac{1}{2} \chi_0(\omega) \nu]^{-1} \chi_0(\omega)$. Finally, the screened Coulomb potential experienced by each electron is

$$W^{\text{PGG}}(\omega) = \nu + \nu \delta n_s(\omega) \quad (61a)$$

$$= \nu + \frac{1}{2} \nu \chi^{\text{PGG}}(\omega) \nu \quad (61b)$$

$$= \left[1 - \frac{1}{2} \nu \chi_0(\omega) \right]^{-1} \nu, \quad (61c)$$

as expected.

The self-energy $\tilde{\Sigma}_{\text{xc}}$ appearing in Eq. (38) is thus the GW self-energy with vertex corrections coming from the two-electron x-OEP potential [5,19,20]. As for the asymptotic behavior of the ACFD-PGG potential, we find, following the lines of Sec. IV A, that in the He atom:

$$v_{\text{sex}}^{\text{ss}}(\mathbf{r}) = -\frac{1}{r} + O(\exp). \quad (62)$$

The corrections to this leading $-1/r$ term decay exponentially, because both the $1s$ orbital of He and the induced screening charge density in Eq. (49) have spherical symmetry thus no multipole moments. Moreover, it follows from Eq. (47b) with $W_s^{\text{PGG}}(iu) = \frac{1}{2} \nu \chi^{\text{PGG}}(iu) \nu$ that

$$v_{\text{coh}}^{\text{ss}}(\mathbf{r}) \sim \frac{1}{2} W_s^{\text{PGG}}(\mathbf{r}, \mathbf{r}; iu=0) \quad (63)$$

$$= -\frac{\tilde{\alpha}^{\text{PGG}}}{2r^4} + O\left(\frac{1}{r^5}\right), \quad (64)$$

where $\tilde{\alpha}^{\text{PGG}}$ is half the static PGG polarizability of the He atom:

$$\tilde{\alpha}^{\text{PGG}} = -\frac{1}{2} \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 z_1 z_2 \chi^{\text{PGG}}(\mathbf{r}_1, \mathbf{r}_2; iu=0). \quad (65)$$

We thus finally get [$v_{\text{xc}}(\mathbf{r}) = v_{\text{xc}}^{\text{ss}}(\mathbf{r})$ since $v_c^{\text{dk}}(\mathbf{r}) = 0$ for PGG in two-electron systems]

$$v_{\text{xc}}(\mathbf{r}) = -\frac{1}{r} - \frac{\tilde{\alpha}^{\text{PGG}}}{2r^4} + O\left(\frac{1}{r^5}\right). \quad (66)$$

Let us comment on this result: $W_s^{\text{PGG}}(\mathbf{r}, \mathbf{r}; iu=0) = [\nu \delta n_s](\mathbf{r}; iu=0)$ is the potential created at \mathbf{r} by *one* electron, whereas in the He atom $W_s^{\text{RPA}}(\mathbf{r}, \mathbf{r}; iu=0)$ is the potential created at \mathbf{r} by *two* electrons (see Sec. IV A). The PGG kernel is thus a clear step (with respect to the RPA) towards the $-\alpha_{\text{He}^+}/(2r^4)$ behavior expected for $v_c(\mathbf{r})$, where α_{He^+} is the polarizability of the He^+ ion. This feature that $\tilde{W}_s(iu)$ is the potential created by $N-1$ particles might be preserved by the exact-exchange kernel [34] for an arbitrary number of electrons. To be more quantitative, we get from Ref. [54] $\alpha_N^{\text{RPA}} = 1.22$ a.u., while we estimate [61] $\tilde{\alpha}^{\text{PGG}} = 0.68$ a.u., in better agreement with the exact result [62] $\alpha_{\text{He}^+} = 0.28$ a.u. By the way, the ACFD-PGG correlation energy of the He atom [16] (-44 mHa) is much closer to the exact value (-43 mHa) than the far too low ACFD-RPA energy (-78 mHa). However, $\delta n_s(\mathbf{r}; iu=0)$ is still not the response of the He^+ ion to an external test charge. It notably misses the $1s$ orbital relaxation upon ionization, and the remaining electron formally still interacts with two particles. Further inclusion of the correlation into f_{xc} is thus needed to cure these problems.

C. The ACFD-ALDA potential

We now consider the ACFD-ALDA potential. The ALDA kernel $f_{\text{xc}}^{\lambda}(\mathbf{r}, \mathbf{r}'; iu)$ indeed includes correlation, but only approximate exchange (at variance with the PGG kernel in two-electron systems, which is the exact-exchange kernel). It is defined by Eq. (9), where

$$E_{\text{xc}}^{\text{LDA}}[n] = \int d^3\mathbf{r} n(\mathbf{r}) \varepsilon_{\text{xc}}(n(\mathbf{r})), \quad (67)$$

and $\varepsilon_{\text{xc}}(n)$ is the exchange-correlation energy per particle of a homogeneous electron gas with density n . Hence,

$$f_{\text{xc}}^{\lambda}[n](\mathbf{r}, \mathbf{r}'; iu) = \frac{1}{\lambda} \delta(\mathbf{r} - \mathbf{r}') g\left(\frac{1}{\lambda^3} n(\mathbf{r})\right), \quad (68)$$

where

$$g(n) = 2 \frac{d\varepsilon_{\text{xc}}}{dn} + n \frac{d^2\varepsilon_{\text{xc}}}{dn^2}. \quad (69)$$

The following properties of the ALDA kernel are worth to know here. First, $g(n)$ diverges as $n^{-2/3}$ when $n \rightarrow 0$. Indeed,

$$\varepsilon_x(n) = -K_x n^{1/3}, \quad (70)$$

where $K_x = (3/4)(3/\pi)^{1/3}$ a.u. Moreover, $\varepsilon_c(n)$ has the low density-expansion [63]:

$$\varepsilon_c(n) = -K_c n^{1/3} + O(n^{1/2}), \quad (71)$$

with $K_c \approx 0.69883$ a.u. Hence,

$$g(n) = -\frac{4}{9}(K_x + K_c)n^{-2/3} + O(n^{-1/2}) \quad (72)$$

when $n \rightarrow 0$. Second, $f_{xc}^\lambda[n](\mathbf{r}, \mathbf{r}'; iu)$ vanishes (as expected) as λ when $\lambda \rightarrow 0$. This can easily be verified from the high density limit $\varepsilon_{xc}(n) \sim \varepsilon_x(n)$.

We first analyze the asymptotic behavior of $v_{xc}^{ss}(\mathbf{r})$, then the asymptotic behavior of $v_c^{dk}(\mathbf{r})$. As for $v_{xc}^{ss}(\mathbf{r})$, we expect, from Eqs. (47b) and (49),

$$v_{\text{sex}}^{ss}(\mathbf{r}) = -\frac{1}{r} + \frac{Q_{N-1}^{\text{ALDA}}}{r^3} + O\left(\frac{1}{r^5}\right), \quad (73a)$$

$$v_{\text{coh}}^{ss}(\mathbf{r}) \sim \frac{1}{2} \tilde{W}_s^{\text{ALDA}}(\mathbf{r}, \mathbf{r}; iu=0) = -\frac{\tilde{\alpha}^{\text{ALDA}}}{2r^4} + O\left(\frac{1}{r^5}\right), \quad (73b)$$

where $\tilde{W}_s^{\text{ALDA}}(\mathbf{r}, \mathbf{r}'; iu) = \tilde{W}^{\text{ALDA}}(\mathbf{r}, \mathbf{r}'; iu) - v(\mathbf{r}, \mathbf{r}')$ and $\tilde{W}^{\text{ALDA}}(iu)$ is defined by Eq. (34) using the ALDA $\varepsilon_\lambda(iu)$. The closed expressions for Q_{N-1}^{ALDA} and $\tilde{\alpha}^{\text{ALDA}}$ are, unfortunately, not really meaningful. Indeed, the ALDA kernel f_{xc}^λ lacks a physically motivated expansion in powers of $\lambda v(\mathbf{r}, \mathbf{r}')$ which could guide the interpretation. Obviously, however, $\tilde{W}_s^{\text{ALDA}}(iu)$ is not a potential created by $N-1$ particles as is PGG in two-electron systems.

We now investigate the asymptotic behavior of $v_c^{dk}(\mathbf{r})$ [Eq. (27)]. Since the ALDA kernel is local, we get

$$\frac{\delta f_{xc}^\lambda(\mathbf{r}_1, \mathbf{r}_2; iu)}{\delta n(\mathbf{r})} = \frac{1}{\lambda^4} \delta(\mathbf{r} - \mathbf{r}_1) \delta(\mathbf{r} - \mathbf{r}_2) h\left(\frac{1}{\lambda^3} n(\mathbf{r})\right), \quad (74)$$

where

$$h(n) = 3 \frac{d^2 \varepsilon_{xc}}{dn^2} + n \frac{d^3 \varepsilon_{xc}}{dn^3}, \quad (75)$$

which diverges as $n^{-5/3}$ when $n \rightarrow 0$. $v_c^{dk}(\mathbf{r})$ can thus be cast in the form

$$v_c^{dk}[n](\mathbf{r}) = -\frac{1}{2} \int_0^1 d\lambda \frac{1}{\lambda^4} h\left(\frac{1}{\lambda^3} n(\mathbf{r})\right) q_\lambda(\mathbf{r}), \quad (76)$$

with

$$q_\lambda(\mathbf{r}) = \int \frac{du}{2\pi} \int d^3 \mathbf{r}_1 \int d^3 \mathbf{r}_2 \chi_\lambda(\mathbf{r}, \mathbf{r}_1; iu) \times v(\mathbf{r}_1, \mathbf{r}_2) \chi_\lambda(\mathbf{r}_2, \mathbf{r}; iu). \quad (77)$$

The integrand in Eq. (76) vanishes as λ when $\lambda \rightarrow 0$, since $h(n(\mathbf{r})/\lambda^3) \sim \lambda^5$. However, the density decays [25] like $e^{-2\sqrt{2}r}$ (up to a power law prefactor) in the vacuum, where

$I = -\varepsilon_{N/2}$ is the ionization energy [assuming $v_{xc}(\mathbf{r}) \sim -1/r$], so that $h(n(\mathbf{r})/\lambda^3)$ will blow up like $e^{10\sqrt{2}r/3}$ when $r \rightarrow \infty$. Nonetheless,

$$\int d^3 \mathbf{r}' \chi_\lambda(\mathbf{r}, \mathbf{r}'; iu) v(\mathbf{r}') \sim e^{-2\sqrt{2}r} \quad (78)$$

up to a power-law prefactor, provided $v(\mathbf{r})$ does not diverge exponentially when $r \rightarrow \infty$. This relation can be shown for $\chi_0(\mathbf{r}, \mathbf{r}'; iu)$ following the lines of Refs. [51,56], then for arbitrary λ using the Dyson equation [Eq. (7)]. Thus $q_\lambda(\mathbf{r})$ is expected to behave like $e^{-4\sqrt{2}r}$ when $r \rightarrow \infty$, so that $v_c^{dk}(\mathbf{r})$ is finally expected to decay exponentially like $e^{-2\sqrt{2}r/3}$ (up to a power-law prefactor).

The ACFD-ALDA potential hence behaves as given by Eq. (73) when $r \rightarrow \infty$, $v_c^{dk}(\mathbf{r})$ being asymptotically negligible with respect to $v_c^{ss}(\mathbf{r})$. As discussed previously, the detailed physics brought by the ALDA kernel is, however, not clear. In the homogeneous electron gas, the ACFD-ALDA is known to strongly overcorrect the ACFD-RPA error on total energies [11]. The calculation of $\tilde{W}_s^{\text{ALDA}}(\mathbf{r}, \mathbf{r}; iu=0)$ in the He atom could show whether there is any improvement on the asymptotic behavior of the potential (with respect to RPA and PGG).

One may wonder about the asymptotic behavior of the exact $v_c^{dk}(\mathbf{r})$ (calculated using the true f_{xc} , which is highly nonlocal and frequency dependent, unlike the crude ALDA kernel). It seems hardly possible to get both the exact Q_{N-1} and α_{N-1} from Eqs. (47b) and (49). We therefore conjecture that the exact $v_c^{dk}(\mathbf{r})$ also behaves as $a/r^3 + b/r^4 + O(1/r^5)$ when $r \rightarrow \infty$, although we give no rigorous proof here.

In the following section, we discuss approximate ACFD potentials for practical use.

V. APPROXIMATE ACFD POTENTIALS

The calculation of the ACFD potentials for arbitrary systems is a very demanding computational effort. In this section, we discuss two approximate ACFD potentials that are much simpler to compute while having the same asymptotic behavior as the exact ACFD-RPA, ACFD-PGG (for two-electron systems), and ACFD-ALDA potentials. These approximate potentials both neglect $v_c^{dk}(\mathbf{r})$ and have a clear physical interpretation at least in the RPA. The first one is based on an approximate solution of the linear-response Sham-Schlüter equation (“x-OEP-like” approximation), while the second one is based on an approximate $\tilde{\Sigma}_{xc}$ (“statically screened” approximation). We give further details below.

A. The x-OEP-like approximation

The “x-OEP-like” potential (whose name will be justified later) is an approximate solution of the linear-response Sham-Schlüter equation. Indeed, the integration over imaginary frequencies in Eq. (32) can be performed closing the contour of integration on the left of the imaginary axis. This contour encloses the poles of G_0 related to the occupied KS

states, as well as some poles of the self-energy. We thus split $v_{xc}^{ss}(\mathbf{r}) = v_{xc,pG}^{ss}(\mathbf{r}) + v_{c,p\Sigma}^{ss}(\mathbf{r})$ in two parts, where $v_{xc,pG}^{ss}(\mathbf{r})$ is the contribution of the simple poles coming from both KS Green functions G_0 , and $v_{c,p\Sigma}^{ss}(\mathbf{r})$ is the contribution of the poles of $\tilde{\Sigma}_{xc}(iu)$ plus the double poles coming from the KS Green functions. In Ref. [56], we have shown the following points.

(i) $v_{xc,pG}^{ss}(\mathbf{r})$ can be written as

$$v_{xc,pG}^{ss}(\mathbf{r}) = 2 \int d^3\mathbf{r}_1 \chi_0^{-1}(\mathbf{r}, \mathbf{r}_1; iu=0) \times \left\{ \sum_{j=1}^{N/2} \int d^3\mathbf{r}_2 \varphi_j^*(\mathbf{r}_2) u_{xcj}(\mathbf{r}_2) G_j(\mathbf{r}_2, \mathbf{r}_1) \times \varphi_j(\mathbf{r}_1) + \text{c.c.} \right\}, \quad (79)$$

where $u_{xcj}(\mathbf{r})$ is the orbital-dependent potential:

$$u_{xcj}(\mathbf{r}) = \frac{1}{\varphi_j^*(\mathbf{r})} \int d^3\mathbf{r}' \tilde{\Sigma}_{xc}(\mathbf{r}', \mathbf{r}; \varepsilon_j) \varphi_j^*(\mathbf{r}') \quad (80)$$

and the Green function $G_j(\mathbf{r}, \mathbf{r}')$ is defined by

$$G_j(\mathbf{r}, \mathbf{r}') = \sum_{k \neq j} \frac{\varphi_k(\mathbf{r}) \varphi_k^*(\mathbf{r}')}{\varepsilon_j - \varepsilon_k}. \quad (81)$$

Using Eq. (12), Eq. (79) can also be cast in the form

$$\sum_{j=1}^{N/2} \int d^3\mathbf{r}' \varphi_j^*(\mathbf{r}') [v_{xc,pG}^{ss}(\mathbf{r}') - u_{xcj}(\mathbf{r}')] G_j(\mathbf{r}', \mathbf{r}) \varphi_j(\mathbf{r}) + \text{c.c.} = 0, \quad (82)$$

which appears as a generalization of the x-OEP equation to the correlated case. Indeed, it yields the exact $v_x(\mathbf{r})$ in the exchange-only approximation for the self-energy [5] [thus $v_{xc,pG}^{ss}(\mathbf{r})$ still includes exact exchange].

(ii) For a GW -like self-energy such as Eq. (38), $v_{c,p\Sigma}^{ss}(\mathbf{r})$ is asymptotically negligible with respect to $v_{c,pG}^{ss}(\mathbf{r})$, so that $v_{xc,pG}^{ss}(\mathbf{r})$ has the same asymptotic behavior as $v_c^{ss}(\mathbf{r})$. Also, $v_{c,p\Sigma}^{ss}(\mathbf{r})$ has no influence on the energy of the highest occupied orbital(s), i.e., $\langle \hat{\varphi}_m | v_{c,p\Sigma}^{ss} | \hat{\varphi}_m \rangle = 0$.

Moreover, $v_{xc,pG}^{ss}(\mathbf{r})$ has a simple physical interpretation in the RPA [22,56]: it can be obtained from a quasiparticle approximation to the linear-response Sham-Schlüter equation. In this quasiparticle approximation, $v_{xc}(\mathbf{r})$ is calculated so that the first-order variation of the density (computed from the quasiparticle amplitudes) is zero under the perturbation $\tilde{\Sigma}_{xc} - v_{xc}$ that transforms the KS equation into the quasiparticle equation (here $\tilde{\Sigma}_{xc} \equiv GW$), which directly yields Eq. (82). This interpretation as well as point (ii) above clearly support the use of $v_{xc,pG}^{ss}(\mathbf{r})$ as a meaningful approximation to the RPA potential. We expect $v_{xc,pG}^{ss}(\mathbf{r})$ to be a reasonable approximation to $v_{xc}^{ss}(\mathbf{r})$ also beyond RPA, although the link with MBPT will be lost in most cases. This, of course, re-

mains to be tested, but is beyond the scope of this paper. The effect of $v_c^{dk}(\mathbf{r})$ (in the ACFD-ALDA, for example) should also be investigated, since the x-OEP-like approximation may benefit from partial cancellations between $v_{c,p\Sigma}^{ss}(\mathbf{r})$ and $v_c^{dk}(\mathbf{r})$ (though these cancellations are unclear at this stage). Anyway, $v_{xc,pG}^{ss}(\mathbf{r})$ is much simpler to compute than the exact ACFD potential, even if it still requires the calculation of the GW -like self-energy $\tilde{\Sigma}_{xc}$ [Eq. (38)] for the occupied KS states. Once this is done, the potential can be evaluated using any existing x-OEP code. If needed, $v_{xc,pG}^{ss}(\mathbf{r})$ also lends itself to the Krieger-Li-Iafrate (KLI) approximation [5], which proved to be very accurate in the x-OEP case. We conjecture that KLI will remain a good approximation to $v_{xc,pG}^{ss}(\mathbf{r})$ in the ACFD framework.

B. The “statically screened” approximation

This potential, which also neglects $v_c^{dk}(\mathbf{r})$, follows from the use of an approximate $\tilde{\Sigma}_{xc}$ in the linear-response Sham-Schlüter equation [56]. The prototype of this approximate $\tilde{\Sigma}_{xc}$ is the static Coulomb hole and screened exchange (COHSEX) self-energy [28], which is a frequency-independent approximation to the GW self-energy that neglects dynamical correlations. The static COHSEX screened exchange part $\Sigma_{ssex}(\mathbf{r}, \mathbf{r}')$ and Coulomb hole part $\Sigma_{scoh}(\mathbf{r}, \mathbf{r}')$ read

$$\Sigma_{ssex}(\mathbf{r}, \mathbf{r}') = - \sum_{j=1}^{N/2} \varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}') W^{\text{RPA}}(\mathbf{r}, \mathbf{r}'; iu=0), \quad (83a)$$

$$\Sigma_{scoh}(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \delta(\mathbf{r} - \mathbf{r}') W_s^{\text{RPA}}(\mathbf{r}, \mathbf{r}; iu=0). \quad (83b)$$

Compared to Eq. (46), Σ_{ssex} is now statically screened while Σ_{scoh} is just half the potential felt by an electron at \mathbf{r} and due to the “Coulomb hole” that forms around it. We can make a similar approximation for arbitrary GW -like $\tilde{\Sigma}_{xc}$'s [Eq. (38)], replacing $W^{\text{RPA}}(\mathbf{r}, \mathbf{r}'; iu=0)$ with $\tilde{W}(\mathbf{r}, \mathbf{r}'; iu=0)$ and $W_s^{\text{RPA}}(\mathbf{r}, \mathbf{r}'; iu=0)$ with $\tilde{W}_s(\mathbf{r}, \mathbf{r}; iu=0)$. We then plug this “statically screened” approximation for $\tilde{\Sigma}_{xc}$ into the linear-response Sham-Schlüter equation and split (with obvious definitions) $v_{xc}^{ss}(\mathbf{r}) = v_{ssex}^{ss}(\mathbf{r}) + v_{scoh}^{ss}(\mathbf{r})$ in two parts. On one hand, we directly get, with the help of Eq. (12):

$$v_{scoh}^{ss}(\mathbf{r}) = \frac{1}{2} \tilde{W}_s(\mathbf{r}, \mathbf{r}; iu=0), \quad (84)$$

since $\tilde{\Sigma}_{scoh}$ is local [note that Eq. (84) only holds asymptotically when dynamical correlations are included, see Eq. (47b) for $v_{scoh}^{ss}(\mathbf{r})$]. On the other hand, $v_{ssex}^{ss}(\mathbf{r})$ satisfies the same equation as the x-OEP potential with $\nu(\mathbf{r}, \mathbf{r}')$ replaced by $\tilde{W}(\mathbf{r}, \mathbf{r}'; iu=0)$, i.e., it satisfies Eq. (82) with

$$u_{\text{ssex}j}(\mathbf{r}) = -\frac{1}{\varphi_j^*(\mathbf{r})} \sum_{k=1}^{N/2} \varphi_k^*(\mathbf{r}) \int d^3\mathbf{r}' \varphi_j^*(\mathbf{r}') \times \tilde{W}(\mathbf{r}, \mathbf{r}'; iu=0) \varphi_k(\mathbf{r}'). \quad (85)$$

Therefore, all what is needed starting from an existing x-OEP code is to calculate the statically screened Coulomb interaction $\tilde{W}(\mathbf{r}, \mathbf{r}'; iu=0)$ (whose ingredients are already computed when evaluating the total energy). The KLI approximation [5] may be used if appropriate and can be expected quite accurate. The statically screened approximation to $v_{\text{xc}}^{\text{ss}}(\mathbf{r})$ also follows from Eq. (82) if $\tilde{\Sigma}_{\text{ssex}}$ and $\tilde{\Sigma}_{\text{scoh}}$ are used as input.

$v_{\text{sxc}}^{\text{ss}}(\mathbf{r})$ should be a reasonable approximation to $v_{\text{xc}}^{\text{ss}}(\mathbf{r})$ for many practical purposes. We emphasize that both have the same asymptotic behavior. This is evident from Eqs. (47b) and (84) for the Coulomb hole parts $v_{\text{coh}}^{\text{ss}}(\mathbf{r})$ and $v_{\text{scoh}}^{\text{ss}}(\mathbf{r})$. Moreover, Eq. (47a) still holds for $v_{\text{ssex}}^{\text{ss}}(\mathbf{r})$ using $\tilde{\Sigma}_{\text{ssex}}$ in Eq. (48), which directly yields Eq. (49).

The statically screened approximation to the RPA potential has been calculated by Kotani [64] in some bulk metals (Cu, Ni, Fe, and Co). It was found rather close to the LDA potential in these metals, in agreement with Godby's conclusions in bulk Si. However, we stress that in finite systems, the statically screened approximation to the RPA potential, which includes exact exchange and thus exhibits the expected $-1/r$ behavior, should perform better than the LDA potential.

VI. CONCLUSION

We have derived the exchange-correlation potential $v_{\text{xc}}(\mathbf{r})$ in the adiabatic connection fluctuation-dissipation framework, for arbitrary TDDFT kernels f_{xc} . We have shown that this potential is the sum of two terms, one of which has the structure of the linear-response Sham-Schlüter equation. We have investigated the asymptotic behavior of $v_{\text{xc}}(\mathbf{r})$ in three relevant approximations: the random-phase approximation, the exact-exchange kernel for two-electron systems, and the adiabatic local-density approximation. The exchange-correlation potential exhibits the expected $-1/r + Q/r^3 - \alpha/(2r^4)$ tail (in closed-shell systems with spherical symmetry), where Q and α depend on the choice for f_{xc} . We have discussed the underlying physics for each of the three approximations. Finally, we have proposed a “x-OEP-like” approximation and a statically screened approximation to the ACFD potentials, which are much simpler to compute than the exact ones. The accuracy of these approximate potentials should now be tested on real molecules or solids.

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 [50] Note that proper infinitesimals must be included (as usual) in all poles when going from the imaginary to the real frequency axis. For example, the real frequency Green function $G_0(\mathbf{r},\mathbf{r}';\omega)$ reads

$$G_0(\mathbf{r},\mathbf{r}';\omega)=\sum_j\frac{\varphi_j(\mathbf{r})\varphi_j^*(\mathbf{r}')}{\omega-\varepsilon_j\pm i\eta},$$

where η is a positive infinitesimal and the sign $-$ (resp. $+$) holds for occupied (resp. empty) KS states. The analytical continuation of $\chi_0(\mathbf{r},\mathbf{r}';iu)$ from the positive imaginary frequency axis to the positive real frequency axis, and from the negative imaginary frequency axis to the negative real frequency axis, reads in the same way:

$$\chi_0(\mathbf{r},\mathbf{r}';\omega)=2\sum_{j=1}^{N/2}\sum_{k>N/2}\frac{\varphi_j^*(\mathbf{r})\varphi_k(\mathbf{r})\varphi_k^*(\mathbf{r}')\varphi_j(\mathbf{r}')}{\omega-(\varepsilon_k-\varepsilon_j)+i\eta}-2\sum_{j=1}^{N/2}\sum_{k>N/2}\frac{\varphi_j^*(\mathbf{r})\varphi_k(\mathbf{r})\varphi_k^*(\mathbf{r}')\varphi_j(\mathbf{r}')}{\omega+(\varepsilon_k-\varepsilon_j)-i\eta}. \quad (86)$$

This is in fact the Fourier transform of the time-ordered (rather than causal) density-density response function.

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