

Asymptotic behaviour of the exchange-correlation potentials from the linear-response Sham-Schlüter equation

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Abstract

The linear-response Sham-Schlüter equation can be used to calculate an exchange-correlation potential starting from a given approximation for the self-energy. The asymptotic behaviour of these potentials is however much debated, a recent work suggesting that they could blow up in finite systems. Here we investigate the asymptotic behaviour of the linear-response Sham-Schlüter potentials in the GW and second-order approximations for the self-energy. We show that these potentials do not diverge, and that the correlation potential itself has a $-\alpha/(2r^4)$ tail (under appropriate conditions), where α depends on the self-energy. We also provide further justification for the quasiparticle approximation to the linear-response Sham-Schlüter equation, that is much simpler to solve while being likely of comparable accuracy. Calculations for real molecules or solids using this approximation should be within the reach of present computers.

I. INTRODUCTION

Density functional theory (DFT) has now become an efficient and widely used tool to calculate the ground-state properties of atoms, molecules and solids¹⁻³. In the usual Kohn-Sham² (KS) implementation of DFT, the system of interacting electrons is replaced with a fictitious system of non-interacting particles moving in a local potential $v^{\text{KS}}(\mathbf{r})$. Far from a finite system with spherical symmetry and orbitally non-degenerate N and $N - 1$ electron ground-states (such as a He atom), the exchange-correlation part of this potential, $v_{\text{xc}}(\mathbf{r})$, is expected to behave as^{4,5} :

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

where α_{N-1} is the static ground-state polarizability of the $N - 1$ electron system. In the same way, $v_{\text{xc}}(\mathbf{r})$ is expected to behave⁴ as $-1/(4z)$ far from a metal surface located at $z = 0$. The local density approximation^{1,2} (LDA) and the generalized gradient approximations⁶ (GGAs), that are the simplest approximations for the exchange-correlation energy, do not yield accurate exchange-correlation potentials. Indeed, these potentials vanish exponentially⁷, at variance with the expected behaviour. This results in inaccurate empty KS states, which is an inadequate starting point for Time-Dependent DFT⁸⁻¹¹. These shortcomings have thus stimulated the search for better, fully non-local approximations to the exchange-correlation energy and/or potential.

Many-Body Perturbation Theory¹² (MBPT) is one way to improve on the LDA and GGAs. In 1985, Sham and Schlüter¹³ derived an equation that yields the exchange-correlation potential corresponding to a given approximation for the self-energy. Although the exact Sham-Schlüter equation is of little practical interest, its simpler, “linear-response” (LR) form has attracted much attention. It reverts back to the standard x-OEP (Optimized Effective Potential) equation¹⁴⁻¹⁷ for the exact KS exchange potential in the exchange-only approximation for the self-energy. Beyond the exchange-only treatment, the LR Sham-Schlüter equation can be used to include correlations in the KS potential, e.g., at the level of the *GW* self-energy^{18,19}. Importantly, expressions similar to the LR Sham-Schlüter equation also appear in other formalisms for the exchange-correlation potential, such as the Görling-Levy perturbation theory^{20,21} (GLPT), or the Adiabatic-Connection Fluctuation-Dissipation (ACFD) framework^{22,23}. There is therefore a clear need for a detailed assessment and a bet-

ter understanding of the properties of this equation, in particular the asymptotic behaviour of its solutions that has remained controversial.

Indeed, in 1992, Eguiluz *et al.*¹⁸ solved the LR Sham-Schlüter equation for a jellium surface, in the *GW* approximation for the self-energy^{24,25}. The calculated exchange-correlation potential exhibits the expected $-1/(4z)$ behaviour, unlike most other potentials so far. However, Facco Bonnetti *et al.*²⁶ recently investigated the asymptotic behaviour of the exchange-correlation potential from the second-order GLPT. In the He-like systems they considered, it amounts to the LR Sham-Schlüter potential in the second-order [MBPT(2)] approximation for the self-energy. They claim that this potential blows up exponentially far from a finite system, which casts serious doubts on the physical relevance of the LR Sham-Schlüter equation. Their demonstration was mainly based on numerical considerations. In the present paper, we analytically study the asymptotic behaviour of the LR Sham-Schlüter potential in the *GW* and second-order approximations for the self-energy (LRSS-*GW* and LRSS-MBPT(2) potentials). We show that these potentials have the expected $-1/r$ behaviour in finite systems (due to exchange), while the correlation potential itself has a $-\alpha/(2r^4)$ tail (where α depends on the self-energy). By a detailed analysis, we trace this discrepancy with the work of Facco Bonnetti *et al.* back to a (numerically) problematic splitting of the potential into two parts that diverge asymptotically, whereas their sum remains finite. In addition, we provide further justification for the quasiparticle approximation to the LR Sham-Schlüter equation²⁹, that is much easier to solve than the usual LR form, while being likely of comparable accuracy. Its application to small real molecules should be within the reach of present computers.

This paper is organized as follows : in section II, we briefly review the derivation of the LR Sham-Schlüter equation. In section III, we show that the correlation potential has a $-\alpha/(2r^4)$ tail. We focus on the LRSS-*GW* potential, although the results can easily be extended to many other approximations, including LRSS-MBPT(2). Then, in section IV, we discuss the implications of these results and compare with the work of Facco Bonnetti *et al.* Last, in section V, we provide further support for the quasiparticle approximation to the LR Sham-Schlüter equation. For computational purposes, we also recall the simpler KLI form of this quasiparticle approximation, and discuss the static COHSEX approximation to the LRSS-*GW* potential.

II. THE LINEAR-RESPONSE SHAM-SCHLÜTER EQUATION

In this section, we briefly review the basics of the linear-response Sham-Schlüter equation and recall the expression of the associated exchange-correlation functional $E_{xc}[n]$ (when available).

A. The Sham-Schlüter equation

The Sham-Schlüter equation¹³ was derived in the framework of the many-body Green functions formalism¹². It gives the exchange-correlation potential $v_{xc\sigma}(\mathbf{r})$ that corresponds to a given approximation for the self-energy. It is based on the fact that $v_{xc\sigma}(\mathbf{r})$ is the only local potential that yields the many-body ground-state spin density $n_\sigma(\mathbf{r})$. This directly translates into the following relation between the interacting many-body Green function³⁰ $G_\sigma(\mathbf{r}, \mathbf{r}'; \omega)$ and the Kohn-Sham (KS) Green function $G_\sigma^{\text{KS}}(\mathbf{r}, \mathbf{r}'; \omega)$:

$$n_\sigma(\mathbf{r}) = \int \frac{d\omega}{2i\pi} e^{i\omega\delta} G_\sigma(\mathbf{r}, \mathbf{r}'; \omega) = \int \frac{d\omega}{2i\pi} e^{i\omega\delta} G_\sigma^{\text{KS}}(\mathbf{r}, \mathbf{r}'; \omega), \quad (2)$$

where the limits $\delta \rightarrow 0^+$, $\mathbf{r}' \rightarrow \mathbf{r}$ are implied, and³¹ :

$$G_\sigma^{\text{KS}}(\mathbf{r}, \mathbf{r}'; \omega) = \sum_n \frac{\varphi_{n\sigma}(\mathbf{r})\varphi_{n\sigma}^*(\mathbf{r}')}{\omega - \varepsilon_{n\sigma} \pm i\eta}. \quad (3)$$

η is a positive infinitesimal and the sign $-$ (resp. $+$) holds for occupied (resp. empty) KS states, whose orbitals $\varphi_{n\sigma}(\mathbf{r})$ and energies $\varepsilon_{n\sigma}$ satisfy the set of KS equations² :

$$-\frac{1}{2}\nabla^2\varphi_{n\sigma}(\mathbf{r}) + v_\sigma^{\text{KS}}(\mathbf{r})\varphi_{n\sigma}(\mathbf{r}) = \varepsilon_{n\sigma}\varphi_{n\sigma}(\mathbf{r}), \quad (4)$$

where $v_\sigma^{\text{KS}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{h}}(\mathbf{r}) + v_{xc\sigma}(\mathbf{r})$ is the KS potential, $v_{\text{ext}}(\mathbf{r})$ is the external (ionic) potential, and $v_{\text{h}}(\mathbf{r})$ is the Hartree potential. Moreover, G_σ and G_σ^{KS} are related by the Dyson equation (written in matrix form for compactness) :

$$G_\sigma(\omega) = G_\sigma^{\text{KS}}(\omega) + G_\sigma^{\text{KS}}(\omega) \left\{ \Sigma_{xc\sigma}[G](\omega) - v_{xc\sigma} \right\} G_\sigma(\omega), \quad (5)$$

where $\Sigma_{xc\sigma}[G](\mathbf{r}, \mathbf{r}'; \omega)$ is the exchange-correlation self-energy. It must conserve the number of particles for Eq. (2) to be meaningful. One possible (though not the only) way to build particle-number conserving approximations for the self-energy is to sum³² selected “skeleton diagrams” (see paragraph II B). In that case, $\Sigma_{xc\sigma}[G](\mathbf{r}, \mathbf{r}'; \omega)$ is an explicit functional of the

interacting Green function G , which is emphasized in the notation. The self-consistent GW self-energy^{24,25} is one well-known approximation of this kind. Insertion of Eq. (5) into Eq. (2) yields the Sham-Schlüter equation for $v_{xc\sigma}(\mathbf{r})$:

$$0 = \int \frac{d\omega}{2i\pi} \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 G_\sigma^{\text{KS}}(\mathbf{r}, \mathbf{r}_1; \omega) \left\{ \Sigma_{xc\sigma}[G](\mathbf{r}_1, \mathbf{r}_2; \omega) - v_{xc\sigma}(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2) \right\} G_\sigma(\mathbf{r}_2, \mathbf{r}; \omega). \quad (6)$$

The Sham-Schlüter equation thus appears as a complex non-linear integral equation. Although it can be used to discuss general properties of the exchange-correlation potential, it is of little practical interest. Indeed, the calculation of the self-consistent interacting Green function G_σ is in general far beyond present computational capabilities. Anyway, G_σ , if known, already gives access to most single-particle ground-state properties¹², which makes DFT useless. The Sham-Schlüter equation is therefore usually solved in the linear response (LR) approximation²⁹. Treating $\lambda\{\Sigma_{xc\sigma}[G] - v_{xc\sigma}\}$ as a perturbation in Eq. (5), where $\lambda \rightarrow 1$ is a coupling constant, yields to first-order :

$$0 = \int \frac{d\omega}{2i\pi} \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 G_\sigma^{\text{KS}}(\mathbf{r}, \mathbf{r}_1; \omega) \left\{ \Sigma_{xc\sigma}[G^{\text{KS}}](\mathbf{r}_1, \mathbf{r}_2; \omega) - v_{xc\sigma}(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2) \right\} G_\sigma^{\text{KS}}(\mathbf{r}_2, \mathbf{r}; \omega). \quad (7)$$

The LR Sham-Schlüter equation is thought to be a very good approximation to the exact Sham-Schlüter equation, although there has been little work to assess its accuracy. To enlighten the physics behind this equation, we introduce the static KS density-density response function $\chi_\sigma^{\text{KS}}(\mathbf{r}, \mathbf{r}')$:

$$\chi_\sigma^{\text{KS}}(\mathbf{r}, \mathbf{r}') = \int \frac{d\omega'}{2i\pi} G_\sigma^{\text{KS}}(\mathbf{r}, \mathbf{r}'; \omega') G_\sigma^{\text{KS}}(\mathbf{r}', \mathbf{r}; \omega') \quad (8a)$$

$$= \sum_{n=1}^{N_\sigma} \sum_{m>N_\sigma} \frac{\varphi_{n\sigma}^*(\mathbf{r}) \varphi_{m\sigma}(\mathbf{r}) \varphi_{m\sigma}^*(\mathbf{r}') \varphi_{n\sigma}(\mathbf{r}')}{\varepsilon_{n\sigma} - \varepsilon_{m\sigma}} + \text{c.c.} \quad (8b)$$

N_σ is the total number of electrons with spin σ . Eq. (7) can thus be cast in the following form, characteristic of all OEP formalisms^{15-17,20,21,23} :

$$\int d^3\mathbf{r}' \chi_\sigma^{\text{KS}}(\mathbf{r}, \mathbf{r}') v_{xc\sigma}(\mathbf{r}') = \rho_{xc\sigma}(\mathbf{r}), \quad (9)$$

where :

$$\rho_{xc\sigma}(\mathbf{r}) = \int \frac{d\omega}{2i\pi} \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 G_\sigma^{\text{KS}}(\mathbf{r}, \mathbf{r}_1; \omega) \Sigma_{xc\sigma}[G^{\text{KS}}](\mathbf{r}_1, \mathbf{r}_2; \omega) G_\sigma^{\text{KS}}(\mathbf{r}_2, \mathbf{r}; \omega). \quad (10)$$

The properties of the kernel $\chi_\sigma^{\text{KS}}(\mathbf{r}, \mathbf{r}')$ have been thoroughly discussed in the literature^{17,21}. It is singular since the response of the density to a uniform potential is zero and :

$$\int d^3\mathbf{r} \int d^3\mathbf{r}' \chi_\sigma^{\text{KS}}(\mathbf{r}, \mathbf{r}') v(\mathbf{r}') = 0 \quad (11)$$

whatever $v(\mathbf{r}')$. Therefore, *i*) Eq. (9) has solutions only if $\rho_{\text{xc}\sigma}(\mathbf{r})$ has vanishing integral (this is the counterpart of the particle number conservation requirement for the exact Sham-Schlüter equation), and *ii*) $v_{\text{xc}\sigma}(\mathbf{r})$ is defined by Eq. (9) only up to an arbitrary constant. In principle, Eq. (9) must be solved together with Eq. (4) until self-consistency is achieved.

The LR Sham-Schlüter equation has been solved in the *GW* approximation^{24,25} by Eguiluz *et al.*¹⁸ for a jellium surface, and by Godby *et al.*¹⁹ in bulk silicon (albeit not up to full self-consistency). Godby *et al.* showed that the LDA and LRSS-*GW* potentials in silicon are very close, which may explain the success of the LDA for the calculation of the ground-state properties of solids. They also showed that the bandgap energy is not improved by the LRSS-*GW* potential, which suggests that the discontinuity in the (exact) exchange-correlation potential upon addition or removal of an electron in bulk silicon is large^{13,34} (see however Ref. 33). The LR Sham-Schlüter equation (as derived above) is a “direct” approach to the exchange-correlation potential that does not proceed by functional differentiation of an approximate exchange-correlation energy. This means, however, that the functional $E_{\text{xc}}[n]$ that corresponds to the calculated $v_{\text{xc}\sigma}(\mathbf{r})$ is *a priori* unknown. Nonetheless, particle-number conserving approximations for the self-energy are usually obtained from truncated series of skeleton diagrams, in which case the exchange-correlation energy $E_{\text{xc}}[n]$ whose potential is given by Eq. (9) is known²⁹. This will be the subject of the next paragraph.

B. The Nozières energy functional

In principle, the self-energy $\Sigma_{\text{xc}\sigma}[G]$ can be expanded as a sum of “skeleton” diagrams involving the bare Coulomb interaction $v(\mathbf{r}, \mathbf{r}') = 1/|\mathbf{r} - \mathbf{r}'|$ and the interacting Green function G . The rules for drawing and evaluating these diagrams can be found in standard textbooks dealing with many-body perturbation theory¹². Approximate self-energies can be obtained by summing only a subset of these diagrams. Casida has shown that the LR Sham-Schlüter equation then yields the potential $v_{\text{xc}\sigma}(\mathbf{r}) = \delta E_{\text{xc}}[n]/\delta n_\sigma(\mathbf{r})$ that corresponds to the following

exchange-correlation energy²⁹ :

$$E_{xc}[n] = \Phi[G^{\text{KS}}] = \sum_{\sigma} \sum_{n=1}^{\infty} \frac{1}{2n} \int \frac{d\omega}{2i\pi} e^{i\omega\delta} \text{Tr} \left\{ \Sigma_{xc\sigma}^{(n)}[G^{\text{KS}}] G_{\sigma}^{\text{KS}} \right\}. \quad (12)$$

$\Sigma_{xc\sigma}^{(n)}[G^{\text{KS}}]$ is the (truncated) sum of all skeleton diagrams of order n (i.e., that involve n explicit electron-electron interactions), where the interacting Green function G has been replaced with the KS Green function G^{KS} . The symbol Tr stands for :

$$\text{Tr}\{AB\} = \int d^3\mathbf{r} d^3\mathbf{r}' A(\mathbf{r}, \mathbf{r}'; \omega) B(\mathbf{r}', \mathbf{r}; \omega). \quad (13)$$

Eq. (12) is just Nozières' energy functional³⁵ evaluated at the KS Green function (Note that Nozières' energy functional differs from the original Luttinger-Ward³⁶ energy functional : although both are equal when evaluated at the self-consistent, interacting Green function G_{σ} , they differ away from self-consistency. Compare for example Ref. 29, which actually uses Nozières' functional, and Ref. 37).

In the exchange-only approximation :

$$\Sigma_{xc\sigma}[G^{\text{KS}}](\mathbf{r}, \mathbf{r}') = - \sum_{n=1}^{N_{\sigma}} v(\mathbf{r}, \mathbf{r}') \varphi_{n\sigma}(\mathbf{r}) \varphi_{n\sigma}^*(\mathbf{r}'), \quad (14)$$

Eq. (12) is the usual Fock energy and the LR Sham-Schlüter equation amounts to the standard x-OEP equation, as derived (from other starting points) in Refs. 15 or 16. In this paper, we focus on the second-order [MBPT(2)] and GW self-energies, that both include correlations. The second-order $\Sigma_{xc\sigma}[G^{\text{KS}}]$ is the sum of the first-order exchange diagram and of the two second-order diagrams represented in Fig. 1. The expression of the associated correlation energy, obtained from Eq. (12), can be found in Ref. 26. It has the same functional form as the second-order Møller-Plesset (MP2) correction²⁷. The GW self-energy^{24,25} reads :

$$\Sigma_{xc\sigma}[G^{\text{KS}}](\mathbf{r}, \mathbf{r}'; \omega) = i \int \frac{d\omega'}{2\pi} e^{i\omega'\delta} G_{\sigma}^{\text{KS}}(\mathbf{r}, \mathbf{r}'; \omega + \omega') W(\mathbf{r}, \mathbf{r}'; \omega'), \quad (15)$$

where $W(\omega) = [1 - vP^{\text{KS}}(\omega)]^{-1}v$ is the time-ordered RPA screened Coulomb interaction and $P^{\text{KS}}(\omega) = \sum_{\sigma} P_{\sigma}^{\text{KS}}(\omega)$ is the time-ordered KS density-density response function³⁸ [$P_{\sigma}^{\text{KS}}(\omega)$ is given by Eq. (8a) where one of the two $G_{\sigma}^{\text{KS}}(\omega')$ has been replaced with a $G_{\sigma}^{\text{KS}}(\omega + \omega')$]. We stress that Eq. (12) in the GW approximation is strictly equivalent to the well-known RPA expression for the exchange-correlation energy. It has been used early to discuss the total energy of the homogeneous electron gas^{39,40}, and, more recently, in calculations of the van

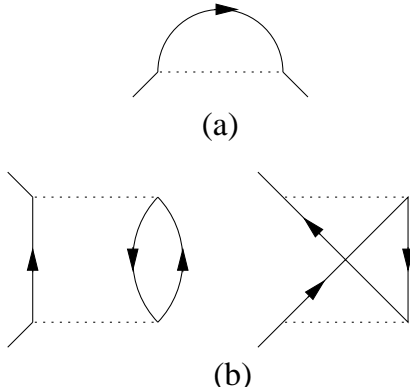


FIG. 1: (a) The first-order exchange diagram. (b) The two second-order diagrams. The solid line is the (KS) Green function, and the dotted line the bare Coulomb interaction.

der Waals interaction between jellium slabs⁴¹, as well as in calculation on real molecules^{42–45} (although not self-consistently, i.e., with LDA orbitals and energies as input).

To conclude this paragraph, we note that $E_{xc}[n] \equiv E_{xc}[\{\varphi_{n\sigma}, \varepsilon_{n\sigma}\}]$ may also be considered as an explicit functional of the KS orbitals $\varphi_{n\sigma}$ and KS energies $\varepsilon_{n\sigma}$. This allows to establish useful links between the LR Sham-Schlüter equation and the xc-OEP formalism of Engel *et al.*²⁸, and to compare our work with the one of Ref. 26. Details can be found in Appendix A. In the next section, we discuss the asymptotic behaviour of the LR Sham-Schlüter potential taking the GW approximation as an example, though the results can be extended to many other approximations, including LRSS-MBPT(2).

III. ASYMPTOTIC BEHAVIOUR OF THE LRSS- GW POTENTIAL

We now analyze the asymptotic behaviour of the LRSS- GW potential in finite systems. We first show that the LR Sham-Schlüter potential can be split into a “quasiparticle” term, that comes from the simple poles of the Green functions, and a dynamical correction, that comes from the other poles. We then briefly review the basics of the GW approximation (for notational purposes) in paragraph III B. We further investigate the long-range behaviour of the quasiparticle term and of the dynamical correction in paragraphs III C and III D. We show that the dynamical correction is asymptotically negligible with respect to the quasiparticle term, and that the latter has a finite limit when $r \rightarrow \infty$.

A. Decomposition of the LR Sham-Schlüter potential

For the sake of simplicity, we now assume that the KS states are non degenerate (except possibly for spin). The extension to the degenerate case is straightforward, but involves notational complications. In systems with spherical symmetry, the asymptotic behaviour of the potential can be discussed from the equations below provided the Kohn-Sham HOMO (Highest Occupied Molecular Orbital) is *s*-like.

To begin with, we rewrite Eq. (10) so as to make explicit the contributions from the poles of the KS Green functions and self-energy. Following Ref. 29, we split $\Sigma_{c\sigma}(\mathbf{r}, \mathbf{r}'; \omega)$ into a “hole” and a “particle” part. The hole part :

$$\Sigma_{h\sigma}(\mathbf{r}, \mathbf{r}'; \omega) = \sum_k \frac{R_{k\sigma}(\mathbf{r}, \mathbf{r}')}{\omega - \Omega_{k\sigma} - i\eta} \quad (16)$$

is the contribution from all poles $\Omega_{k\sigma}$ [with residues $R_{k\sigma}(\mathbf{r}, \mathbf{r}')$] that lie above the real axis⁴⁶. The particle part $\Sigma_{p\sigma}(\mathbf{r}, \mathbf{r}'; \omega) = \Sigma_{c\sigma}(\mathbf{r}, \mathbf{r}'; \omega) - \Sigma_{h\sigma}(\mathbf{r}, \mathbf{r}'; \omega)$ is the remainder. The expressions for $\Omega_{k\sigma}$ and $R_{k\sigma}(\mathbf{r}, \mathbf{r}')$ in the *GW* approximation will be given in paragraph III B. We then calculate $\rho_{xc\sigma}(\mathbf{r})$ closing the contour of integration in the upper part of the complex plane. This contour thus encloses all poles of $\Sigma_{h\sigma}$ and all poles of G_{σ}^{KS} related to the occupied KS states. Accordingly, we make the following decomposition of $\rho_{xc\sigma}(\mathbf{r})$:

$$\rho_{xc\sigma}(\mathbf{r}) = \rho_{xc\sigma}^{(1)}(\mathbf{r}) + \rho_{c\sigma}^{(2)}(\mathbf{r}) \text{ and } \rho_{c\sigma}^{(2)}(\mathbf{r}) = \rho_{c\sigma}^{(21)}(\mathbf{r}) + \rho_{c\sigma}^{(22)}(\mathbf{r}), \quad (17)$$

where $\rho_{xc\sigma}^{(1)}(\mathbf{r})$ is the contribution of all simple poles coming from the G_{σ}^{KS} 's, $\rho_{c\sigma}^{(21)}(\mathbf{r})$ is the contribution of all double poles coming from the G_{σ}^{KS} 's, and $\rho_{c\sigma}^{(22)}(\mathbf{r})$ is the contribution of the poles of $\Sigma_{h\sigma}$ (since $\rho_{c\sigma}^{(2)}$ is zero in the x-only approximation, it only contributes to the correlation potential). A straightforward calculation yields²⁹ :

$$\rho_{xc\sigma}^{(1)}(\mathbf{r}) = \sum_{n=1}^{N_{\sigma}} \sum_{m \neq n} \varphi_{n\sigma}(\mathbf{r}) \varphi_{m\sigma}^*(\mathbf{r}) \frac{\Sigma_{xc\sigma}^{nm}(\varepsilon_{n\sigma})}{\varepsilon_{n\sigma} - \varepsilon_{m\sigma}} + \text{c.c.} \quad (18a)$$

$$\rho_{c\sigma}^{(21)}(\mathbf{r}) = \sum_{n=1}^{N_{\sigma}} \varphi_{n\sigma}(\mathbf{r}) \varphi_{n\sigma}^*(\mathbf{r}) \left. \frac{\partial \Sigma_{c\sigma}^{nn}}{\partial \omega} \right|_{\varepsilon_{n\sigma}} \quad (18b)$$

$$\rho_{c\sigma}^{(22)}(\mathbf{r}) = \sum_n \sum_m \varphi_{n\sigma}(\mathbf{r}) \varphi_{m\sigma}^*(\mathbf{r}) \sum_k \frac{1}{\Omega_{k\sigma} - \varepsilon_{n\sigma}} R_{k\sigma}^{nm} \frac{1}{\Omega_{k\sigma} - \varepsilon_{m\sigma}}, \quad (18c)$$

where we have defined for a generic kernel $A_{\sigma}(\mathbf{r}, \mathbf{r}')$:

$$A_{\sigma}^{nm} = \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \varphi_{n\sigma}^*(\mathbf{r}_1) A_{\sigma}(\mathbf{r}_1, \mathbf{r}_2) \varphi_{m\sigma}(\mathbf{r}_2). \quad (19)$$

Further manipulation of these equations leads back to the xc-OEP formalism of Engel *et al.*²⁸, as shown in Appendix A (for the class of functionals defined in paragraph II B). $\rho_{xc\sigma}^{(1)}(\mathbf{r})$ has vanishing integral (since the KS orbitals are orthogonal), so that $\rho_{c\sigma}^{(2)}(\mathbf{r})$ also has vanishing integral (because $\rho_{xc\sigma}(\mathbf{r})$ has). Therefore, we can split $v_{xc\sigma}(\mathbf{r}) = v_{xc\sigma}^{(1)}(\mathbf{r}) + v_{c\sigma}^{(2)}(\mathbf{r})$, where $v_{xc\sigma}^{(1)}(\mathbf{r})$ and $v_{c\sigma}^{(2)}(\mathbf{r})$ are solutions of Eq. (9) with $\rho_{xc\sigma}^{(1)}(\mathbf{r})$ and $\rho_{c\sigma}^{(2)}(\mathbf{r})$ as the right-hand side respectively. Trying to associate a physical meaning with this decomposition, we note that $\rho_{c\sigma}^{(2)}(\mathbf{r})$ and $v_{c\sigma}^{(2)}(\mathbf{r})$ are zero if the self-energy is frequency-independent. We will therefore refer to $v_{c\sigma}^{(2)}(\mathbf{r})$ as a “dynamical correction” to the potential. Its long-range behaviour will be discussed in paragraph III D. Moreover, the equation satisfied by $v_{xc\sigma}^{(1)}(\mathbf{r})$ can be cast in a more familiar form using the following expression for $\chi_{\sigma}^{\text{KS}}(\mathbf{r}, \mathbf{r}')$:

$$\chi_{\sigma}^{\text{KS}}(\mathbf{r}, \mathbf{r}') = \sum_{n=1}^{N_{\sigma}} \varphi_{n\sigma}^*(\mathbf{r}) G_{n\sigma}(\mathbf{r}, \mathbf{r}') \varphi_{n\sigma}(\mathbf{r}') + \text{c.c.}, \quad (20)$$

where the Green function $G_{n\sigma}(\mathbf{r}, \mathbf{r}')$ is defined by :

$$G_{n\sigma}(\mathbf{r}, \mathbf{r}') = \sum_{m \neq n} \frac{\varphi_{m\sigma}(\mathbf{r}) \varphi_{m\sigma}^*(\mathbf{r}')}{\varepsilon_{n\sigma} - \varepsilon_{m\sigma}}. \quad (21)$$

Eq. (9) for $v_{xc\sigma}^{(1)}(\mathbf{r})$ can indeed be written¹⁷ :

$$\sum_{n=1}^{N_{\sigma}} \int d^3\mathbf{r}' \varphi_{n\sigma}^*(\mathbf{r}') \left[v_{xc\sigma}^{(1)}(\mathbf{r}') - u_{xcn\sigma}(\mathbf{r}') \right] G_{n\sigma}(\mathbf{r}', \mathbf{r}) \varphi_{n\sigma}(\mathbf{r}) + \text{c.c.} = 0, \quad (22)$$

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

$$u_{xcn\sigma}(\mathbf{r}) = \frac{1}{\varphi_{n\sigma}^*(\mathbf{r})} \int d^3\mathbf{r}' \Sigma_{xc\sigma}(\mathbf{r}', \mathbf{r}; \varepsilon_{n\sigma}) \varphi_{n\sigma}^*(\mathbf{r}'). \quad (23)$$

Eq. (22) is a generalization of the x-OEP equation to the correlated case (it yields the exact $v_{xc\sigma}(\mathbf{r})$ in the x-only approximation¹⁶). As shown by Casida²⁹ (and discussed in paragraph V A), $v_{xc\sigma}^{(1)}(\mathbf{r})$ can be obtained from a quasiparticle approximation to the linear-response Sham-Schlüter equation. We will thus refer to $v_{xc\sigma}^{(1)}(\mathbf{r})$ as the “quasiparticle” term. Before discussing its asymptotic behaviour, we specify $\Omega_{k\sigma}$ and $R_{k\sigma}(\mathbf{r}, \mathbf{r}')$ in the *GW* approximation.

B. The *GW* approximation

In this paragraph, we provide explicit expressions for the hole and particle parts of the *GW* self-energy (needed to calculate $\rho_{c\sigma}^{(2)}(\mathbf{r})$). We also introduce the physically meaningful

decomposition of the GW self-energy into a screened exchange plus a Coulomb hole term^{24,25}. This decomposition will be used later to analyze the long-range behaviour of $v_{xc\sigma}^{(1)}(\mathbf{r})$.

We start from the spectral representation of the RPA screened Coulomb interaction $W(\omega) = [1 - vP^{\text{KS}}(\omega)]^{-1}v$. The latter can be written as the sum of the bare Coulomb interaction $v(\mathbf{r}, \mathbf{r}')$ and a response part :

$$W_s(\mathbf{r}, \mathbf{r}'; \omega) = [vP^{\text{RPA}}(\omega)v](\mathbf{r}, \mathbf{r}'), \quad (24)$$

where $P^{\text{RPA}}(\omega) = [1 - P^{\text{KS}}(\omega)v]^{-1}P^{\text{KS}}(\omega)$ is the time-ordered RPA density-density response function³⁸, whose spectral representation reads⁸ :

$$P^{\text{RPA}}(\mathbf{r}, \mathbf{r}'; \omega) = \sum_s \rho_s(\mathbf{r})\rho_s^*(\mathbf{r}') \left[\frac{1}{\omega - \omega_s + i\eta} - \frac{1}{\omega + \omega_s - i\eta} \right]. \quad (25)$$

The ω_s 's are the poles of $P^{\text{RPA}}(\omega)$; the $\rho_s(\mathbf{r})$'s have vanishing integral and decay exponentially in the vacuum (with a typical $\propto e^{-\sqrt{-2I}r}$ tail, where I is the ionization energy). The spectral representation of $W_s(\omega)$ is therefore the same as that of $P^{\text{RPA}}(\omega)$, with $\rho_s(\mathbf{r})$ replaced by :

$$v_s(\mathbf{r}) = \int d^3\mathbf{r}' v(\mathbf{r}, \mathbf{r}')\rho_s(\mathbf{r}'). \quad (26)$$

Performing the frequency integration in Eq. (15) thus yields :

$$\Sigma_{xc\sigma}(\mathbf{r}, \mathbf{r}'; \omega) = \Sigma_{x\sigma}(\mathbf{r}, \mathbf{r}') + \Sigma_{h\sigma}(\mathbf{r}, \mathbf{r}'; \omega) + \Sigma_{p\sigma}(\mathbf{r}, \mathbf{r}'; \omega), \quad (27)$$

where $\Sigma_{x\sigma}(\mathbf{r}, \mathbf{r}')$ is the bare exchange contribution to the self-energy [Eq. (14)] and :

$$\Sigma_{h\sigma}(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{m=1}^{N_\sigma} \varphi_{m\sigma}(\mathbf{r})\varphi_{m\sigma}^*(\mathbf{r}') \sum_s \frac{v_s(\mathbf{r})v_s^*(\mathbf{r}')}{\omega - \varepsilon_{m\sigma} + \omega_s - i\eta} \quad (28a)$$

$$\Sigma_{p\sigma}(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{m>N_\sigma} \varphi_{m\sigma}(\mathbf{r})\varphi_{m\sigma}^*(\mathbf{r}') \sum_s \frac{v_s(\mathbf{r})v_s^*(\mathbf{r}')}{\omega - \varepsilon_{m\sigma} - \omega_s + i\eta}. \quad (28b)$$

Eqs. (28a) and (16) readily allow to identify $\Omega_{k\sigma} \equiv \varepsilon_{m\sigma} - \omega_s$, $R_{k\sigma}(\mathbf{r}, \mathbf{r}') \equiv v_s(\mathbf{r})\varphi_{m\sigma}(\mathbf{r})v_s^*(\mathbf{r}')\varphi_{m\sigma}^*(\mathbf{r}')$ and $\sum_k \equiv \sum_{m=1}^{N_\sigma} \sum_s \rho_{c\sigma}^{(22)}(\mathbf{r})$ thus reads⁴⁷ :

$$\rho_{c\sigma}^{(22)}(\mathbf{r}) = \sum_{n=1}^{N_\sigma} \sum_s \left| \sum_m \frac{v_{s\sigma}^{nm}}{\varepsilon_{n\sigma} - \varepsilon_{m\sigma} - \omega_s} \varphi_{m\sigma}^*(\mathbf{r}) \right|^2, \quad (29)$$

with $v_{s\sigma}^{nm}$ defined by Eq. (19).

Moreover, a straightforward manipulation of Eqs. (28) leads back to the usual decomposition of the GW self-energy into a screened exchange term $\Sigma_{\text{sex}\sigma}(\mathbf{r}, \mathbf{r}'; \omega)$ plus a Coulomb hole term $\Sigma_{\text{coh}\sigma}(\mathbf{r}, \mathbf{r}'; \omega)$:

$$\Sigma_{\text{sex}\sigma}(\mathbf{r}, \mathbf{r}'; \omega) = - \sum_{m=1}^{N_\sigma} \varphi_{m\sigma}(\mathbf{r}) \varphi_{m\sigma}^*(\mathbf{r}') W(\mathbf{r}, \mathbf{r}'; \omega - \varepsilon_{m\sigma}) \quad (30)$$

$$\Sigma_{\text{coh}\sigma}(\mathbf{r}, \mathbf{r}'; \omega) = \sum_m \varphi_{m\sigma}(\mathbf{r}) \varphi_{m\sigma}^*(\mathbf{r}') \sum_s \frac{v_s(\mathbf{r}) v_s^*(\mathbf{r}')}{\omega - \varepsilon_{m\sigma} - \omega_s + i\eta}. \quad (31)$$

The interpretation of $\Sigma_{\text{coh}\sigma}(\mathbf{r}, \mathbf{r}'; \omega)$ as a Coulomb hole term is made obvious in the simpler static COHSEX approximation^{24,25}. This approximation, which neglects dynamical correlations, is at best valid around the chemical potential. It relies on the fact that the most important contributions to $\Sigma_{\text{coh}\sigma}$ and $\Sigma_{\text{sex}\sigma}$ usually come from single particle states m with energies $|\omega - \varepsilon_{m\sigma}|$ much lower than those of the plasmon poles of W . Discarding $\omega - \varepsilon_{m\sigma}$ in Eqs. (30) and (31) and using the closure relation then yields :

$$\Sigma_{\text{sex}\sigma}(\mathbf{r}, \mathbf{r}'; \omega) = - \sum_{m=1}^{N_\sigma} \varphi_{m\sigma}(\mathbf{r}) \varphi_{m\sigma}^*(\mathbf{r}') W(\mathbf{r}, \mathbf{r}'; \omega = 0) \quad (32)$$

$$\begin{aligned} \Sigma_{\text{coh}\sigma}(\mathbf{r}, \mathbf{r}'; \omega) &= -\delta(\mathbf{r} - \mathbf{r}') \sum_s \frac{|v_s(\mathbf{r})|^2}{\omega_s} \\ &= \frac{1}{2} \delta(\mathbf{r} - \mathbf{r}') W_s(\mathbf{r}, \mathbf{r}; \omega = 0). \end{aligned} \quad (33)$$

In the static COHSEX approximation, $\Sigma_{\text{coh}\sigma}$ is thus half the classical image potential felt by a test charge at \mathbf{r} (and due to the Coulomb hole that forms around it). The factor 1/2 comes from the adiabatic building of the screening charge.

C. Asymptotic behaviour of the quasiparticle term

In this paragraph, we discuss the asymptotic behaviour of the quasiparticle term $v_{\text{xc}\sigma}^{(1)}(\mathbf{r})$. We first recall some general results about the long-range behaviour of the solutions of Eq. (22) before focusing on the GW approximation.

1. Generalities about the long-range behaviour of the solutions of the x -OEP like equation

The long-range behaviour of $v_{\text{x}\sigma}(\mathbf{r})$ and $v_{\text{c}\sigma}^{(1)}(\mathbf{r})$ in finite systems has been discussed by T. Grabo *et al.*¹⁷. We only consider here the case of a non-degenerate HOMO that has

no nodal planes or lines extending up to infinity⁴⁸. We first assume that $v_\sigma^{\text{KS}}(\mathbf{r})$ has the expected $-1/r$ tail (which must be checked *a posteriori*). The bound KS orbitals thus behave asymptotically as :

$$\varphi_{n\sigma}(\mathbf{r}) \sim \frac{A_{n\sigma}}{r} r^{1/\beta_{n\sigma}} e^{-\beta_{n\sigma}r} \hat{\varphi}_{n\sigma}(\hat{\mathbf{r}}), \quad (34)$$

where $\beta_{n\sigma} = \sqrt{-2\varepsilon_{n\sigma}}$ and $\hat{\mathbf{r}} = \mathbf{r}/r$ [in the following, $\hat{f}(\hat{\mathbf{r}})$ will always refer to the asymptotic angular part of a function $f(\mathbf{r})$]. We also assume (in order to fix the undetermined constant in the potential) that $v_{x\sigma}(\mathbf{r})$ and $v_{c\sigma}^{(1)}(\mathbf{r})$ both tend to zero when $r \rightarrow \infty$. We define the average potentials :

$$\bar{u}_{xcn\sigma} = \int d^3\mathbf{r} |\varphi_{n\sigma}(\mathbf{r})|^2 u_{xcn\sigma}(\mathbf{r}) \quad (35)$$

and :

$$\bar{v}_{xcn\sigma}^{(1)} = \int d^3\mathbf{r} |\varphi_{n\sigma}(\mathbf{r})|^2 v_{xc\sigma}^{(1)}(\mathbf{r}). \quad (36)$$

Under these assumptions, T. Grabo *et al.*¹⁷ proved the following theorems for $v_{x\sigma}(\mathbf{r})$ and $v_{c\sigma}^{(1)}(\mathbf{r})$ respectively :

(i) $\bar{v}_{xN_\sigma\sigma} = \bar{u}_{xN_\sigma\sigma}$, and $|v_{x\sigma}(\mathbf{r}) - u_{xN_\sigma\sigma}(\mathbf{r})|$ vanishes asymptotically as least as fast as :

$$r \left(\frac{1}{\beta_{(N_\sigma-1)\sigma}} - \frac{1}{\beta_{N_\sigma\sigma}} - 2 \right) e^{-(\beta_{(N_\sigma-1)\sigma} - \beta_{N_\sigma\sigma})r}. \quad (37)$$

(ii) If $u_{cn\sigma}(\mathbf{r})$ has a finite limit when $r \rightarrow \infty$, then $\bar{v}_{cN_\sigma\sigma}^{(1)} = \bar{u}_{cN_\sigma\sigma}$, and $|v_{c\sigma}^{(1)}(\mathbf{r}) - u_{cN_\sigma\sigma}(\mathbf{r})|$ vanishes asymptotically as least as fast as :

$$r \left(\frac{2}{\beta_{(N_\sigma-1)\sigma}} - \frac{2}{\beta_{N_\sigma\sigma}} + 1 \right) e^{-2(\beta_{(N_\sigma-1)\sigma} - \beta_{N_\sigma\sigma})r}. \quad (38)$$

In the x-only approximation¹⁷, we finally get $v_{x\sigma}(\mathbf{r}) \sim -1/r$ and $v_\sigma^{\text{KS}}(\mathbf{r}) \sim -1/r$ (as initially assumed), since $u_{xN_\sigma\sigma}(\mathbf{r}) \sim -1/r$ [Eq. (23) with (14)] and $v_{\text{ext}}(\mathbf{r}) + v_{\text{h}}(\mathbf{r})$ vanishes as least as fast as $1/r^2$ in neutral systems.

2. Application to the GW approximation

We now use these two theorems to discuss the asymptotic behaviour of the LRSS-GW potential. Following Eqs. (30) and (31), we split (with obvious definitions) $u_{xcn\sigma}(\mathbf{r}) = u_{\text{sexn}\sigma}(\mathbf{r}) + u_{\text{cohn}\sigma}(\mathbf{r})$ and $v_{xc\sigma}^{(1)}(\mathbf{r}) = v_{\text{sex}\sigma}^{(1)}(\mathbf{r}) + v_{\text{coh}\sigma}^{(1)}(\mathbf{r})$ into a screened exchange and a Coulomb

hole part. We first focus on the screened exchange potential $v_{\text{sex}\sigma}^{(1)}(\mathbf{r})$. Using Eqs. (23) and (30), $u_{\text{sex}n\sigma}(\mathbf{r})$ can be written :

$$u_{\text{sex}n\sigma}(\mathbf{r}) = - \sum_{m=1}^{N_\sigma} \frac{\varphi_{m\sigma}^*(\mathbf{r})}{\varphi_{n\sigma}^*(\mathbf{r})} W_{nm\sigma}(\mathbf{r}), \quad (39)$$

where :

$$W_{nm\sigma}(\mathbf{r}) = \int d^3\mathbf{r}' \varphi_{n\sigma}^*(\mathbf{r}') W(\mathbf{r}, \mathbf{r}'; \varepsilon_{n\sigma} - \varepsilon_{m\sigma}) \varphi_{m\sigma}(\mathbf{r}') \quad (40)$$

is the screened Coulomb potential due to the charge distribution $\rho_{nm\sigma}(\mathbf{r}) = \varphi_{n\sigma}^*(\mathbf{r})\varphi_{m\sigma}(\mathbf{r})$ oscillating with frequency $\varepsilon_{n\sigma} - \varepsilon_{m\sigma}$. If $m \neq n$, this charge distribution has zero sum (since the KS orbitals are orthogonal), so that $W_{nm\sigma}(\mathbf{r})$ vanishes as $1/r^q$ ($q \geq 2$ is an integer that depends on n and m). If $m = n$, this charge distribution sums up to 1, so that $W_{nm\sigma}(\mathbf{r}) \sim 1/r$. Since $\varphi_{N_\sigma\sigma}(\mathbf{r})$ has the slowest decay, we finally get :

$$u_{\text{sex}n\sigma}(\mathbf{r}) \sim - \frac{\varphi_{N_\sigma\sigma}^*(\mathbf{r})}{\varphi_{n\sigma}^*(\mathbf{r})} W_{nN_\sigma\sigma}(\mathbf{r}). \quad (41)$$

Hence,

$$u_{\text{sex}n\sigma}(\mathbf{r}) \sim -r^{\left(\frac{1}{\beta_{N_\sigma\sigma}} - \frac{1}{\beta_{n\sigma}} - q\right)} e^{(\beta_{n\sigma} - \beta_{N_\sigma\sigma})r} \hat{u}_{\text{sex}n\sigma}(\hat{\mathbf{r}}) \text{ if } n < N_\sigma, \quad (42a)$$

$$u_{\text{sex}N_\sigma\sigma}(\mathbf{r}) \sim -\frac{1}{r}. \quad (42b)$$

The same asymptotic behaviour as in the x-only approximation is found¹⁷ [i.e. with $W(\mathbf{r}, \mathbf{r}'; \omega)$ replaced by $v(\mathbf{r}, \mathbf{r}')$] : while $u_{\text{sex}N_\sigma\sigma}(\mathbf{r}) \rightarrow 0$ when $r \rightarrow \infty$, $u_{\text{sex}n\sigma}(\mathbf{r})$ ($n < N_\sigma$) diverges exponentially. Therefore, the theorem (i) above is applicable : $v_{\text{sex}\sigma}^{(1)}(\mathbf{r})$ satisfies the relation $\bar{v}_{\text{sex}N_\sigma\sigma}^{(1)} = \bar{u}_{\text{sex}N_\sigma\sigma}$ and $v_{\text{sex}\sigma}^{(1)}(\mathbf{r}) \sim u_{\text{sex}N_\sigma\sigma}(\mathbf{r}) \sim -1/r$. The latter behaviour is of course due to the bare exchange contribution to $\Sigma_{\text{sex}\sigma}$. Moreover, in a system with spherical symmetry and a doubly occupied s -like HOMO, the corrections to the leading $-1/r$ term are exponentially vanishing. Indeed, $\rho_{N_\sigma N_\sigma\sigma}(\mathbf{r})$ and the induced screening charge density both have spherical symmetry, and thus no multipole moments.

We now turn to the potential $v_{\text{coh}\sigma}^{(1)}(\mathbf{r})$. We start with the following expression for $u_{\text{coh}n\sigma}(\mathbf{r})$ [see Eqs. (23) and (31)] :

$$u_{\text{coh}n\sigma}(\mathbf{r}) = \frac{1}{\varphi_{n\sigma}^*(\mathbf{r})} \sum_s v_s^*(\mathbf{r}) w_{sn\sigma}(\mathbf{r}), \quad (43)$$

where :

$$w_{sn\sigma}(\mathbf{r}) = \sum_m \frac{v_{s\sigma}^{nm}}{\varepsilon_{n\sigma} - \varepsilon_{m\sigma} - \omega_s} \varphi_{m\sigma}^*(\mathbf{r}), \quad (44)$$

and $v_{s\sigma}^{nm}$ is defined by :

$$v_{s\sigma}^{nm} = \int d^3\mathbf{r} \varphi_{n\sigma}^*(\mathbf{r}) v_s(\mathbf{r}) \varphi_{m\sigma}(\mathbf{r}). \quad (45)$$

We first analyze the asymptotic behaviour of the $w_{sn\sigma}(\mathbf{r})$'s. Owing to the closure relation, each $w_{sn\sigma}(\mathbf{r})$ satisfies a dynamic Sternheimer-like⁴⁹ equation :

$$\left\{ \varepsilon_{n\sigma} - \omega_s + \frac{1}{2} \nabla^2 - v_{\sigma}^{\text{KS}}(\mathbf{r}) \right\} w_{sn\sigma}(\mathbf{r}) = v_s(\mathbf{r}) \varphi_{n\sigma}^*(\mathbf{r}). \quad (46)$$

The associated homogeneous equation has no normalizable solutions (otherwise $\varepsilon_{n\sigma} - \omega_s$ would be a KS energy⁴⁶), so that $w_{sn\sigma}(\mathbf{r})$ is the only solution of Eq. (46) whose squared modulus is integrable. We insert the following ansatz into Eq. (46) :

$$w_{sn\sigma}(\mathbf{r}) = \varphi_{n\sigma}^*(\mathbf{r}) p_{sn\sigma}(\mathbf{r}). \quad (47)$$

Since $\varphi_{n\sigma}(\mathbf{r})$ satisfies the KS equation [Eq. (4)], we are left with :

$$-\omega_s \varphi_{n\sigma}^*(\mathbf{r}) p_{sn\sigma}(\mathbf{r}) + \frac{1}{2} \varphi_{n\sigma}^*(\mathbf{r}) \nabla^2 p_{sn\sigma}(\mathbf{r}) + \nabla \varphi_{n\sigma}^*(\mathbf{r}) \nabla p_{sn\sigma}(\mathbf{r}) = v_s(\mathbf{r}) \varphi_{n\sigma}^*(\mathbf{r}). \quad (48)$$

$v_s(\mathbf{r})$ is the potential created by a charge distribution with zero sum [see Eq. (26)], and thus decays like $1/r^q$, where $q \geq 2$ is an integer. Therefore, the long-range behaviour of $p_{sn\sigma}(\mathbf{r})$ is easily shown to be :

$$p_{sn\sigma}(\mathbf{r}) \sim -\frac{v_s(\mathbf{r})}{\omega_s}. \quad (49)$$

Eq. (34) indeed yields :

$$\nabla \varphi_{n\sigma}^*(\mathbf{r}) \nabla p_{sn\sigma}(\mathbf{r}) \sim -\beta_{n\sigma} \varphi_{n\sigma}^*(\mathbf{r}) \frac{\partial}{\partial r} p_{sn\sigma}(\mathbf{r}), \quad (50)$$

so that the second and third term on the left hand side of Eq. (48) are asymptotically negligible with respect to the first one. Hence, we finally get from Eqs. (47) and (49) :

$$w_{sn\sigma}(\mathbf{r}) \sim -\frac{1}{\omega_s} v_s(\mathbf{r}) \varphi_{n\sigma}^*(\mathbf{r}), \quad (51)$$

and from Eqs. (24)–(26) and (43) :

$$u_{\text{coh}n\sigma}(\mathbf{r}) \sim -\sum_s \frac{|v_s(\mathbf{r})|^2}{\omega_s} \quad (52)$$

$$\sim \frac{1}{2} W_s(\mathbf{r}, \mathbf{r}; \omega = 0). \quad (53)$$

In principle, the mathematical validity of Eq. (52) is subject to the nature of the convergence of the series in Eq. (43) (e.g. uniform convergence, ...). This issue however appears very

difficult to address in the general case. Nonetheless, we emphasize that Eq. (52) is also supported by the static COHSEX approximation, which is expected to be exact in the asymptotic regime⁵⁰. Indeed, since $\Sigma_{\text{coh}\sigma}$ is local in this approximation [Eq. (33)], we directly get :

$$u_{\text{coh}n\sigma}(\mathbf{r}) = \frac{1}{2}W_s(\mathbf{r}, \mathbf{r}; \omega = 0), \quad (54)$$

independently of the KS orbital $\varphi_{n\sigma}(\mathbf{r})$. We shall say more about the static COHSEX approximation in paragraph V B.

Since $u_{\text{coh}n\sigma}(\mathbf{r}) \rightarrow 0$ when $r \rightarrow \infty$, the theorem (ii) is applicable. Therefore, $\bar{v}_{\text{coh}N\sigma\sigma}^{(1)} = \bar{u}_{\text{coh}N\sigma\sigma}$ and $v_{\text{coh}\sigma}^{(1)}(\mathbf{r}) \sim u_{\text{coh}N\sigma\sigma}(\mathbf{r})$. We can further expand the Coulomb interaction in powers of $1/r$ in Eq. (24) to show that in a system with spherical symmetry and a doubly occupied s -like HOMO :

$$v_{\text{coh}\sigma}^{(1)}(\mathbf{r}) \sim -\frac{\alpha_N^{\text{RPA}}}{2r^4}, \quad (55)$$

where α_N^{RPA} is the static polarizability of the N electron system (in the RPA) :

$$\alpha_N^{\text{RPA}} = -\int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 z_1 z_2 P^{\text{RPA}}(\mathbf{r}_1, \mathbf{r}_2; \omega = 0). \quad (56)$$

Before discussing the physics behind this result, we analyze the asymptotic behaviour of $v_{c\sigma}^{(2)}(\mathbf{r})$ in the following paragraph.

D. Asymptotic behaviour of the dynamical correction to the potential

The asymptotic behaviours of $v_{c\sigma}^{(2)}(\mathbf{r})$ and $\rho_{c\sigma}^{(2)}(\mathbf{r})$ are related through Eq. (9). We first rewrite this equation in a way better suited to the discussion of the long-range behaviour of $v_{c\sigma}^{(2)}(\mathbf{r})$ before focusing on the GW approximation.

1. General considerations

In this paragraph, we derive the basic equations needed to determine the asymptotic behaviour of $v_{c\sigma}^{(2)}(\mathbf{r})$. The latter satisfies the equation :

$$\int d^3\mathbf{r}' \chi_{\sigma}^{\text{KS}}(\mathbf{r}, \mathbf{r}') v_{c\sigma}^{(2)}(\mathbf{r}') = \rho_{c\sigma}^{(2)}(\mathbf{r}), \quad (57)$$

where $\rho_{c\sigma}^{(2)}(\mathbf{r})$ is defined by Eqs. (18b) and (18c). Using Eq. (20) for $\chi_{\sigma}^{\text{KS}}$, this can be written¹⁷ :

$$\sum_{n=1}^{N_{\sigma}} \varphi_{n\sigma}^*(\mathbf{r}) \delta\varphi_{n\sigma}(\mathbf{r}) + \text{c.c.} = \rho_{c\sigma}^{(2)}(\mathbf{r}), \quad (58)$$

where :

$$\delta\varphi_{n\sigma}(\mathbf{r}) = \int d^3\mathbf{r}' G_{n\sigma}(\mathbf{r}, \mathbf{r}') v_{c\sigma}^{(2)}(\mathbf{r}') \varphi_{n\sigma}(\mathbf{r}') \quad (59)$$

is the first-order change of the KS orbital $\varphi_{n\sigma}(\mathbf{r})$ in response to the perturbation $v_{c\sigma}^{(2)}(\mathbf{r})$. $\delta\varphi_{n\sigma}(\mathbf{r})$ is orthogonal to $\varphi_{n\sigma}(\mathbf{r})$ ($\langle\varphi_{n\sigma}|\delta\varphi_{n\sigma}\rangle = 0$) and satisfies the Sternheimer⁴⁹ equation :

$$\left\{ \varepsilon_{n\sigma} + \frac{1}{2} \nabla^2 - v_{\sigma}^{\text{KS}}(\mathbf{r}) \right\} \delta\varphi_{n\sigma}(\mathbf{r}) = \varphi_{n\sigma}(\mathbf{r}) \left\{ v_{c\sigma}^{(2)}(\mathbf{r}) - \bar{v}_{cn\sigma}^{(2)} \right\}, \quad (60)$$

with $\bar{v}_{cn\sigma}^{(2)}$ defined by Eq. (36). $\delta\varphi_{n\sigma}(\mathbf{r})$ is uniquely determined¹⁷ by the orthogonality constraint and the physical boundary condition $\delta\varphi_{n\sigma}(\mathbf{r}) \rightarrow 0$ when $r \rightarrow \infty$.

We now analyze the asymptotic behaviour of $\delta\varphi_{n\sigma}(\mathbf{r})$ and $\rho_{c\sigma}^{(2)}(\mathbf{r})$ as a function of $v_{c\sigma}^{(2)}(\mathbf{r})$. This will later be inverted to get the asymptotic behaviour of $v_{c\sigma}^{(2)}(\mathbf{r})$ as a function of $\rho_{c\sigma}^{(2)}(\mathbf{r})$. We assume here that $v_{c\sigma}^{(2)}(\mathbf{r}) \rightarrow 0$ when $r \rightarrow \infty$, which will be checked *a posteriori*. As in paragraph III C, we make the ansatz :

$$\delta\varphi_{n\sigma}(\mathbf{r}) = \varphi_{n\sigma}(\mathbf{r}) q_{n\sigma}(\mathbf{r}), \quad (61)$$

which leaves the following equation for $q_{n\sigma}(\mathbf{r})$:

$$\frac{1}{2} \varphi_{n\sigma}(\mathbf{r}) \nabla^2 q_{n\sigma}(\mathbf{r}) + \nabla \varphi_{n\sigma}(\mathbf{r}) \nabla q_{n\sigma}(\mathbf{r}) = \varphi_{n\sigma}(\mathbf{r}) \{ v_{c\sigma}^{(2)}(\mathbf{r}) - \bar{v}_{cn\sigma}^{(2)} \}. \quad (62)$$

We must distinguish between two cases. First, if $\bar{v}_{cn\sigma}^{(2)} \neq 0$, $q_{n\sigma}(\mathbf{r})$ can be shown to satisfy the asymptotic equation¹⁷ [use Eq. (50)] :

$$-\beta_{n\sigma} \frac{\partial}{\partial r} q_{n\sigma}(\mathbf{r}) = -\bar{v}_{cn\sigma}^{(2)}. \quad (63)$$

We therefore readily get :

$$q_{n\sigma}(\mathbf{r}) \sim \frac{\bar{v}_{cn\sigma}^{(2)}}{\beta_{n\sigma}} r. \quad (64)$$

Second, if $\bar{v}_{cn\sigma}^{(2)} = 0$ and $v_{c\sigma}^{(2)}(\mathbf{r})$ decays faster than $1/r$, it is straightforward to show that¹⁷ :

$$q_{n\sigma}(\mathbf{r}) = q'_{n\sigma}(\mathbf{r}) + C_{n\sigma}, \quad (65)$$

where $q'_{n\sigma}(\mathbf{r}) \rightarrow 0$ when $r \rightarrow \infty$ and $C_{n\sigma}$ is a constant. Eqs. (62), (63) and (64) will prove sufficient to determine the asymptotic behaviour of $v_{c\sigma}^{(2)}(\mathbf{r})$ in the *GW* approximation. As a corollary of these equations, we already note (assuming $v_{c\sigma}^{(2)}(\mathbf{r}) \rightarrow 0$ when $r \rightarrow \infty$) that :

$$\rho_{c\sigma}^{(2)}(\mathbf{r}) \sim \frac{\bar{v}_{cN_{\sigma\sigma}}^{(2)}}{\beta_{N_{\sigma\sigma}}} r |\varphi_{N_{\sigma\sigma}}(\mathbf{r})|^2 \quad (66)$$

if $\bar{v}_{cN_{\sigma\sigma}}^{(2)} \neq 0$, and that $\rho_{c\sigma}^{(2)}(\mathbf{r})$ decays faster than Eq. (66) if $\bar{v}_{cN_{\sigma\sigma}}^{(2)} = 0$. Conversely, $\rho_{c\sigma}^{(2)}(\mathbf{r})$ must decrease as least as fast as $r |\varphi_{N_{\sigma\sigma}}(\mathbf{r})|^2$ for $v_{c\sigma}^{(2)}(\mathbf{r})$ to have a finite limit when $r \rightarrow \infty$.

2. Application to the *GW* approximation

We now apply the results of the former paragraph to the LRSS-*GW* dynamical correction $v_{c\sigma}^{(2)}(\mathbf{r})$. $\rho_{c\sigma}^{(2)}(\mathbf{r})$ is the sum of two terms [Eqs. (18b) and (18c)]. The first one, $\rho_{c\sigma}^{(21)}(\mathbf{r})$, is the contribution of all double poles coming from the KS Green functions in Eq. (10). Its behaviour is obvious. We thus now focus on the second term, $\rho_{c\sigma}^{(22)}(\mathbf{r})$, which is the contribution of the poles of $\Sigma_{h\sigma}$ [Eq. (29)] :

$$\begin{aligned} \rho_{c\sigma}^{(22)}(\mathbf{r}) &= \sum_{n=1}^{N_{\sigma}} \sum_s \left| \sum_m \frac{v_{s\sigma}^{nm}}{\varepsilon_{n\sigma} - \varepsilon_{m\sigma} - \omega_s} \varphi_{m\sigma}^*(\mathbf{r}) \right|^2 \\ &= \sum_{n=1}^{N_{\sigma}} \sum_s |w_{sn\sigma}(\mathbf{r})|^2, \end{aligned} \quad (67)$$

with $w_{sn\sigma}(\mathbf{r})$ given by Eq. (44). The asymptotic behaviour of $\rho_{c\sigma}^{(22)}(\mathbf{r})$ is easily obtained from Eq. (51) :

$$\begin{aligned} \rho_{c\sigma}^{(22)}(\mathbf{r}) &\sim \sum_{n=1}^{N_{\sigma}} \sum_s |\varphi_{n\sigma}(\mathbf{r})|^2 \frac{|v_s(\mathbf{r})|^2}{\omega_s^2} \\ &\sim |\varphi_{N_{\sigma\sigma}}(\mathbf{r})|^2 u(\mathbf{r}), \end{aligned} \quad (68)$$

where :

$$u(\mathbf{r}) = \sum_s \frac{|v_s(\mathbf{r})|^2}{\omega_s^2}. \quad (69)$$

We can further majorate $u(\mathbf{r})$ as follows :

$$\begin{aligned} \sum_s \frac{|v_s(\mathbf{r})|^2}{\omega_s^2} &\leq \frac{1}{\omega_1} \sum_s \frac{|v_s(\mathbf{r})|^2}{\omega_s} \\ &\leq \frac{1}{2\omega_1} W_s(\mathbf{r}, \mathbf{r}; \omega = 0), \end{aligned} \quad (70)$$

where ω_1 is the lowest ω_s . Therefore, $u(\mathbf{r})$ decreases as least as fast as $1/r^4$.

We finally get with the help of Eqs. (18b) and (68) :

$$\rho_{c\sigma}^{(2)}(\mathbf{r}) \sim |\varphi_{N\sigma\sigma}(\mathbf{r})|^2 \left\{ u(\mathbf{r}) + \frac{\partial \Sigma_{c\sigma}^{N\sigma N\sigma}}{\partial \omega} \Big|_{\varepsilon_{N\sigma\sigma}} \right\}. \quad (71)$$

Since $\rho_{c\sigma}^{(2)}(\mathbf{r})$ decays faster than Eq. (66), we must necessarily have $\bar{v}_{cN\sigma\sigma}^{(2)} = 0$, which means that $v_{c\sigma}^{(2)}(\mathbf{r})$ has no influence on the energy of the HOMO. Identification with Eqs. (58) and (65) further yields :

$$q'_{N\sigma\sigma}(\mathbf{r}) \sim \frac{1}{2} u(\mathbf{r}) \quad (72a)$$

$$C_{N\sigma\sigma} = \frac{1}{2} \frac{\partial \Sigma_{c\sigma}^{N\sigma N\sigma}}{\partial \omega} \Big|_{\varepsilon_{N\sigma\sigma}}. \quad (72b)$$

Insertion of the ansatz (65) with (72a) into Eq. (62) then readily allows to show that $v_{c\sigma}^{(2)}(\mathbf{r})$ decreases one power of $1/r$ faster than $u(\mathbf{r})$, that is as least as fast as $1/r^5$. $v_{c\sigma}^{(2)}(\mathbf{r})$ is thus found asymptotically negligible with respect to $v_{xc\sigma}^{(1)}(\mathbf{r})$. We discuss other implications of these results in the next paragraph.

IV. DISCUSSION

Gathering the results of paragraphs III C and III D, we finally get, in the *GW* approximation for the self-energy :

$$v_{xc\sigma}(\mathbf{r}) = -\frac{1}{r} + \text{exp. decreasing terms} \quad (73)$$

$$v_{c\sigma}(\mathbf{r}) \sim -\frac{\alpha_N^{\text{RPA}}}{2r^4}, \quad (74)$$

for a system with spherical symmetry and a doubly occupied *s*-like HOMO. The LRSS-*GW* potential thus has the expected $-1/r$ behaviour (consistent with the hypothesis of paragraph III C). We stress that the same conclusion can be drawn in the second-order approximation for the self-energy, following the lines of paragraphs III C and III D. This is in contrast with Ref. 26. We first examine possible reasons for the apparent divergent behaviour found in that work, before further discussing the asymptotic behaviour of the correlation potential.

A. Comparison with the usual OEP formalism

Facco Bonnetti *et al.* calculated the LRSS-MBPT(2) potential in a xc-OEP formalism²⁸ where the exchange-correlation energy $E_{xc}[n] \equiv E_{xc}[\{\varphi_{k\sigma}, \varepsilon_{k\sigma}\}]$ is considered as a functional of the KS orbitals $\varphi_{k\sigma}$ and KS energies $\varepsilon_{k\sigma}$. In a system with a discrete spectrum⁵¹, the equation for the potential can be written :

$$\int d^3\mathbf{r}' \chi_{\sigma}^{\text{KS}}(\mathbf{r}, \mathbf{r}') v_{xc\sigma}(\mathbf{r}') = Q_{xc\sigma}^{(a)}(\mathbf{r}) + Q_{c\sigma}^{(b)}(\mathbf{r}), \quad (75)$$

where $Q_{xc\sigma}^{(a)}(\mathbf{r})$ involves the functional derivatives $\delta E_{xc}/\delta\varphi_{n\sigma}(\mathbf{r})$:

$$Q_{xc\sigma}^{(a)}(\mathbf{r}) = \sum_{n=1}^{\infty} \varphi_{n\sigma}(\mathbf{r}) \int d^3\mathbf{r}' G_{n\sigma}(\mathbf{r}', \mathbf{r}) \frac{\delta E_{xc}}{\delta\varphi_{n\sigma}(\mathbf{r}')} + \text{c.c.}, \quad (76a)$$

and $Q_{c\sigma}^{(b)}(\mathbf{r})$ involves the functional derivatives $\partial E_c/\partial\varepsilon_{n\sigma}$:

$$Q_{c\sigma}^{(b)}(\mathbf{r}) = \sum_{n=1}^{\infty} \varphi_{n\sigma}(\mathbf{r}) \varphi_{n\sigma}^*(\mathbf{r}) \frac{\partial E_c}{\partial\varepsilon_{n\sigma}}. \quad (76b)$$

In Appendix A, we give the explicit expressions of $\delta E_{xc}/\delta\varphi_{n\sigma}(\mathbf{r})$ and $\partial E_c/\partial\varepsilon_{n\sigma}$ as a function of the self-energy, for the class of functionals defined in paragraph II B (to which LRSS-MBPT(2) belongs). We further show that Eqs. (76a)–(76b) and Eqs. (18a)–(18c) are equivalent for this class of functionals and can be obtained one from each other by a simple rearrangement of the terms. We can define the potentials $v_{xc\sigma}^{(a)}(\mathbf{r})$ and $v_{c\sigma}^{(b)}(\mathbf{r})$ solutions of Eq. (75) with either $Q_{xc\sigma}^{(a)}(\mathbf{r})$ or $Q_{c\sigma}^{(b)}(\mathbf{r})$ as the right hand side, since both have vanishing integral. We show in Appendix B that $v_{xc\sigma}^{(a)}(\mathbf{r})$ and $v_{c\sigma}^{(b)}(\mathbf{r})$ *both diverge* far from a finite system⁵², although *their sum is finite*. The fact that $v_{c\sigma}^{(b)}(\mathbf{r})$ is divergent has long been anticipated²⁸, being understood that the squared empty KS orbitals in Eq. (76b) make $Q_{c\sigma}^{(b)}(\mathbf{r})$ decay too slowly. It has even sometimes been suggested²⁸ to simply discard $Q_{c\sigma}^{(b)}(\mathbf{r})$ in Eq. (75). However, the divergence of $v_{c\sigma}^{(b)}(\mathbf{r})$ compensates for an equivalent one in $v_{xc\sigma}^{(a)}(\mathbf{r})$, so that this procedure is doomed to fail. This compensation does not arise, unfortunately, from a simple “term by term” cancellation between $Q_{xc\sigma}^{(a)}(\mathbf{r})$ and $Q_{c\sigma}^{(b)}(\mathbf{r})$, but slowly builds up over the whole range of the KS spectrum (thanks to the closure relation). We believe that these subtle cancellations have been missed in Ref. 26, thereby leading to the wrong conclusion that $v_{xc\sigma}(\mathbf{r})$ blows up. Indeed, we point out that $Q_{c\sigma}(\mathbf{r}) = Q_{xc\sigma}^{(a)}(\mathbf{r}) + Q_{c\sigma}^{(b)}(\mathbf{r})$ has vanishing integral and thus must tend to zero when $r \rightarrow \infty$, which is not the case on Fig.

1 of that reference. Facco Bonnetti *et al.* also gave another hint for the divergence of the LRSS-MBPT(2) potential, based on a KLI-like approximation neglecting $Q_{c\sigma}^{(b)}(\mathbf{r})$. We agree that this KLI-like approximation does diverge, as also diverges the exact solution of Eq. (75) if we neglect $Q_{c\sigma}^{(b)}(\mathbf{r})$. A proper KLI-like approximation to the xc-OEP equation will be given in section VB.

We now discuss the implications of these results for practical calculations of the LR Sham-Schlüter (or GLPT) potentials. Obviously $v_{xc\sigma}(\mathbf{r})$ can not diverge in any finite basis set implementation²¹ of Eqs. (9) or (75). It can however show unphysical bumps (that can be viewed as the “projection” of a divergence). To avoid such instabilities, the same number of KS states must be included in the calculation of both the left and right-hand sides of Eqs. (9) or (75). In these conditions, the potential should behave smoothly with increasing the basis size.

B. Asymptotic behaviour of $v_{c\sigma}(\mathbf{r})$

The correlation potential $v_{c\sigma}(\mathbf{r})$ has the expected $-\alpha/(2r^4)$ behaviour. Obviously, the coefficient α will depend on the approximation chosen for the self-energy. In the *GW* approximation, $\alpha = \alpha_N^{\text{RPA}}$ is clearly consistent with the underlying physics, the N electron RPA polarisability being contained in the screened Coulomb interaction W . The fact that α_N appears instead of α_{N-1} can be traced back to the neglect of vertex corrections. This is quite well illustrated by the comparison between MBPT(2) and a second-order approximation for the *GW* self-energy. Indeed, the exchange diagram of Fig. 1a and the first correlation (bubble) diagram of Fig. 1b both belong to the expansion of the *GW* self-energy. If we only keep these two diagrams, we get :

$$\Sigma_{xc\sigma}(\mathbf{r}, \mathbf{r}'; \omega) = i \int \frac{d\omega'}{2\pi} e^{i\omega'\delta} G_{\sigma}^{\text{KS}}(\mathbf{r}, \mathbf{r}'; \omega + \omega') W^{\text{KS}}(\mathbf{r}, \mathbf{r}'; \omega'), \quad (77)$$

where $W^{\text{KS}}(\omega) = v + vP^{\text{KS}}(\omega)v$ is the screened Coulomb interaction obtained from the non-interacting KS density-density response function. Eq. (77) has the same functional form as the *GW* self-energy [Eq. (15)], with W replaced by W^{KS} . The corresponding LR Sham-Schlüter potential thus behaves asymptotically as :

$$v_{c\sigma}(\mathbf{r}) \sim \frac{1}{2} W_s^{\text{KS}}(\mathbf{r}, \mathbf{r}; \omega = 0) \sim -\frac{\alpha_N^{\text{KS}}}{2r^4}, \quad (78)$$

where $W_s^{\text{KS}}(\omega) = vP^{\text{KS}}(\omega)v$ and α_N^{KS} is the static non-interacting KS polarizability of the N -electron system. It is given by Eq. (56) using $P^{\text{KS}}(0)$ instead of the RPA $P^{\text{RPA}}(0)$ [see³⁸ Eq. (8a)]. Next, the second-order exchange diagram of Fig. 1b belongs to the expansion of the vertex. Inclusion of this diagram into the self-energy now yields the LRSS-MBPT(2) potential. Following the lines of paragraphs III C and III D (see details in appendix C), we get :

$$v_{c\sigma}^{\text{MBPT}(2)}(\mathbf{r}) \sim -\frac{\tilde{\alpha}^{\text{KS}}}{2r^4}. \quad (79)$$

where in a spin-compensated system, $\tilde{\alpha}^{\text{KS}}$ is given by Eq. (56) using $\tilde{P}^{\text{KS}}(\mathbf{r}, \mathbf{r}'; \omega = 0)$ defined by :

$$\begin{aligned} \tilde{P}^{\text{KS}}(\mathbf{r}, \mathbf{r}'; \omega = 0) = & 2 \sum_{j=1}^{N/2-1} \sum_{k>N/2} \frac{\varphi_j^*(\mathbf{r})\varphi_k(\mathbf{r})\varphi_k^*(\mathbf{r}')\varphi_j(\mathbf{r}')}{\varepsilon_j - \varepsilon_k} \\ & + \sum_{k>N/2} \frac{\varphi_{N/2}^*(\mathbf{r})\varphi_k(\mathbf{r})\varphi_k^*(\mathbf{r}')\varphi_{N/2}(\mathbf{r}')}{\varepsilon_{N/2} - \varepsilon_k} + \text{c.c.} \end{aligned} \quad (80)$$

We have dropped the spin index since the KS orbitals and energies are the same for both spins. Compared to P^{KS} , the strength of the transitions from the HOMO to the empty KS orbitals is divided by 2, i.e. these transitions are suppressed in one spin channel. This clearly marks a shift towards a $N - 1$ electron-like polarizability.

The dynamical correction $v_{c\sigma}^{(2)}(\mathbf{r})$ decays faster than $v_{c\sigma}^{(1)}(\mathbf{r})$ and has no influence on the energy of the HOMO. This suggests to neglect $v_{c\sigma}^{(2)}(\mathbf{r})$ in actual calculations of the correlation potential. This is strongly supported by the simple and appealing interpretation of $v_{c\sigma}^{(1)}(\mathbf{r})$, that we recall in the next subsection.

V. THE QUASIPARTICLE APPROXIMATION TO THE LINEAR-RESPONSE SHAM-SCHLÜTER EQUATION

In this section, we further discuss the physical interpretation of the quasiparticle term $v_{xc\sigma}^{(1)}(\mathbf{r})$. For computational purposes, we also recall the related KLI approximation¹⁶, and introduce the static COHSEX approximation to the LRSS-GW potential.

A. Interpretation of the potential $v_{xc\sigma}^{(1)}(\mathbf{r})$

The potential $v_{xc\sigma}^{(1)}(\mathbf{r})$ results from a quasiparticle approximation to the LR Sham-Schlüter equation, as stated in paragraph III A and first pointed out by Casida²⁹ in 1995. Indeed, the many-body ground-state spin density $n_\sigma(\mathbf{r})$ can be calculated from the set of quasiparticle (QP) amplitudes $\psi_{k\sigma}(\mathbf{r})$ that satisfy the equation¹² :

$$-\frac{1}{2}\nabla^2\psi_{k\sigma}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r})\psi_{k\sigma}(\mathbf{r}) + v_{\text{h}}(\mathbf{r})\psi_{k\sigma}(\mathbf{r}) + \int d^3\mathbf{r}'\Sigma_{xc\sigma}[G](\mathbf{r},\mathbf{r}';E_{k\sigma})\psi_{k\sigma}(\mathbf{r}') = E_{k\sigma}\psi_{k\sigma}(\mathbf{r}). \quad (81)$$

$E_{k\sigma}$ is the QP energy and may be complex. $n_\sigma(\mathbf{r})$ reads :

$$n_\sigma(\mathbf{r}) = \sum_{\text{Re}(E_{k\sigma}) \leq \mu} |\psi_{k\sigma}(\mathbf{r})|^2, \quad (82)$$

where Re is the real part and μ is the chemical potential. The Sham-Schlüter equation just states that the KS spin density $n_\sigma(\mathbf{r}) = \sum_{k=1}^{N_\sigma} |\varphi_{k\sigma}(\mathbf{r})|^2$ must be equal to Eq. (82). We now look for $v_{xc\sigma}(\mathbf{r})$ such that the first-order variation of the KS spin density [calculated from Eq. (82)] is zero under the perturbation $\Sigma_{xc\sigma}[G](E) - v_{xc\sigma}$ that transforms the KS equation [Eq. (4)] into the QP equation [Eq. (81)]. We get from simple perturbation theory :

$$\delta n_\sigma(\mathbf{r}) = 0 = \sum_{n=1}^{N_\sigma} \varphi_{n\sigma}(\mathbf{r})\delta\varphi_{n\sigma}^*(\mathbf{r}) + \text{c.c.}, \quad (83)$$

where (still assuming non degenerate orbitals) :

$$\delta\varphi_{n\sigma}(\mathbf{r}) = \sum_{m \neq n} \frac{\varphi_{m\sigma}(\mathbf{r})}{\varepsilon_{n\sigma} - \varepsilon_{m\sigma}} \langle \varphi_{m\sigma} | \Sigma_{xc\sigma}[G^{\text{KS}}](\varepsilon_{n\sigma}) - v_{xc\sigma} | \varphi_{n\sigma} \rangle. \quad (84)$$

Further manipulation of the former two equations leads back to Eq. (22) for $v_{xc\sigma}^{(1)}(\mathbf{r})$. The application to degenerate orbitals is straightforward (see Ref. 16 for example). Eq. (22) is still a non-linear equation, which is however much simpler to solve than the LR Sham-Schlüter equation. Indeed, it only involves the $u_{xcn\sigma}(\mathbf{r})$'s for the occupied KS states. The calculation of $v_{xc\sigma}^{(1)}(\mathbf{r})$ for small real molecules or solids, though demanding, should therefore be within the reach of present computers (starting from an existing x-OEP code). If needed, $v_{xc\sigma}^{(1)}(\mathbf{r})$ also lends itself to the KLI approximation¹⁶ (see next paragraph), that proved to be very good in the x-only case.

The major difference between the LR Sham-Schlüter equation [Eq. (7)] and its quasiparticle approximation [Eq. (22)] is that in the former the density is calculated from the

first-order Green function while in the latter it is calculated from the first-order quasiparticle amplitudes. The first-order Green function additionally yields the dynamical correction $v_{c\sigma}^{(2)}(\mathbf{r})$ (coming from the poles of the self-energy), whose physical interpretation is not clear. However, such additional terms should disappear when the perturbation expansion is carried out to infinite order because both expressions for the density (Green function or quasiparticle amplitudes) must give the same result. Indeed, we can provide further support for the use of the quasiparticle approximation as follows : the right-hand side of the LR Sham-Schlüter equation [Eq. (7)] has poles coming from the two KS Green functions and from the self-energy. The right-hand side of the exact Sham-Schlüter equation [Eq. (6)], however, is just the difference between the interacting Green function $G_{\sigma}(\mathbf{r}, \mathbf{r}'; \omega)$ and the KS Green function $G_{\sigma}^{\text{KS}}(\mathbf{r}, \mathbf{r}'; \omega)$ [see Eq. (2)]. Therefore, it has only simple poles coming from G_{σ} and G_{σ}^{KS} (i.e., the contribution from the poles of the self-energy cancels because of the Dyson equation). The quasiparticle approximation [Eq. (22)] is precisely that equation obtained by keeping only the simple poles coming from the KS Green functions in the LR Sham-Schlüter equation.

One of the minor drawbacks of the quasiparticle approximation is that the corresponding exchange-correlation functional $E_{\text{xc}}[n]$ is unknown except in the x-only approximation. However, $v_{\text{xc}\sigma}^{(1)}(\mathbf{r})$ should be a very good starting point for self-consistent calculations with the exchange-correlation functionals defined in paragraph IIB [see Eq. (12)], provided it is not too far from the exact solution of the LR Sham-Schlüter equation. This, of course, remains to be tested, but is beyond the scope of the present paper.

B. KLI and further approximations

The solution of the Eq. (22) remains computationally intensive so that simplified schemes would be welcome. In this paragraph, we discuss two further approximations to the potential $v_{\text{xc}\sigma}^{(1)}(\mathbf{r})$. The first one is the well-known KLI approximation, which can be used with any self-energy, and the second one is the static COHSEX approximation to the LRSS-GW potential.

The simplest approach to the KLI approximation¹⁶ is to replace the energy denominators of the Green functions $G_{n\sigma}(\mathbf{r}, \mathbf{r}')$ by a constant $\Delta\varepsilon$ in Eq. (22). This constant then simplifies,

which leaves :

$$v_{xc\sigma}^{\text{KLI}}(\mathbf{r}) = \frac{1}{2n_{\sigma}(\mathbf{r})} \sum_{n=1}^{N_{\sigma}} |\varphi_{n\sigma}(\mathbf{r})|^2 [u_{xcn\sigma}(\mathbf{r}) + \bar{v}_{xcn\sigma}^{\text{KLI}} - \bar{u}_{xcn\sigma}] + \text{c.c.} \quad (85)$$

Eq. (85) is still an integral equation because $v_{xc\sigma}^{\text{KLI}}(\mathbf{r})$ appears on the right hand side in the coefficients $\bar{v}_{xcn\sigma}^{\text{KLI}}$. The relation $\bar{v}_{xcN_{\sigma}\sigma}^{\text{KLI}} = \bar{u}_{xcN_{\sigma}\sigma}$ directly stems from the condition $v_{xc\sigma}^{\text{KLI}}(\mathbf{r}) \rightarrow 0$ when $r \rightarrow \infty$. The other $\bar{v}_{xcn\sigma}^{\text{KLI}}$'s can be determined multiplying Eq. (85) by $|\varphi_{m\sigma}(\mathbf{r})|^2$ and integrating over \mathbf{r} . This yields the following linear system of equations :

$$\sum_{m=1}^{N_{\sigma}-1} [\delta_{nm} - M_{nm\sigma}] [\bar{v}_{xcm\sigma}^{\text{KLI}} - \text{Re}(\bar{u}_{xcm\sigma})] = \bar{v}_{xcn\sigma}^{\text{S}} - \text{Re}(\bar{u}_{xcn\sigma}), \quad (86)$$

where :

$$\bar{v}_{xcn\sigma}^{\text{S}} = \sum_{m=1}^{N_{\sigma}} \int d^3\mathbf{r} \frac{|\varphi_{n\sigma}(\mathbf{r})|^2 |\varphi_{m\sigma}(\mathbf{r})|^2}{n_{\sigma}(\mathbf{r})} \text{Re}(u_{xcm\sigma}(\mathbf{r})), \quad (87)$$

and :

$$M_{nm\sigma} = \int d^3\mathbf{r} \frac{|\varphi_{n\sigma}(\mathbf{r})|^2 |\varphi_{m\sigma}(\mathbf{r})|^2}{n_{\sigma}(\mathbf{r})}. \quad (88)$$

Grabo *et al.*¹⁷ showed that $v_{xc\sigma}^{(1)}(\mathbf{r})$ and its KLI counterpart have the same asymptotic behaviour. The x-only KLI potential proved to be an excellent approximation to the exact x-OEP. We conjecture that the KLI potential will remain a good approximation to $v_{xc\sigma}^{(1)}(\mathbf{r})$ if correlations are included.

An approximate LRSS-GW potential can also be obtained from the static COHSEX self-energy introduced in section III C [Eqs. (32) and (33)]. Since the static COHSEX self-energy is frequency-independent, $\rho_{c\sigma}^{(2)}(\mathbf{r}) = 0$. Therefore, the static COHSEX potential can either be obtained directly from the LR Sham-Schlüter equation [Eq. (7)] or from Eq. (22). It splits in two parts $v_{xc\sigma}(\mathbf{r}) = v_{\text{sex}\sigma}(\mathbf{r}) + v_{\text{coh}}(\mathbf{r})$, where :

$$v_{\text{coh}}(\mathbf{r}) = \frac{1}{2} W_s(\mathbf{r}, \mathbf{r}; \omega = 0) \quad (89)$$

is half the classical image potential felt by a test charge at \mathbf{r} , and $v_{\text{sex}\sigma}(\mathbf{r})$ satisfies Eq. (22) with the self-energy :

$$\Sigma_{\text{sex}\sigma}(\mathbf{r}, \mathbf{r}') = - \sum_{n=1}^{N_{\sigma}} \varphi_{n\sigma}(\mathbf{r}) \varphi_{n\sigma}^*(\mathbf{r}') W(\mathbf{r}, \mathbf{r}'; \omega = 0). \quad (90)$$

This is just the x-only OEP equation with $v(\mathbf{r}, \mathbf{r}')$ replaced by $W(\mathbf{r}, \mathbf{r}'; \omega = 0)$. Therefore, all what is needed starting from an existing x-OEP code is to calculate the static RPA

screened Coulomb interaction $W(\mathbf{r}, \mathbf{r}'; \omega = 0)$. If needed, $v_{\text{sex}\sigma}(\mathbf{r})$ also lends itself to the KLI approximation. The static COHSEX potential has been used by Kotani⁵³ in some bulk metals (Cu, Ni, Fe and Co).

VI. CONCLUSION

We have investigated the asymptotic behaviour of the exchange-correlation potentials calculated with the linear-response Sham-Schlüter equation in the GW and second-order approximations for the self-energy. We have shown that these potentials have the expected $-1/r$ tail in finite systems. This contrasts with a previous work where a divergent behaviour was found. The reasons for this discrepancy have been analyzed in detail. We have also shown that the correlation potential itself has a $-\alpha/(2r^4)$ tail, where α depends on the self-energy. In addition, we have given physical motivations for the quasiparticle approximation to the linear-response Sham-Schlüter equation, that is much simpler to solve and should be within the reach of present computers. We have briefly discussed the related KLI approximation, as well as the static COHSEX approximation to the LRSS- GW potential. The accuracy of this hierarchy of approximations should now be tested on real molecules or solids.

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APPENDIX A: LINK WITH THE XC-OEP FORMALISM

In this appendix, we make the connection between the LR Sham-Schlüter equation and the OEP formalism of Engel *et al.*²⁸ for the class of functionals defined in paragraph II B. This allows a detailed comparison between our work and the one of Ref. 26.

The functional $E_{xc}[n]$ defined by Eq. (12) can either be considered as an explicit functional of the KS Green function G^{KS} or as an explicit functional of the KS orbitals $\varphi_{n\sigma}(\mathbf{r})$ and KS energies $\varepsilon_{n\sigma}$. From the latter point of view, the exchange-correlation potential satisfies the OEP equations (75) and (76). To calculate the functional derivatives of E_{xc} with respect to the $\varphi_{n\sigma}(\mathbf{r})$'s and $\varepsilon_{n\sigma}$'s, we make use of the following property^{29,35,36} of the functional $\Phi[G^{\text{KS}}]$:

$$\frac{\delta\Phi[G^{\text{KS}}]}{\delta G_{\sigma}^{\text{KS}}(\mathbf{r}, \mathbf{r}'; \omega)} = \frac{1}{2i\pi} \Sigma_{xc\sigma}[G^{\text{KS}}](\mathbf{r}', \mathbf{r}; \omega). \quad (\text{A1})$$

Therefore,

$$\begin{aligned} \frac{\delta E_{xc}}{\delta \varphi_{n\sigma}(\mathbf{r})} &= \int d\omega e^{i\omega\delta} \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \frac{\delta\Phi[G^{\text{KS}}]}{\delta G_{\sigma}^{\text{KS}}(\mathbf{r}_1, \mathbf{r}_2; \omega)} \frac{\delta G_{\sigma}^{\text{KS}}(\mathbf{r}_1, \mathbf{r}_2; \omega)}{\delta \varphi_{n\sigma}(\mathbf{r})} \\ &= \int \frac{d\omega}{2i\pi} e^{i\omega\delta} \int d^3\mathbf{r}_2 \frac{\Sigma_{xc\sigma}(\mathbf{r}_2, \mathbf{r}; \omega)}{\omega - \varepsilon_{n\sigma} \pm i\eta} \varphi_{n\sigma}^*(\mathbf{r}_2). \end{aligned} \quad (\text{A2})$$

Performing the frequency integration thus yields⁴⁶:

$$\begin{aligned} \frac{\delta E_{xc}}{\delta \varphi_{n\sigma}(\mathbf{r})} &= f_{n\sigma} \int d^3\mathbf{r}' \Sigma_{xc\sigma}(\mathbf{r}', \mathbf{r}; \varepsilon_{n\sigma}) \varphi_{n\sigma}^*(\mathbf{r}') \\ &\quad - \int d^3\mathbf{r}' \sum_k \frac{R_{k\sigma}(\mathbf{r}', \mathbf{r})}{\varepsilon_{n\sigma} - \Omega_{k\sigma}} \varphi_{n\sigma}^*(\mathbf{r}') \end{aligned} \quad (\text{A3a})$$

$$= \int d^3\mathbf{r}' \{f_{n\sigma} \Sigma_{xc\sigma}(\mathbf{r}', \mathbf{r}; \varepsilon_{n\sigma}) - \Sigma_{h\sigma}(\mathbf{r}', \mathbf{r}; \varepsilon_{n\sigma})\} \varphi_{n\sigma}^*(\mathbf{r}'), \quad (\text{A3b})$$

where $f_{n\sigma} = 0$ (resp. $f_{n\sigma} = 1$) for the empty (resp. occupied) KS states and the second term on the right-hand side of Eq. (A3a) comes from the poles of the self-energy. Hence,

$$\frac{\delta E_{xc}}{\delta \varphi_{n\sigma}(\mathbf{r})} = \int d^3\mathbf{r}' \Sigma_{xp\sigma}(\mathbf{r}', \mathbf{r}; \varepsilon_{n\sigma}) \varphi_{n\sigma}^*(\mathbf{r}') \quad (\text{A4a})$$

for the occupied KS states, and :

$$\frac{\delta E_{xc}}{\delta \varphi_{n\sigma}(\mathbf{r})} = - \int d^3\mathbf{r}' \Sigma_{h\sigma}(\mathbf{r}', \mathbf{r}; \varepsilon_{n\sigma}) \varphi_{n\sigma}^*(\mathbf{r}') \quad (\text{A4b})$$

for the empty KS states. Here $\Sigma_{xp\sigma}$ is the sum of the exchange and particle parts of the

self-energy (see paragraph III A). In the same way,

$$\begin{aligned}\frac{\partial E_{\text{xc}}}{\partial \varepsilon_{n\sigma}} &= \int d\omega e^{i\omega\delta} \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \frac{\delta\Phi[G^{\text{KS}}]}{\delta G_{\sigma}^{\text{KS}}(\mathbf{r}_1, \mathbf{r}_2; \omega)} \frac{\partial G_{\sigma}^{\text{KS}}(\mathbf{r}_1, \mathbf{r}_2; \omega)}{\partial \varepsilon_{n\sigma}} \\ &= \int \frac{d\omega}{2i\pi} e^{i\omega\delta} \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \varphi_{n\sigma}^*(\mathbf{r}_1) \frac{\Sigma_{\text{xc}\sigma}(\mathbf{r}_1, \mathbf{r}_2; \omega)}{(\omega - \varepsilon_{n\sigma} \pm i\eta)^2} \varphi_{n\sigma}(\mathbf{r}_2).\end{aligned}\quad (\text{A5})$$

Therefore,

$$\frac{\partial E_{\text{xc}}}{\partial \varepsilon_{n\sigma}} = \left. \frac{\partial \Sigma_{\text{p}\sigma}^{nn}}{\partial \omega} \right|_{\varepsilon_{n\sigma}} \quad \text{for the occupied KS states,} \quad (\text{A6a})$$

$$\frac{\partial E_{\text{xc}}}{\partial \varepsilon_{n\sigma}} = - \left. \frac{\partial \Sigma_{\text{h}\sigma}^{nn}}{\partial \omega} \right|_{\varepsilon_{n\sigma}} \quad \text{for the empty KS states.} \quad (\text{A6b})$$

Gathering Eqs. (76), (A4) and (A6), we finally get, in a system with a discrete spectrum^{51,54} :

$$\begin{aligned}Q_{\text{xc}\sigma}^{(a)}(\mathbf{r}) &= \sum_{n=1}^{N_{\sigma}} \sum_{m \neq n} \varphi_{n\sigma}(\mathbf{r}) \varphi_{m\sigma}^*(\mathbf{r}) \frac{\Sigma_{\text{xp}\sigma}^{nm}(\varepsilon_{n\sigma})}{\varepsilon_{n\sigma} - \varepsilon_{m\sigma}} + \text{c.c.} \\ &\quad - \sum_{n > N_{\sigma}} \sum_{m \neq n} \varphi_{n\sigma}(\mathbf{r}) \varphi_{m\sigma}^*(\mathbf{r}) \frac{\Sigma_{\text{h}\sigma}^{nm}(\varepsilon_{n\sigma})}{\varepsilon_{n\sigma} - \varepsilon_{m\sigma}} + \text{c.c.}\end{aligned}\quad (\text{A7a})$$

$$\begin{aligned}Q_{\text{c}\sigma}^{(b)}(\mathbf{r}) &= \sum_{n=1}^{N_{\sigma}} \varphi_{n\sigma}^*(\mathbf{r}) \varphi_{n\sigma}(\mathbf{r}) \left. \frac{\partial \Sigma_{\text{p}\sigma}^{nn}}{\partial \omega} \right|_{\varepsilon_{n\sigma}} \\ &\quad - \sum_{n > N_{\sigma}} \varphi_{n\sigma}^*(\mathbf{r}) \varphi_{n\sigma}(\mathbf{r}) \left. \frac{\partial \Sigma_{\text{h}\sigma}^{nn}}{\partial \omega} \right|_{\varepsilon_{n\sigma}}.\end{aligned}\quad (\text{A7b})$$

$Q_{\text{xc}\sigma}^{(a)}(\mathbf{r}) + Q_{\text{c}\sigma}^{(b)}(\mathbf{r})$ is equal to $\rho_{\text{xc}\sigma}(\mathbf{r})$ [Eqs. (18)]. Indeed, one can recover Eqs. (A7) splitting $1/[(\Omega_{k\sigma} - \varepsilon_{n\sigma})(\Omega_{k\sigma} - \varepsilon_{m\sigma})]$ into simple elements in $\rho_{\text{c}\sigma}^{(22)}(\mathbf{r})$. As discussed in paragraph IV A, this shows that $Q_{\text{xc}\sigma}^{(a)}(\mathbf{r})$ and $Q_{\text{c}\sigma}^{(b)}(\mathbf{r})$ are intricately matched one to each other for the class of functionals defined in paragraph II B. This peculiar matching leads to large cancellations between $v_{\text{xc}\sigma}^{(a)}(\mathbf{r})$ and $v_{\text{c}\sigma}^{(b)}(\mathbf{r})$, so that their sum remains finite when $r \rightarrow \infty$.

As stated in paragraph II A, $\rho_{\text{xc}\sigma}(\mathbf{r})$ must have vanishing integral (otherwise Eq. (9) has no solutions), which translates into the following condition for the self-energy⁵⁴ [see Eqs. (A7)] :

$$\sum_{n=1}^{N_{\sigma}} \left. \frac{\partial \Sigma_{\text{p}\sigma}^{nn}}{\partial \omega} \right|_{\varepsilon_{n\sigma}} - \sum_{n > N_{\sigma}} \left. \frac{\partial \Sigma_{\text{h}\sigma}^{nn}}{\partial \omega} \right|_{\varepsilon_{n\sigma}} = 0. \quad (\text{A8})$$

If $\Sigma_{\text{xc}\sigma}[G^{\text{KS}}]$ is build from a truncated series of skeleton diagrams, this is equivalent to [see Eqs. (A6)] :

$$\sum_{n=1}^{\infty} \frac{\partial E_{\text{xc}}}{\partial \varepsilon_{n\sigma}} = 0, \quad (\text{A9})$$

where E_{xc} is the associated exchange-correlation functional defined in paragraph II B. This condition is obviously satisfied, because E_{xc} only depends on KS energies differences.

APPENDIX B: ASYMPTOTIC BEHAVIOUR OF $v_{c\sigma}^{(a)}(\mathbf{r})$ AND $v_{c\sigma}^{(b)}(\mathbf{r})$

In this appendix, we show that $v_{c\sigma}^{(a)}(\mathbf{r})$ (resp. $v_{c\sigma}^{(b)}(\mathbf{r})$) diverges exponentially to $+\infty$ (resp. $-\infty$) in the GW approximation for the self-energy.

To proceed, we consider a finite system with hard-wall boundary conditions at $r = R$, calculate $v_{c\sigma}^{(a)}(\mathbf{r})$ and $v_{c\sigma}^{(b)}(\mathbf{r})$ for this given R and for $r < R$, then take the limit $R \rightarrow \infty$. We first discuss the asymptotic behaviour of $v_{c\sigma}^{(b)}(\mathbf{r})$. $v_{c\sigma}^{(b)}(\mathbf{r})$ satisfies the equation :

$$\int d^3\mathbf{r}' \chi_{\sigma}^{\text{KS}}(\mathbf{r}, \mathbf{r}') v_{c\sigma}^{(b)}(\mathbf{r}') = Q_{c\sigma}^{(b)}(\mathbf{r}), \quad (\text{B1})$$

where $Q_{c\sigma}^{(b)}(\mathbf{r})$ is defined by Eq. (A7b) with the GW $\Sigma_{p\sigma}$ and $\Sigma_{h\sigma}$ given by Eqs. (28). $Q_{c\sigma}^{(b)}(\mathbf{r}) = Q_{c\sigma}^{(b-)}(\mathbf{r}) + Q_{c\sigma}^{(b+)}(\mathbf{r})$ can be split in two parts, where $Q_{c\sigma}^{(b-)}(\mathbf{r})$ is the sum over the occupied KS states in Eq. (A7b) and $Q_{c\sigma}^{(b+)}(\mathbf{r})$ is the sum over the empty KS states. Moreover,

$$\left. \frac{\partial \Sigma_{h\sigma}^{nn}}{\partial \omega} \right|_{\varepsilon_{n\sigma}} = - \sum_{m=1}^{N_{\sigma}} \sum_s \frac{|v_{s\sigma}^{nm}|^2}{(\varepsilon_{n\sigma} - \varepsilon_{m\sigma} + \omega_s)^2} < 0, \quad (\text{B2})$$

so that all terms in $Q_{c\sigma}^{(b+)}(\mathbf{r})$ are positive. Hence we can minorate $Q_{c\sigma}^{(b+)}(\mathbf{r})$ as follows :

$$Q_{c\sigma}^{(b+)}(\mathbf{r}) > -|\varphi_{k\sigma}(\mathbf{r})|^2 \left. \frac{\partial \Sigma_{h\sigma}^{kk}}{\partial \omega} \right|_{\varepsilon_{k\sigma}}, \quad (\text{B3})$$

where k is any of the empty KS states. We now look at the divergence due to such a $\propto |\varphi_{k\sigma}(\mathbf{r})|^2$ term on the right hand side of Eq. (B1). We thus set $Q_{c\sigma}^{(b)}(\mathbf{r}) = -|\varphi_{k\sigma}(\mathbf{r})|^2 [\partial \Sigma_{h\sigma}^{kk} / \partial \omega] (\varepsilon_{k\sigma}) + f_{\text{sr}}(\mathbf{r})$, where $f_{\text{sr}}(\mathbf{r})$ is an arbitrary short-range function such that $Q_{c\sigma}^{(b)}(\mathbf{r})$ has vanishing integral. Using Eq. (20) for $\chi_{\sigma}^{\text{KS}}(\mathbf{r}, \mathbf{r}')$, Eq. (B1) can be written :

$$\sum_{n=1}^{N_{\sigma}} \varphi_{n\sigma}^*(\mathbf{r}) \delta \varphi_{n\sigma}(\mathbf{r}) + \text{c.c.} = -|\varphi_{k\sigma}(\mathbf{r})|^2 \left. \frac{\partial \Sigma_{h\sigma}^{kk}}{\partial \omega} \right|_{\varepsilon_{k\sigma}} + f_{\text{sr}}(\mathbf{r}), \quad (\text{B4})$$

where $\delta \varphi_{n\sigma}(\mathbf{r})$ is defined by Eq. (59) with $v_{c\sigma}^{(2)}(\mathbf{r})$ replaced by $v_{c\sigma}^{(b)}(\mathbf{r})$. We again make the ansatz $\delta \varphi_{n\sigma}(\mathbf{r}) = q_{n\sigma}(\mathbf{r}) \varphi_{n\sigma}(\mathbf{r})$, which yields Eq. (62) for $q_{n\sigma}(\mathbf{r})$. Assuming that the long-range behaviour of the left-hand side of Eq. (B1) is still driven by the HOMO (which can easily be checked *a posteriori*), we get for large enough $R' < r < R$:

$$q_{N_{\sigma}\sigma}(\mathbf{r}) \simeq -\frac{1}{2} \frac{|\varphi_{k\sigma}(\mathbf{r})|^2}{|\varphi_{N_{\sigma}\sigma}(\mathbf{r})|^2} \left. \frac{\partial \Sigma_{h\sigma}^{kk}}{\partial \omega} \right|_{\varepsilon_{k\sigma}}. \quad (\text{B5})$$

Inserting Eq. (B5) into Eq. (62), then taking the limit $R \rightarrow \infty$ yields :

$$v_{c\sigma}^{(b)}(\mathbf{r}) \sim -r^{\left(\frac{1}{\beta_{k\sigma}} - \frac{1}{\beta_{N\sigma\sigma}}\right)} e^{2(\beta_{N\sigma\sigma} - \beta_{k\sigma})r} \hat{v}_{c\sigma}^{(b)}(\hat{\mathbf{r}}), \quad (\text{B6})$$

where $\hat{v}_{c\sigma}^{(b)}(\hat{\mathbf{r}})$ is a positive function. This suggests that $v_{c\sigma}^{(b)}(\mathbf{r})$ diverges to $-\infty$ nearly as fast as $e^{2\beta_{N\sigma\sigma}r}$. Since $v_{xc\sigma}(\mathbf{r})$ decays to zero, $v_{c\sigma}^{(a)}(\mathbf{r})$ must diverge to $+\infty$ with the same exponential behaviour. The KLI approximation as performed by Facco Bonnetti *et al.*²⁶ provides a clear hint to this divergence. Indeed, using Eqs. (20) and (76a), the equation satisfied by $v_{c\sigma}^{(a)}(\mathbf{r})$ can be cast in the form :

$$\sum_{n=1}^{\infty} \int d^3\mathbf{r}' \varphi_{n\sigma}^*(\mathbf{r}') \left[f_{n\sigma} v_{c\sigma}^{(a)}(\mathbf{r}') - u_{cn\sigma}^{(a)}(\mathbf{r}') \right] G_{n\sigma}(\mathbf{r}', \mathbf{r}) \varphi_{n\sigma}(\mathbf{r}) + \text{c.c.} = 0, \quad (\text{B7})$$

where $f_{n\sigma} = 0$ (resp. $f_{n\sigma} = 1$) for the empty (resp. occupied) KS states and $u_{cn\sigma}^{(a)}(\mathbf{r})$ is defined by :

$$\begin{aligned} u_{cn\sigma}^{(a)}(\mathbf{r}) &= \frac{1}{\varphi_{n\sigma}^*(\mathbf{r})} \frac{\delta E_c}{\delta \varphi_{n\sigma}(\mathbf{r})} \\ &= \frac{1}{\varphi_{n\sigma}^*(\mathbf{r})} \int d^3\mathbf{r}' \Sigma_{p\sigma}(\mathbf{r}', \mathbf{r}; \varepsilon_{n\sigma}) \varphi_{n\sigma}^*(\mathbf{r}') \end{aligned} \quad (\text{B8a})$$

for the occupied KS states, and by :

$$u_{cn\sigma}^{(a)}(\mathbf{r}) = -\frac{1}{\varphi_{n\sigma}^*(\mathbf{r})} \int d^3\mathbf{r}' \Sigma_{h\sigma}(\mathbf{r}', \mathbf{r}; \varepsilon_{n\sigma}) \varphi_{n\sigma}^*(\mathbf{r}') \quad (\text{B8b})$$

for the empty KS states [see Eqs. (A4)]. Eq. (B7) is basically the same OEP equation as for $v_{xc\sigma}^{(1)}(\mathbf{r})$ [Eq. (22)], except that the sum over n now extends over the whole KS spectrum. Replacing the energy denominators in the Green functions $G_{n\sigma}$ [Eq. (21)] with a constant $\Delta\varepsilon$ yields :

$$v_{c\sigma}^{(a),\text{KLI}}(\mathbf{r}) = \frac{1}{2n_{\sigma}(\mathbf{r})} \left\{ \sum_{n=1}^{\infty} |\varphi_{n\sigma}(\mathbf{r})|^2 [u_{cn\sigma}^{(a)}(\mathbf{r}) - \bar{u}_{cn\sigma}^{(a)}] + \sum_{n=1}^{N_{\sigma}} |\varphi_{n\sigma}(\mathbf{r})|^2 \bar{v}_{cn\sigma}^{(a),\text{KLI}} \right\} + \text{c.c.}, \quad (\text{B9})$$

with $\bar{u}_{cn\sigma}^{(a)}$ and $\bar{v}_{cn\sigma}^{(a),\text{KLI}}$ defined by Eqs. (35) and (36).

Explicit expressions for the $u_{cn\sigma}^{(a)}(\mathbf{r})$'s in the *GW* approximation are easily obtained from Eqs. (28) :

$$u_{cn\sigma}^{(a)}(\mathbf{r}) = \frac{1}{\varphi_{n\sigma}^*(\mathbf{r})} \sum_{m>N_{\sigma}} \sum_s \frac{v_{s\sigma}^{nm}}{\varepsilon_{n\sigma} - \varepsilon_{m\sigma} - \omega_s} v_s^*(\mathbf{r}) \varphi_{m\sigma}^*(\mathbf{r}) \quad (\text{B10a})$$

for the occupied KS states, and :

$$u_{cn\sigma}^{(a)}(\mathbf{r}) = -\frac{1}{\varphi_{n\sigma}^*(\mathbf{r})} \sum_{m=1}^{N_\sigma} \sum_s \frac{v_{s\sigma}^{nm}}{\varepsilon_{n\sigma} - \varepsilon_{m\sigma} + \omega_s} v_s^*(\mathbf{r}) \varphi_{m\sigma}^*(\mathbf{r}) \quad (\text{B10b})$$

for the empty KS states. With these expressions in hand, it is moreover straightforward to show that :

$$\sum_{n>N_\sigma} |\varphi_{n\sigma}(\mathbf{r})|^2 u_{cn\sigma}^{(a)}(\mathbf{r}) = \sum_{n=1}^{N_\sigma} |\varphi_{n\sigma}(\mathbf{r})|^2 u_{cn\sigma}^{(a)}(\mathbf{r}). \quad (\text{B11})$$

Therefore,

$$v_{c\sigma}^{(a),\text{KLI}}(\mathbf{r}) = \frac{1}{2n_\sigma(\mathbf{r})} \left\{ \sum_{n=1}^{N_\sigma} |\varphi_{n\sigma}(\mathbf{r})|^2 [2u_{cn\sigma}^{(a)}(\mathbf{r}) - \bar{u}_{cn\sigma}^{(a)} + \bar{v}_{cn\sigma}^{(a),\text{KLI}}] - \sum_{n>N_\sigma} |\varphi_{n\sigma}(\mathbf{r})|^2 \bar{u}_{cn\sigma}^{(a)} \right\} + \text{c.c.} \quad (\text{B12})$$

On one hand, we can further write for the occupied KS states :

$$u_{cn\sigma}^{(a)}(\mathbf{r}) = u_{\text{cohn}\sigma}(\mathbf{r}) - \frac{1}{\varphi_{n\sigma}^*(\mathbf{r})} \sum_{m=1}^{N_\sigma} \sum_s \frac{v_{s\sigma}^{nm}}{\varepsilon_{n\sigma} - \varepsilon_{m\sigma} - \omega_s} v_s^*(\mathbf{r}) \varphi_{m\sigma}^*(\mathbf{r}), \quad (\text{B13})$$

with $u_{\text{cohn}\sigma}(\mathbf{r})$ defined by Eq. (43). Hence, the first sum in Eq. (B12) is easily shown to have a finite limit when $r \rightarrow \infty$. On the other hand, we get for the empty KS states :

$$\bar{u}_{cn\sigma}^{(a)} = -\sum_{m=1}^{N_\sigma} \frac{|v_{s\sigma}^{nm}|^2}{\varepsilon_{n\sigma} - \varepsilon_{m\sigma} + \omega_s} < 0. \quad (\text{B14})$$

Since all terms in the sum over the empty KS states in Eq. (B12) are negative, we finally conclude that $v_{c\sigma}^{(a),\text{KLI}}(\mathbf{r})$ diverges to $+\infty$ nearly as fast as $e^{2\beta N_\sigma \sigma r}$.

APPENDIX C: ASYMPTOTIC BEHAVIOUR OF THE EXCHANGE-CORRELATION POTENTIAL IN THE SECOND-ORDER APPROXIMATION FOR THE SELF-ENERGY

In this appendix, we give some details about the asymptotic behaviour of the exchange-correlation potential in the second-order approximation for the self-energy.

The second-order self-energy is the sum of the diagrams represented on Fig. 1. If we only keep the second-order bubble-like diagram (along with the first-order exchange one), the asymptotic behaviour of the correlation potential is given by Eq. (78) [see paragraph IV B]. We thus now focus on the so-called ‘‘second-order exchange diagram’’, which, despite its name, only contributes to the correlation potential.

The particle and hole parts of the second-order exchange self-energy $\Sigma_{\text{sox}\sigma}(\mathbf{r}, \mathbf{r}'; \omega)$ read :

$$\Sigma_{\text{h}\sigma}(\mathbf{r}, \mathbf{r}'; \omega) = - \sum_{i=1}^{N_\sigma} \sum_{j=1}^{N_\sigma} \sum_{k>N_\sigma} \varphi_{j\sigma}(\mathbf{r}) \varphi_{i\sigma}^*(\mathbf{r}') \frac{v_{ik\sigma}^*(\mathbf{r}) v_{jk\sigma}(\mathbf{r}')}{\omega - \varepsilon_{i\sigma} + (\varepsilon_{k\sigma} - \varepsilon_{j\sigma}) - i\eta} \quad (\text{C1a})$$

$$\Sigma_{\text{p}\sigma}(\mathbf{r}, \mathbf{r}'; \omega) = - \sum_{i>N_\sigma} \sum_{j=1}^{N_\sigma} \sum_{k>N_\sigma} \varphi_{k\sigma}(\mathbf{r}) \varphi_{i\sigma}^*(\mathbf{r}') \frac{v_{ji\sigma}(\mathbf{r}) v_{jk\sigma}^*(\mathbf{r}')}{\omega - \varepsilon_{i\sigma} - (\varepsilon_{k\sigma} - \varepsilon_{j\sigma}) + i\eta}, \quad (\text{C1b})$$

where :

$$v_{ij\sigma}(\mathbf{r}) = \int d^3\mathbf{r}' v(\mathbf{r}, \mathbf{r}') \varphi_{i\sigma}^*(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r}'). \quad (\text{C2})$$

We first discuss the long-range behaviour of $v_{\text{sox}\sigma}^{(1)}(\mathbf{r})$, which is the solution of Eq. (22) with $u_{\text{soxn}\sigma}(\mathbf{r})$ defined by :

$$u_{\text{soxn}\sigma}(\mathbf{r}) = \frac{1}{\varphi_{n\sigma}^*(\mathbf{r})} \int d^3\mathbf{r}' \Sigma_{\text{sox}\sigma}(\mathbf{r}', \mathbf{r}; \varepsilon_{n\sigma}) \varphi_{n\sigma}^*(\mathbf{r}'). \quad (\text{C3})$$

To proceed, we split $\Sigma_{\text{sox}\sigma}(\mathbf{r}, \mathbf{r}'; \omega) = \Sigma'_{\text{sox}\sigma}(\mathbf{r}, \mathbf{r}'; \omega) + \Sigma''_{\text{sox}\sigma}(\mathbf{r}, \mathbf{r}'; \omega)$, where :

$$\Sigma'_{\text{sox}\sigma}(\mathbf{r}, \mathbf{r}'; \omega) = - \sum_{i=1}^{N_\sigma} \varphi_{i\sigma}^*(\mathbf{r}') \left\{ \sum_{j=1}^{N_\sigma} \sum_{k>N_\sigma} \varphi_{j\sigma}(\mathbf{r}) \frac{v_{ik\sigma}^*(\mathbf{r}) v_{jk\sigma}(\mathbf{r}')}{\omega - \varepsilon_{i\sigma} + (\varepsilon_{k\sigma} - \varepsilon_{j\sigma}) - i\eta} - \sum_{j=1}^{N_\sigma} \sum_{k>N_\sigma} \varphi_{k\sigma}(\mathbf{r}) \frac{v_{ji\sigma}(\mathbf{r}) v_{jk\sigma}^*(\mathbf{r}')}{\omega - \varepsilon_{i\sigma} - (\varepsilon_{k\sigma} - \varepsilon_{j\sigma}) + i\eta} \right\} \quad (\text{C4a})$$

$$\Sigma''_{\text{sox}\sigma}(\mathbf{r}, \mathbf{r}'; \omega) = - \sum_i \varphi_{i\sigma}^*(\mathbf{r}') \sum_{j=1}^{N_\sigma} \sum_{k>N_\sigma} \varphi_{k\sigma}(\mathbf{r}) \frac{v_{ji\sigma}(\mathbf{r}) v_{jk\sigma}^*(\mathbf{r}')}{\omega - \varepsilon_{i\sigma} - (\varepsilon_{k\sigma} - \varepsilon_{j\sigma}) + i\eta}. \quad (\text{C4b})$$

In the same way, we split (with obvious definitions) $u_{\text{soxn}\sigma}(\mathbf{r}) = u'_{\text{soxn}\sigma}(\mathbf{r}) + u''_{\text{soxn}\sigma}(\mathbf{r})$. First, $u''_{\text{soxn}\sigma}(\mathbf{r})$ can be written :

$$u''_{\text{soxn}\sigma}(\mathbf{r}) = - \frac{1}{\varphi_{n\sigma}^*(\mathbf{r})} \sum_{j=1}^{N_\sigma} \sum_{k>N_\sigma} v_{jk\sigma}^*(\mathbf{r}) w_{jkn\sigma}(\mathbf{r}), \quad (\text{C5})$$

where :

$$w_{jkn\sigma}(\mathbf{r}) = \sum_i \frac{v_{ji\sigma}^{nk}}{\varepsilon_{j\sigma} - \varepsilon_{i\sigma} - (\varepsilon_{k\sigma} - \varepsilon_{n\sigma})} \varphi_{i\sigma}^*(\mathbf{r}), \quad (\text{C6})$$

and :

$$v_{ij\sigma}^{kl} = \int d^3\mathbf{r} \varphi_{k\sigma}^*(\mathbf{r}) v_{ij\sigma}(\mathbf{r}) \varphi_{l\sigma}(\mathbf{r}). \quad (\text{C7})$$

Eq. (C5) has basically the same structure as Eq. (44) with ω_s replaced by $\varepsilon_{k\sigma} - \varepsilon_{n\sigma}$ and $v_s(\mathbf{r})$ replaced by $v_{nk\sigma}(\mathbf{r})$. We therefore readily get :

$$w_{jkn\sigma}(\mathbf{r}) \sim - \frac{1}{\varepsilon_{k\sigma} - \varepsilon_{n\sigma}} v_{nk\sigma}(\mathbf{r}) \varphi_{j\sigma}^*(\mathbf{r}), \quad (\text{C8})$$

and :

$$u''_{\text{soxn}\sigma}(\mathbf{r}) \sim -\frac{1}{\varphi_{n\sigma}^*(\mathbf{r})} \sum_{j=1}^{N_\sigma} \varphi_{j\sigma}^*(\mathbf{r}) \sum_{k>N_\sigma} \frac{v_{jk\sigma}^*(\mathbf{r})v_{nk\sigma}(\mathbf{r})}{\varepsilon_{n\sigma} - \varepsilon_{k\sigma}}. \quad (\text{C9})$$

The same behaviour as in the x-only approximation is found : while $u''_{\text{soxn}\sigma}(\mathbf{r})$ diverges exponentially if $n < N_\sigma$ [see Eq. (42a)], $u''_{\text{soxn}\sigma}(\mathbf{r})$ vanishes when $r \rightarrow \infty$:

$$u''_{\text{soxn}\sigma}(\mathbf{r}) \sim -\sum_{k>N_\sigma} \frac{|v_{N_\sigma k\sigma}(\mathbf{r})|^2}{\varepsilon_{N_\sigma\sigma} - \varepsilon_{k\sigma}} \propto \frac{1}{r^4}. \quad (\text{C10})$$

The $1/r^4$ tail follows from a development of $v(\mathbf{r}, \mathbf{r}')$ in powers of $1/r$ in $v_{N_\sigma k\sigma}(\mathbf{r})$.

Second, $u'_{\text{soxn}\sigma}(\mathbf{r})$ can be written :

$$u'_{\text{soxn}\sigma}(\mathbf{r}) = -\frac{1}{\varphi_{n\sigma}^*(\mathbf{r})} \sum_{i=1}^{N_\sigma} \varphi_{i\sigma}^*(\mathbf{r}) f_{ni\sigma}(\mathbf{r}), \quad (\text{C11})$$

where :

$$\begin{aligned} f_{ni\sigma}(\mathbf{r}) &= \sum_{j=1}^{N_\sigma} \sum_{k>N_\sigma} v_{jk\sigma}(\mathbf{r}) \frac{v_{ki\sigma}^{nj}}{\varepsilon_{n\sigma} - \varepsilon_{i\sigma} + (\varepsilon_{k\sigma} - \varepsilon_{j\sigma})} \\ &\quad - \sum_{j=1}^{N_\sigma} \sum_{k>N_\sigma} v_{jk\sigma}^*(\mathbf{r}) \frac{v_{ji\sigma}^{nk}}{\varepsilon_{n\sigma} - \varepsilon_{i\sigma} - (\varepsilon_{k\sigma} - \varepsilon_{j\sigma})}. \end{aligned} \quad (\text{C12})$$

$u'_{\text{soxn}\sigma}(\mathbf{r})$ again diverges exponentially if $n < N_\sigma$. As for $u'_{\text{soxn}\sigma}(\mathbf{r})$, we investigate the asymptotic behaviour of $f_{N_\sigma N_\sigma\sigma}(\mathbf{r})$:

$$\begin{aligned} f_{N_\sigma N_\sigma\sigma}(\mathbf{r}) &\sim \sum_{j=1}^{N_\sigma} \sum_{k>N_\sigma} \frac{1}{\varepsilon_{k\sigma} - \varepsilon_{j\sigma}} v_{jk\sigma}(\mathbf{r}) v_{kN_\sigma\sigma}^{N_\sigma j} + \text{c.c.} \\ &\sim \int d^3\mathbf{r}' v(\mathbf{r}, \mathbf{r}') \rho_\sigma(\mathbf{r}'), \end{aligned} \quad (\text{C13})$$

where :

$$\rho_\sigma(\mathbf{r}) = \sum_{j=1}^{N_\sigma} \sum_{k>N_\sigma} \frac{c_{jk\sigma}}{\varepsilon_{k\sigma} - \varepsilon_{j\sigma}} \varphi_{j\sigma}^*(\mathbf{r}) \varphi_{k\sigma}(\mathbf{r}) + \text{c.c.}, \quad (\text{C14})$$

with :

$$c_{jk\sigma} = v_{kN_\sigma\sigma}^{N_\sigma j} = \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \varphi_{k\sigma}^*(\mathbf{r}_1) [\varphi_{N_\sigma\sigma}(\mathbf{r}_1) v(\mathbf{r}_1, \mathbf{r}_2) \varphi_{N_\sigma\sigma}^*(\mathbf{r}_2)] \varphi_{j\sigma}(\mathbf{r}_2). \quad (\text{C15})$$

$\rho_\sigma(\mathbf{r})$ has vanishing integral since the KS orbitals are orthogonal, and decays exponentially when $r \rightarrow \infty$ (its behaviour is driven by $j = N_\sigma$ term). Moreover, in a system with spherical symmetry and a s -like HOMO, it follows from straightforward considerations that $\rho_\sigma(\mathbf{r})$ also has spherical symmetry. Therefore, $f_{N_\sigma N_\sigma\sigma}(\mathbf{r})$ will vanish exponentially when

$r \rightarrow \infty$, as the potential created by a charge distribution with spherical symmetry, zero sum, and exponential decay. $u'_{\text{sox}N_\sigma\sigma}(\mathbf{r})$ is thus found asymptotically negligible with respect to $u''_{\text{sox}N_\sigma\sigma}(\mathbf{r})$. Hence, we conclude from theorem *i*) of paragraph III C that $\bar{v}_{\text{sox}\sigma}^{(1)} = \bar{u}_{\text{sox}N_\sigma\sigma}$ and that $v_{\text{sox}\sigma}^{(1)}(\mathbf{r}) \sim u''_{\text{sox}N_\sigma\sigma}(\mathbf{r})$ [Eq. (C10)].

The asymptotic behaviour of $v_{\text{sox}\sigma}^{(2)}(\mathbf{r})$ can be obtained using the same line of thought as in paragraph III D. Indeed, $\rho_{\text{sox}\sigma}^{(2)}(\mathbf{r})$ reads :

$$\rho_{\text{sox}\sigma}^{(2)}(\mathbf{r}) = - \sum_{i=1}^{N_\sigma} \sum_{j=1}^{N_\sigma} \sum_{k>N_\sigma} w_{jki\sigma}^*(\mathbf{r}) w_{ikj\sigma}(\mathbf{r}), \quad (\text{C16})$$

with $w_{ijk\sigma}(\mathbf{r})$ defined by Eq. (C6). The long-range behaviour of $\rho_{\text{sox}\sigma}^{(2)}(\mathbf{r})$ easily follows from Eq. (C8) :

$$\rho_{\text{sox}\sigma}^{(2)}(\mathbf{r}) \sim -|\varphi_{N_\sigma\sigma}(\mathbf{r})|^2 u(\mathbf{r}), \quad (\text{C17})$$

where :

$$u(\mathbf{r}) = \sum_{k>N_\sigma} \frac{|v_{N_\sigma k\sigma}(\mathbf{r})|^2}{(\varepsilon_{N_\sigma\sigma} - \varepsilon_{k\sigma})^2} \quad (\text{C18a})$$

$$\leq \frac{1}{\varepsilon_{(N_\sigma+1)\sigma} - \varepsilon_{N_\sigma\sigma}} \sum_{k>N_\sigma} \frac{|v_{N_\sigma k\sigma}(\mathbf{r})|^2}{\varepsilon_{k\sigma} - \varepsilon_{N_\sigma\sigma}}. \quad (\text{C18b})$$

$u(\mathbf{r})$ thus decreases as least as fast as $1/r^4$ [see Eq. (C10)]. Hence we can show (as in the *GW* approximation) that $v_{\text{sox}\sigma}^{(2)}(\mathbf{r})$ decreases as least as fast as $1/r^5$ and is asymptotically negligible with respect to $v_{\text{sox}\sigma}^{(1)}(\mathbf{r})$.

Finally, adding Eq. (C10) to Eq. (78) yields (for a system with spherical symmetry and a doubly occupied *s*-like HOMO) :

$$v_{c\sigma}^{\text{MBPT}(2)}(\mathbf{r}) \sim \frac{1}{2} \tilde{W}_s^{\text{KS}}(\mathbf{r}, \mathbf{r}; \omega = 0) \sim -\frac{\tilde{\alpha}^{\text{KS}}}{2r^4}, \quad (\text{C19})$$

where $\tilde{W}_s^{\text{KS}}(\omega = 0) \equiv v \tilde{P}^{\text{KS}}(\omega = 0) v$, $\tilde{P}^{\text{KS}}(\omega = 0)$ is defined by Eq. (80), and $\tilde{\alpha}^{\text{KS}}$ is given by Eq. (56) using $\tilde{P}^{\text{KS}}(\omega = 0)$ instead of $\tilde{P}^{\text{RPA}}(\omega = 0)$.

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