Asymptotic behavior of the Kohn-Sham exchange potential at a metal surface

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The asymptotic structure of the Kohn-Sham exchange potential $v_x(\mathbf{r})$ in the classically forbidden region of a metal surface is investigated, together with that of the Slater exchange potential $V_x^S(\mathbf{r})$ and those of the approximate Krieger-Li-Iafrate $V_x^{\mathrm{KLI}}(\mathbf{r})$ and Harbola-Sahni $W_x(\mathbf{r})$ exchange potentials. Particularly, the former is shown to have the form of $v_x(z\to\infty)=-\alpha_x/z$ with α_x a constant dependent only of bulk electron density. The same result in previous work is thus confirmed; in the meanwhile, a controversy raised recently gets resolved. The structure of the exchange hole $\rho_x(\mathbf{r},\mathbf{r}')$ is examined, and the delocalization of it in the metal bulk when the electron is at large distance from the metal surface is demonstrated with analytical expressions. The asymptotic structures of $v_x(\mathbf{r})$, $V_x^S(\mathbf{r})$, $V_x^{\mathrm{KLI}}(\mathbf{r})$, and $W_x(\mathbf{r})$ at a slab metal surface are also investigated. Particularly, $v_x(z\to\infty)=-1/z$ in the slab case. The distinction, in this respect, between the semi-infinite and the slab metal surfaces is elucidated.

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I. INTRODUCTION

The static (classical) charge potential vanishes exponentially far outside a metal surface. The electronic structure in the classically forbidden region as a consequence depends strongly on exchange and correlation (xc) effects. Quantum-mechanical many-body effects thus play a major role in this region. In the seminal work of the application of the Kohn-Sham (KS) density functional theory (DFT)[1] to the metal surface problem, Lang and Kohn[2] assumed that the KS local xc potential $v_{\mathrm{xc}}(z)$ decays like the classical image potential $V_{\mathrm{im}}(z)=-1/4z$, with z being the distance from the metal surface. (Similar assumption had been made earlier in Bardeen's pioneering study of the electronic properties of the metal surface.)[3] The KS local xc potential $v_{\mathrm{xc}}(\mathbf{r})$ is equal to the functional derivative of the KS xc energy functional $E_{\mathrm{xc}}[\rho]$ with respect to the electron density $\rho(\mathbf{r})$: $v_{\mathrm{xc}}(\mathbf{r})=\delta E_{\mathrm{xc}}[\rho]/\delta\rho(\mathbf{r})$. It was found that $v_{\mathrm{xc}}(z)$ calculated by Lang and Kohn in the local density approximation (LDA) to $E_{\mathrm{xc}}[\rho]$ had an exponential decay at large distance from the metal surface, recognized hence as one of shortcomings of the LDA.[2] The subject of the asymptote of $v_{\mathrm{xc}}(z)$ at the metal surface has thereafter attracted long-standing research interest.[4] It was claimed in Refs. 5 and 6 that $v_{\mathrm{xc}}(z)\sim -1/(4z)$, which was attributed to the correlation potential $v_c(z)$. The exchange potential $v_x(z)$ was claimed to decay exponentially in the former and as $\sim -1/z^2$ in the latter, respectively.

The exponential and the $\sim -1/z^2$ behavior of the exchange potential $v_x(z)$ was questioned in Ref. 7, and it was numerically demonstrated that at least the component of $v_x(z)$ arising purely from the exchange hole, [which is in fact the Harbola-Sahni approximate exchange potential $W_x(z)$ discussed later in this paper] has an image-potential-like behavior though possibly not the exact form of $V_{\mathrm{im}}(z)$. The result in Ref. 7 was corroborated by Solomatin and Sahni[8] who, based on the integral equation for the optimized effective potential (OEP)[9] [also known as the OPM (optimized potential method) in Ref. 8 and various literature], analytically showed that

$$v_x(z\to\infty)=-\alpha_x\frac{1}{z}, \tag{1}$$

with

$$\alpha_x=\frac{\beta^2-1}{2\beta^2}\left[1-\frac{\ln(\beta^2-1)}{\pi(\beta^2-1)^{1/2}}\right], \tag{2}$$

where $\beta=\sqrt{W/\epsilon_F}$, W the surface-barrier height, and ϵ_F the bulk Fermi energy. This result had been further confirmed in Ref. 10. The issue of the asymptote of the full KS exchange-correlation potential $v_{\mathrm{xc}}(z)$ was also addressed in Ref. 10.

Both the calculations in Refs. 8 and 10 for $v_x(z)$ at large z had been carried out exactly (with no approximation employed). The one in Ref. 10 made the use of a different method by solving the Dyson equation with the use of the exact exchange part Σ_x of the electron self-energy. The agreement between Refs. 8 and 10 on the result shown in Eq. (1) strongly indicates its correctness. Recently, Horowitz *et al.*, however, claimed[11] that asymptotically $v_x(z)=-1/z$, but later[12] that $v_x(z)$ has an asymptotic form of $v_x(z)\sim \ln z/z$. The result in Eq. (1) was hence challenged. The method used in Refs. 11 and 12 was the same OEP method used previously in Ref. 8. However, there was a subtle but distinct difference in the technique between the approach in Ref. 8 and that in Refs. 11 and 12. The calculation in Ref. 8 made the direct use of the integral equation for OEP, but those in Refs. 11 and 12 used instead the OEP method formulated in terms of differential equations for the so-called orbital shifts [cf. Eq. (22) below].[13–15] There are certain advantages in this formulation in that the quantities of the orbital-shifts, expressed as the solutions to the differential equations, are comparatively amenable to analytical or numerical study. This will also get illustrated in this work. Indeed, we attempt to resolve the controversy by carrying out further investigation based precisely on this formulation of the OEP method. To this end, we have managed to establish, for limiting large z, an identity between $v_x(z)$ and the planar-momentum averaged orbital-dependent exchange potential $u_{xk}(z)$ at $k=k_F$, where k is the perpendicular component of the electron momentum and k_F the bulk Fermi momentum. The identity, reported in Eq. (42) [for the case of the slab metal surface see instead that in Eq. (41)], is one of the key results, with the aid of which the following development can be made fairly smoothly. The quantity $u_{xk_F}(z)$ is then shown to have the asymptotic form of

$u_{xk_F}(z) = -\alpha_x/z$. In this manner, we confirm once again the result in Eq. (1). The controversy raised in Ref. 12 is hence resolved. It is shown in Sec. V that one component [termed $V_x^{\rm shift}(z)$] of $v_x(z)$, which was ignored in the study in Ref. 12 actually also makes a leading-order contribution to $v_x(z)$. In addition, it is shown that $v_x(z=\infty)=0$ at the semi-infinite metal surface, i.e., Eq. (1) is exact to the leading order. Since $v_{\rm xc}(z=\infty)=0$ (which can always be made true), it follows that $v_c(z=\infty)=0$.

The Slater exchange potential $V_x^S(\mathbf{r})$ (see Ref. 16) has been regarded also as an approximation to the KS exchange potential. In Ref. 8, it was shown that $V_x^S(z)$ has the following asymptotic form at large distance from the metal surface:

$$V_x^S(z\to\infty) = -2\alpha_x\frac{1}{z}. \tag{3}$$

There exists no controversy in the literature over this result. We give further verification of it.

The quite nontrivial asymptotic structure of $v_x(z)$ in Eq. (1) was pointed out to arise from the delocalization of the exchange hole (also known as the Fermi hole) $\rho_x(\mathbf{r},\mathbf{r}')$.[17] It was shown numerically that the exchange hole is spread throughout the entire metal bulk when the electron is in the classically forbidden region.[17] Expressions for the exchange hole with the planar-positions averaged, valid for arbitrary electron positions, are reported. Especially, the delocalization of the exchange hole at the semi-infinite metal surface for limiting large electron positions is illustrated with analytical expressions. This might be of help to shed further light on the curious exchange effects in the classically forbidden region of the metal surface.

Two of other approximate exchange potentials, the Krieger-Li-Iafrate (KLI) $V_x^{\rm KLI}(\mathbf{r})$ potential[18,19] and the Harbola-Sahni (HS) $W_x(\mathbf{r})$ potential,[20] are also surveyed. They will be introduced in Sec. V. $V_x^{\rm KLI}(\mathbf{r})$ is well known as an extensively employed substitute for the OEP. It has the same bulk limit as $v_x(z)$, a fact crucial for calculation practice for the metal surface. $V_x^{\rm KLI}(z)$ turns out to have an asymptotic form of $V_x^{\rm KLI}(z)\sim \ln z/z$ and hence deviate from $v_x(z)$ in the classically forbidden region, indicating that an improvement is required there. On the other side, the asymptotic behavior of $W_x(z)$ has been given a full-fledged study in Ref. 21, and it was shown that $W_x(z)$ deviates from $v_x(z)$ in both the metal bulk and the classically forbidden region, though relatively mildly in the latter in the form of $W_x(z)\sim -\alpha_W/z$, where the constant α_W is given in Eq. (85).

A great deal of work on the electronic structure at the metal surface has been carried out on a jellium metal slab instead. The asymptotic behavior of $v_x(z)$ at large distance from the slab surface is also examined in this work, and it is shown that

$$v_x(z\to\infty) = -\frac{1}{z}. \tag{4}$$

As mentioned previously, the same result was also reported in Ref. 11. In this sense, it gets confirmed here. It is necessary to remark that the study in Ref. 11 was performed on the slab metal surface, but clearly also aimed at obtaining knowledge equally valuable for the semi-infinite metal surface. We, however, point out that Eq. (4) is valid only for the slab surface and can not be naively extrapolated for the semi-infinite surface. In fact, the slab surface can virtually be regarded as a finite system and as a consequence, Eq. (4) can be obtained by a direct multipole expansion of the Coulomb interaction. Furthermore, it is shown that the result in Eq. (4) is in fact subject to a possible difference of nonzero constant, i.e., $v_x(z=\infty)\neq 0$ [see Eq. (103) and the discussion below it], though it can be made to vanish in an exchange-only calculation via a shift in $v_x(z)$.

In Sec. II, we present preliminaries and introduce the OEP method to the metal surface problem. The properties of $v_x(z)$, $V_x^S(z)$, and the exchange energy density $\epsilon_x(z)$ are examined in Sec. III. The properties of $\rho_x(\mathbf{r},\mathbf{r}')$ are examined in Sec. IV, and those of $V_x^{\rm KLI}(z)$ and $W_x(z)$ in Sec. V. The slab surface case is considered in Sec. VI. In Appendix A, we prove a mathematical statement of Eq. (24) proposed in Sec. II. Appendix B contains the calculation for the asymptotic form of $u_{xk_F}(z)$, Appendix C that for $V_x^S(z)$, and Appendix D that for the planar-position averages of $\rho_x(\mathbf{r},\mathbf{r}')$. The paper is concluded in Sec. VII.

II. PRELIMINARIES

In the jellium[3] and structureless-pseudopotential[22] models of a metal surface with a uniform positive background of charge

$$\rho_+(z) = \frac{k_F^3}{3\pi^2}\theta(-z), \tag{5}$$

the KS orbitals are of the form

$$\phi_{\mathbf{k}}(\mathbf{r}) = \sqrt{\frac{2}{AL}}e^{i\mathbf{k}_\parallel\cdot\mathbf{x}_\parallel}\phi_k(z). \tag{6}$$

In Eq. (5), $(\mathbf{k}_\parallel,\mathbf{x}_\parallel)$ are the planar components of the momentum and position, and (k,z) the perpendicular components, i.e., $\mathbf{k}=\mathbf{k}_\parallel+k\mathbf{e}_z$ and $\mathbf{r}=\mathbf{x}_\parallel+z\mathbf{e}_z$, where $\mathbf{e}_z$ is the unit vector perpendicular to the metal surface. The magnitude of $\mathbf{k}$, on the other hand, will be explicitly denoted with $|\mathbf{k}|$ $(=\sqrt{k_\parallel^2+k^2})$. A and L in Eq. (6) denote the planar normalization area and the perpendicular normalization length, respectively.

A. Preparatory materials

The $\phi_k(z)$ obeys the differential equation

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial z^2}+W+V(z)+v_{\rm xc}(z)\right]\phi_k(z)=\frac{1}{2}k^2\phi_k(z), \tag{7}$$

where $V(z)$ is the static (classical) charge potential that vanishes exponentially at large distance from the metal surface. $\phi_k(z)$ has the following asymptotic forms,

$$\phi_k(z)\sim \sin[kz+\delta(k)] \quad \text{for} \quad z\to-\infty, \tag{8a}$$

$$\sim P_k(z)e^{-\kappa z} \quad \text{for} \quad z\to\infty, \tag{8b}$$

where $\delta(k)$ is the phase shift due to the metal surface, $\kappa=\sqrt{2W-k^2}$, and $P_k(z)$ is a power function,[10] and ∞ denotes the positive infinity.

The Dirac density matrix is defined as $\gamma_s(\mathbf{r},\mathbf{r}')=2\sum_i\phi_i(\mathbf{r})\phi_i^*(\mathbf{r}')$. At the metal surface, it has the following

form:

$$\gamma_s(\mathbf{r},\mathbf{r}') = \frac{1}{2\pi^3}\int d\mathbf{k}\ \ \theta(k_F - |\mathbf{k}|)\phi_k^*(z)\phi_k(z')e^{i\mathbf{k}_\parallel\cdot(\mathbf{x}'_\parallel-\mathbf{x}_\parallel)}. \quad (9)$$

By the use of the identities

$$\int d\hat{\mathbf{q}}e^{-i\mathbf{q}\cdot(\mathbf{x}_\parallel-\mathbf{x}'_\parallel)} = 2\pi J_0(q|\mathbf{x}_\parallel - \mathbf{x}'_\parallel|), \quad (10)$$

$$\int_0^\lambda dk_\parallel k_\parallel J_0(k_\parallel|\mathbf{x}_\parallel - \mathbf{x}'_\parallel|) = \lambda\frac{J_1(\lambda|\mathbf{x}_\parallel - \mathbf{x}'_\parallel|)}{|\mathbf{x}_\parallel - \mathbf{x}'_\parallel|}, \quad (11)$$

where $\lambda = \sqrt{k_F^2 - k^2}$, and J_0 and J_1 are the zeroth-order and the first-order Bessel functions, respectively, we can rewrite Eq. (9) as

$$\gamma_s(\mathbf{r},\mathbf{r}') = \frac{2}{\pi^2}\int_0^{k_F} dk\lambda\phi_k(z)\phi_k^*(z')\frac{J_1(\lambda|\mathbf{x}_\parallel - \mathbf{x}'_\parallel|)}{|\mathbf{x}_\parallel - \mathbf{x}'_\parallel|}. \quad (12)$$

The expression for the electron density is

$$\rho(z) = \frac{1}{\pi^2}\int_0^{k_F} dk\lambda^2|\phi_k(z)|^2. \quad (13)$$

[The density is equal to the diagonal component of the density matrix, and Eq. (13) follows directly from Eq. (12) with the aid of the fact that $J_1(x) \to 1/2x$ as $x \to 0$.]

Finally, we formulate for the metal surface problem the exchange hole, which is defined as

$$\rho_x(\mathbf{r},\mathbf{r}') = -\frac{|\gamma_s(\mathbf{r},\mathbf{r}')|^2}{2\rho(\mathbf{r})}. \quad (14)$$

It follows from the substitution of Eq. (9) into Eq. (14) that

$$\rho_x(\mathbf{r},\mathbf{r}') = -\frac{1}{8\pi^6\rho(z)}\int d\mathbf{k}\int d\mathbf{k}'\theta(k_F - |\mathbf{k}|) \times \theta(k_F - |\mathbf{k}'|)\Phi_{k,k'}(z,z')e^{i(\mathbf{k}_\parallel-\mathbf{k}'_\parallel)\cdot(\mathbf{x}'_\parallel-\mathbf{x}_\parallel)}, \quad (15)$$

where

$$\Phi_{k,k'}(z,z') = \phi_k^*(z)\phi_k(z')\phi_{k'}(z)\phi_{k'}^*(z'). \quad (16)$$

Alternatively, the substitution of Eq. (12) instead yields

$$\rho_x(\mathbf{r},\mathbf{r}') = -\frac{2}{\pi^4\rho(z)}\int_0^{k_F} dk\int_0^{k_F} dk'\lambda\lambda'\Phi_{k,k'}(z,z') \times \frac{J_1(\lambda|\mathbf{x}_\parallel - \mathbf{x}'_\parallel|)J_1(\lambda'|\mathbf{x}_\parallel - \mathbf{x}'_\parallel|)}{|\mathbf{x}_\parallel - \mathbf{x}'_\parallel|^2}, \quad (17)$$

where $\lambda' = \sqrt{k_F^2 - k'^2}$.

B. The OEP method

The exchange-only OEP[9] has been proved to be equal to the KS exchange potential $v_x(\mathbf{r})$.[23] We briefly outline the method below, starting with an introduction to the orbital-dependent exchange potentials[13,14]

$$u_{xi}(\mathbf{r}) = \frac{1}{\phi_i(\mathbf{r})}\frac{\delta E_x[\{\phi_j\}]}{\delta\phi_i^*(\mathbf{r})}, \quad (18)$$

and the orbital shifts

$$\psi_i(\mathbf{r}) = \sum_{j\neq i}\frac{\langle\phi_j|v_x - u_{xi}|\phi_i\rangle}{\epsilon_i - \epsilon_j}\phi_j(\mathbf{r}). \quad (19)$$

Here, $\phi_i(\mathbf{r})$ and ϵ_i are the KS orbitals and the corresponding eigenenergies, respectively, and $E_x[\{\phi_j\}]$ is the exchange energy functional of the orbitals. The orbital-dependent exchange potentials $u_{xi}(\mathbf{r})$ in Eq. (18) are of the same form as the Hartree-Fock potentials but constructed from the KS orbitals $\phi_i(\mathbf{r})$. Explicitly,

$$u_{xi}(\mathbf{r}) = -\frac{1}{2\phi_i(\mathbf{r})}\int d\mathbf{r}'\frac{\gamma_s(\mathbf{r},\mathbf{r}')\phi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (20)$$

The central equation in the OEP method is

$$\sum_i^{\text{occ.}}\psi_i^*(\mathbf{r})\phi_i(\mathbf{r}) + \text{c.c.} = 0, \quad (21)$$

where c.c. denotes the complex conjugate of the previous term. Equations (19) and (21), together with the KS equations for the orbitals [cf. Eq. (7)],[1] build the self-consistent calculation scheme for the exchange-only OEP.

In self-consistent calculation for the OEP, evaluating $\psi_i(\mathbf{r})$ from Eq. (19) is highly impractical. Equation (19) therefore is usually rewritten in the form of a differential equation.[13–15] In our case,

$$\left[-\tfrac{1}{2}\bigtriangledown^2 + W + V(z) + v_{\text{xc}}(z) - \tfrac{1}{2}\mathbf{k}^2\right]\psi_\mathbf{k}(\mathbf{r}) = [-v_x(z) + u_{x\mathbf{k}}(\mathbf{r}) + D_\mathbf{k}]\phi_\mathbf{k}(\mathbf{r}), \quad (22)$$

where

$$D_\mathbf{k} = \langle\phi_\mathbf{k}|v_x - u_{x\mathbf{k}}|\phi_\mathbf{k}\rangle. \quad (23)$$

It is demonstrated in Appendix A that $u_{x\mathbf{k}}(\mathbf{r})$ is independent of $\mathbf{x}_\parallel$, i.e., it is a function of z only:

$$u_{x\mathbf{k}}(\mathbf{r}) = u_{x\mathbf{k}}(z). \quad (24)$$

The variables $\mathbf{x}_\parallel$ and z accordingly can be separated in Eq. (22) and $\psi_\mathbf{k}(\mathbf{r})$ hence has the form

$$\psi_\mathbf{k}(\mathbf{r}) = \sqrt{\frac{2}{AL}}e^{i\mathbf{k}_\parallel\cdot\mathbf{x}_\parallel}\psi_\mathbf{k}(z). \quad (25)$$

Correspondingly, with the aid of Eq. (6), it follows that

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial z^2} + W + V(z) + v_{\text{xc}}(z) - \frac{1}{2}k^2\right]\psi_\mathbf{k}(z) = [-v_x(z) + u_{x\mathbf{k}}(z) + D_\mathbf{k}]\phi_k(z). \quad (26)$$

We average over $\mathbf{k}_\parallel$ on both sides of the preceding equation and obtain

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial z^2} + W + V(z) + v_{\text{xc}}(z) - \frac{1}{2}k^2\right]\psi_k(z) = [-v_x(z) + u_{xk}(z) + D_k]\phi_k(z). \quad (27)$$

The planar-momentum averages $u_{xk}(z)$ of the orbital-dependent exchange potentials $u_{x\mathbf{k}}(\mathbf{r})$ [rewritten as $u_{x\mathbf{k}}(z)$ according to Eq. (24)],

$$u_{xk}(z) = \frac{1}{\pi\lambda^2}\int_0^\lambda d\mathbf{k}_\parallel u_{x\mathbf{k}}(z), \quad (28)$$

has been introduced into Eq. (27) together with the similar planar-momentum averages $\psi_k(z)$ of $\psi_\mathbf{k}(z)$, and D_k of $D_\mathbf{k}$.

We write

$$D_\mathbf{k}^a = \langle\phi_\mathbf{k}|v_x|\phi_\mathbf{k}\rangle, \quad D_\mathbf{k}^b = \langle\phi_\mathbf{k}|u_{x\mathbf{k}}|\phi_\mathbf{k}\rangle. \quad (29)$$

Accordingly, it follows from Eq. (23) that

$$D_k = D_k^a - D_k^b, \tag{30}$$

with

$$D_k^a = 2\langle\phi_k|v_x|\phi_k\rangle/L, \quad D_k^b = 2\langle\phi_k|u_{xk}|\phi_k\rangle/L. \tag{31}$$

For the semi-infinite metal surface, D_k^a evidently takes the bulk value $v_x^{\rm bulk} = -k_F/\pi$ of $v_x(z)$ (and is accordingly independent of k.) On the other hand,

$$D_{\mathbf{k}}^b = -\frac{1}{2\pi^2}\int d\mathbf{k}'\frac{1}{|\mathbf{k}-\mathbf{k}'|^2}\theta(k_F - |\mathbf{k}'|). \tag{32}$$

Explicitly,[3,24]

$$D_{\mathbf{k}}^b = -\frac{2k_F}{\pi}F\left(\frac{|\mathbf{k}|}{k_F}\right) \tag{33}$$

with

$$F(x) = \frac{1}{2} + \frac{1-x^2}{4x}\ln\left|\frac{1+x}{1-x}\right|. \tag{34}$$

Solely for later reference, we also list

$$D_{\mathbf{k}} = \frac{k_F}{\pi}\left[2F\left(\frac{|\mathbf{k}|}{k_F}\right) - 1\right], \tag{35}$$

and note that $D_{\mathbf{k}}|_{|\mathbf{k}|=k_F} = 0$. Expression for D_k^b will also be used in the later development:

$$D_k^b = -\frac{2k_F}{\pi^2\lambda^2}\int_0^\lambda d\mathbf{k}_\parallel F\left(\frac{|\mathbf{k}|}{k_F}\right) = -\frac{4k_F^3}{\pi\lambda^2}\int_{k/k_F}^1 dx\, x F(x), \tag{36}$$

explicitly,

$$D_k^b = \frac{1}{3\pi}\left[-2k_F + \frac{(k_F+k)(2k_F-k)}{k_F-k}\ln\frac{k_F+k}{2k_F} + \frac{(k_F-k)(2k_F+k)}{k_F+k}\ln\frac{k_F-k}{2k_F}\right]. \tag{37}$$

C. Identity $v_x(z) = u_{xk_F}(z)$ for $z \to \infty$

We consider Eq. (27) for limiting large z. On the right-hand side of it, the term $u_{xk}(z)\phi_k(z)$, which is due to the orbital-dependent exchange potential, has the asymptotic form of $f_k(z)\phi_{k_F}(z)$ with $f_k(z)$ a power function. Its existence implies that $\psi_k(z)$ must have the analogous asymptotic form:

$$\psi_k(z) = g_k(z)\phi_{k_F}(z), \tag{38}$$

where $g_k(z)$ is also a power function obeying

$$\tfrac{1}{2}\lambda^2 g_k(z) - \phi_{k_F}^{-1}(z)\phi_{k_F}'(z)g_k'(z) - \tfrac{1}{2}g_k''(z) = \phi_{k_F}^{-1}(z)[-v_x(z) + u_{xk}(z) + D_k]\phi_k(z). \tag{39}$$

The primes denote the derivatives with respect to z. Equation (39) is valid for all k. It turns out that its special case at $k = k_F$ solely is sufficient to determine the asymptotic structure of $v_x(z)$. Indeed,

$$\phi_{k_F}^{-1}(z)\phi_{k_F}'(z)g_{k_F}'(z) + \tfrac{1}{2}g_{k_F}''(z) = v_x(z) - u_{xk_F}(z) - D_{k_F}. \tag{40}$$

By using the fact that $g_{k_F}(z) \to 0$, [with the understanding that the homogeneous solution of $\psi_k(z)$ in Eq. (27) is excluded,] one has $g_{k_F}'(z)$, $g_{k_F}''(z) \sim o(1/z)$ for large z. On the other hand, it will be shown later in Eq. (47) that $u_{xk_F}(z) \sim O(1/z)$. One hence obtains, from Eq. (40), for limiting large z,

$$v_x(z) = u_{xk_F}(z) + D_{k_F}. \tag{41}$$

Since $D_k^a = -k_F/\pi$ and $D_{k_F}^b = -k_F/\pi$ according to Eq. (37), one has correspondingly, from Eq. (30), $D_{k_F} = 0$ for the semi-infinite metal surface. This leads to one of the central identities:

$$v_x(z) = u_{xk_F}(z) \quad \text{for} \quad z \to \infty. \tag{42}$$

We remarked that $D_{k_F} \neq 0$ for the slab metal surface, and we then have Eq. (41) only.

Equation (42) suggests that knowledge about the quantity $u_{xk_F}(z)$ could be useful in carrying through the reminder of our task. In this regard, we include here some expressions for it. In general, for $k \to k_F$ and any well behaved function $f(\mathbf{k}) = f(\mathbf{k}_\parallel, k)$ [$u_{x\mathbf{k}}(z)$ in the present case],

$$\int_0^\lambda d\mathbf{k}_\parallel f(\mathbf{k}) = \pi\lambda^2 f(\mathbf{k}_\parallel = 0, k = k_F). \tag{43}$$

Hence from Eq. (28), it follows that

$$u_{xk_F}(z) = u_{x\mathbf{k}}(z)|_{\mathbf{k}_\parallel=0,k=k_F}. \tag{44}$$

Accordingly from Eqs. (20) and (24) one has

$$u_{xk_F}(z) = -\frac{1}{2\phi_{k_F}(z)}\int d\mathbf{r}'\frac{\gamma_s(\mathbf{r},\mathbf{r}')\phi_{k_F}(z')}{|\mathbf{r}-\mathbf{r}'|}. \tag{45}$$

III. ASYMPTOTIC STRUCTURES OF $v_x(z)$ AND $V_x^S(z)$

Quantities similar to $u_{xk_F}(z)$ have been calculated in Refs. 7, 8, and 10. We apply a different approach to perform the calculation, which can serve also as a kind of verification. To this end, we substitute Eq. (12) into Eq. (45). It follows that

$$u_{xk_F}(z) = -\frac{2}{\pi\phi_{k_F}(z)}\int_0^{k_F} dk\lambda\phi_k(z)\int_{-\infty}^{\infty} dz'\phi_k^*(z')\phi_{k_F}(z') \times \int_0^\infty dr_\parallel'\frac{1}{\sqrt{(z-z')^2 + r_\parallel'^2}}J_1(\lambda r_\parallel'). \tag{46}$$

Alternatively, Eq. (46) can also be obtained from the substitution of Eq. (A3) into Eq. (44). The aid of the fact that $J_0(0) = 1$ is needed then.

The asymptotic form of $u_{xk_F}(z)$ is examined in Appendix B with the following result:

$$u_{xk_F}(z \to \infty) = -\alpha_x\frac{1}{z}, \tag{47}$$

which, together with Eq. (42), leads to Eq. (1), fulfilling the main object of this work. (The controversy raised in Ref. 12 will get further elucidated in Sec. V.) Equation (47), which is exact at limiting large z, together with Eq. (42), leads also to the conclusion that $v_x(\infty) = 0$ at the semi-infinite metal surface. In other words, Eq. (1) is exact to the leading order. We assume that $v_{\rm xc}(\infty) = 0$ at the metal surface. Accordingly,

we also have $v_c(\infty) = 0$. Further insight into these facts will be provided in Sec. VI in connection with those for the slab case.

The Slater exchange potential $V_x^S(\mathbf{r})$[16] is defined as

$$V_x^S(\mathbf{r}) = \int d\mathbf{r}' \rho_x(\mathbf{r},\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|}. \tag{48}$$

For our metal surface problem, we substitute Eq. (17) for $\rho_x(\mathbf{r},\mathbf{r}')$ into Eq. (48). It follows that

$$\begin{aligned} V_x^S(z) = & -\frac{4}{\pi^3\rho(z)} \int_0^{k_F} dk \phi_k(z) \int_0^{k_F} dk' \phi_{k'}^*(z) \lambda\lambda' \\ & \times \int_{-\infty}^{\infty} dz' \phi_k^*(z') \phi_{k'}(z') \int_0^{\infty} dr'_{\parallel} \frac{1}{r'_{\parallel}\sqrt{(z-z')^2 + r'^2_{\parallel}}} \\ & \times J_1(\lambda r'_{\parallel}) J_1(\lambda' r'_{\parallel}). \end{aligned} \tag{49}$$

The asymptotic structure of $V_x^S(z)$ at large distance from the metal surface is calculated in Appendix C and the final result is shown in Eq. (3).[8] Correspondingly, the exchange energy density per unit volume $\epsilon_x(\mathbf{r}) = \frac{1}{2}\rho(\mathbf{r}) V_x^S(\mathbf{r})$ has the asymptotic form:[10]

$$\epsilon_x(z \to \infty) = -\alpha_x \frac{\rho(z)}{z}. \tag{50}$$

We note that

$$\rho(z \to \infty) = \frac{k_F}{2\pi^2 c^2} \frac{1}{z^2} |\phi_{k_F}(z)|^2, \tag{51}$$

where $c = 1/\sqrt{\beta^2 - 1}$.

It is well known that in a finite system $v_x(\mathbf{r})$ has a long-range form of $v_x(\mathbf{r} \to \infty) = -1/r$.[5,6,25,26] (For simplicity, only a spherically symmetric system is discussed here. For recent progress made on this subject, see Refs. 14 and 15 and the discussions later in Sec. VI.) The Slater exchange potential has exactly the same long-range form of $V_x^S(\mathbf{r} \to \infty) = -1/r$. The identical long-range form of $v_x(\mathbf{r})$ and $V_x^S(\mathbf{r})$ results from the fact that in the finite system the exchange hole is well localized near the system. The asymptotic structure of $v_x(\mathbf{r})$ is essentially determined by that of the orbital-dependent exchange potential $u_{xm}(\mathbf{r})$ of the highest occupied orbital (denoted by m).[5,6,25,26] The asymptotic structure of both $u_{xm}(\mathbf{r})$ and $V_x^S(\mathbf{r})$ in turn can be attributed to the (orbital-dependent) exchange hole in terms of the leading order contribution of the multipole expansion of the Coulomb interaction. For the semi-infinite metal surface, this is no more true since the exchange hole is delocalized and spread throughout the entire bulk region,[17] and, as a consequence, the multipole expansion argument does not apply anymore. This explains the difference in the asymptotic structures of $v_x(z)$ and $V_x^S(z)$ at large z from the semi-infinite metal surface, as shown in Eqs. (1) and (3), respectively. The delocalization of the exchange hole at large electron positions will be examined in the next section.

IV. DELOCALIZATION OF $\rho_x(\mathbf{r},\mathbf{r}')$

We take planar-position average of $\rho_x(\mathbf{r},\mathbf{r}')$:

$$\rho_x(z,z') = \frac{1}{A} \int d\mathbf{x}_{\parallel} \int d\mathbf{x}'_{\parallel} \rho_x(\mathbf{r},\mathbf{r}'). \tag{52}$$

The information about $\rho_x(z,z')$ clearly is sufficient to serve the present purpose. By the substitution of Eq. (15) into Eq. (52), $\rho_x(z,z')$ can be shown as

$$\begin{aligned} \rho_x(z,z') = & -\frac{2}{\pi^3\rho(z)} \int_0^{k_F} d\lambda \lambda^2 \int_0^{k} dk' [\Phi_{k,k'}(z,z') \\ & + \Phi_{k,k'}(z',z)]. \end{aligned} \tag{53}$$

Equation (53) is valid for all electron positions z. This expression was first reported in Ref. 17, and the reader is referred to that work for detailed derivations. It is not difficult to see that the two terms in Eq. (53) make the same contribution, and hence

$$\rho_x(z,z') = -\frac{4}{\pi^3\rho(z)} \int_0^{k_F} d\lambda \lambda^2 \phi_k^*(z) \phi_k(z') \int_0^{k} dk' \phi_{k'}(z) \phi_{k'}^*(z'). \tag{54}$$

We are interested especially in the asymptotic structure of $\rho_x(z,z')$. It is demonstrated in Appendix D that

$$\rho_x(z \to \infty, z') = -\frac{4}{\pi c} \frac{1}{z} |\phi_{k_F}(z')|^2. \tag{55}$$

Equation (55) displays remarkably the delocalization of the exchange hole in the metal bulk. [The reader is referred to Eq. (8a) for the behavior of $\phi_{k_F}(z')$ in the deep bulk region.] In the meanwhile, the amplitude of $\rho_x(z,z')$ decays as $\sim 1/z$ with the electron position z.

Both planar positions $\mathbf{x}_{\parallel}$ and $\mathbf{x}'_{\parallel}$ of the electron and the hole have been averaged, respectively, in Eq. (52). But, evidently, $\rho_x(\mathbf{r},\mathbf{r}')$ is a function of $\mathbf{x}_{\parallel} - \mathbf{x}'_{\parallel}$ only, rather than of $\mathbf{x}_{\parallel}$ and $\mathbf{x}'_{\parallel}$ separately. Another type of average over the planar positions therefore might be equally capable of featuring the exchange hole at the metal surface, which is defined in the following manner:[27]

$$b_x(z,z') = \int_0^{\infty} d|\mathbf{x}_{\parallel} - \mathbf{x}'_{\parallel}| \rho_x(\mathbf{r},\mathbf{r}'). \tag{56}$$

We substitute Eq. (15) into Eq. (56) and write $b_x(z,z')$ as

$$\begin{aligned} b_x(z,z') = & -\frac{1}{8\pi^6\rho(z)} \int_0^{\infty} d|\mathbf{x}_{\parallel} - \mathbf{x}'_{\parallel}| \\ & \times \int d\mathbf{k} \int d\mathbf{k}' \theta(k_F - |\mathbf{k}|) \theta(k_F - |\mathbf{k}'|) \\ & \times \Phi_{k,k'}(z,z') e^{-i(\mathbf{k}_{\parallel} - \mathbf{k}'_{\parallel})\cdot(\mathbf{x}_{\parallel} - \mathbf{x}'_{\parallel})}, \end{aligned} \tag{57}$$

By introducing the transforms $\mathbf{q} = \mathbf{k}_{\parallel} - \mathbf{k}'_{\parallel}$ and $\mathbf{K} = (\mathbf{k}_{\parallel} + \mathbf{k}'_{\parallel})/2$, one may rewrite $b_x(z,z')$ as

$$\begin{aligned} b_x(z,z') = & -\frac{1}{8\pi^6\rho(z)} \int_{-k_F}^{k_F} dk \int_{-k_F}^{k_F} dk' \Phi_{k,k'}(z,z') \\ & \times \int d\mathbf{q} F(q) \int_0^{\infty} d|\mathbf{x}_{\parallel} - \mathbf{x}'_{\parallel}| e^{-i\mathbf{q}\cdot(\mathbf{x}_{\parallel} - \mathbf{x}'_{\parallel})}, \end{aligned} \tag{58}$$

where the function $F(q)$ is defined as

$$F(q) = \int d\mathbf{K} \theta(\lambda - |\mathbf{K} + \mathbf{q}/2|) \theta(\lambda' - |\mathbf{K} - \mathbf{q}/2|). \tag{59}$$

By using Eq. (10) and further the following identity:

$$\int_0^{\infty} d|\mathbf{x}_{\parallel} - \mathbf{x}'_{\parallel}| J_0(q|\mathbf{x}_{\parallel} - \mathbf{x}'_{\parallel}|) = \frac{1}{q}, \tag{60}$$

Eq. (58) may be further rewritten as

$$b_x(z,z') = -\frac{1}{\pi^5\rho(z)}\int_0^{k_F} dk \int_0^{k_F} dk' \Phi_{k,k'}(z,z') \times \int_0^{\infty} dq\, F(q). \quad (61)$$

Derivation based on Eq. (61), detailed in Appendix D, yields the following result for $b_x(z,z')$:

$$b_x(z,z') = -\frac{16}{3\pi^5\rho(z)}[G(z,z') + G(z',z)], \quad (62)$$

where

$$G(z,z') = \int_0^{k_F} dk \int_k^{k_F} dk' \Phi_{k,k'}(z,z') \times \lambda\left[\mathbf{K}\left(\frac{\lambda'}{\lambda}\right)(\lambda'^2-\lambda^2) + \mathbf{E}\left(\frac{\lambda'}{\lambda}\right)(\lambda^2+\lambda'^2)\right]. \quad (63)$$

K and **E** are the complete elliptic integrals of the first and the second kinds, respectively:[28]

$$\mathbf{K}(t) = \int_0^1 \sqrt{\frac{1}{(1-t^2x^2)(1-x^2)}}\,dx, \quad (64)$$

$$\mathbf{E}(t) = \int_0^1 \sqrt{\frac{1-t^2x^2}{1-x^2}}\,dx. \quad (65)$$

We note that so far all results for $b_x(z,z')$ hold in general for arbitrary position z. Particularly, Eq. (62) evolves into the following asymptotic form for limiting large electron position z (see again Appendix D for the demonstration),

$$b_x(z\to\infty,z') = -\frac{\sqrt{k_F}\gamma}{c^{3/2}}\frac{1}{z^{3/2}}|\phi_{k_F}(z')|^2, \quad (66)$$

where

$$\gamma = \frac{20\sqrt{2}}{\pi^{5/2}}\int_0^1 dy(y+1)^{-7/2}[\mathbf{K}(\sqrt{y})(y-1) + \mathbf{E}(\sqrt{y})(y+1)]. \quad (67)$$

Equation (66) displays similarly the delocalization nature of the exchange hole. The amplitude of $b_x(z,z')$ decays as $\sim 1/z^{3/2}$, a little faster than that of $\rho_x(z,z')$ shown in Eq. (55).

V. ASYMPTOTIC STRUCTURE OF APPROXIMATE EXCHANGE POTENTIALS

The Slater potential $V_x^S(\mathbf{r})$ was proposed as an approximation to the orbital-dependent Hartree-Fock exchange potentials.[16] Upon the arrival of the KS-DFT, $V_x^S(\mathbf{r})$ was regarded naturally also as an approximation to the KS exchange potential $v_x(\mathbf{r})$. The large-distance structure of it at the metal surface is shown in Eq. (3) and discussed in Sec. III. In this section, we survey those of two of other approximate exchange potentials, the KLI potential $V_x^{\mathrm{KLI}}(\mathbf{r})$ and the HS potential $W_x(\mathbf{r})$. The former reads[18,19]

$$V_x^{\mathrm{KLI}}(\mathbf{r}) = V_x^S(\mathbf{r}) + V_x^{\triangle}(\mathbf{r}), \quad (68)$$

where

$$V_x^{\triangle}(\mathbf{r}) = \frac{2}{\rho(\mathbf{r})}\sum_i^{\mathrm{occ.}} |\phi_i(\mathbf{r})|^2\langle\phi_i|v_x - u_{xi}|\phi_i\rangle. \quad (69)$$

In passing, we mention that[19]

$$v_x(\mathbf{r}) = V_x^{\mathrm{KLI}}(\mathbf{r}) + V_x^{\mathrm{shift}}(\mathbf{r}), \quad (70)$$

and the component $V_x^{\mathrm{shift}}(\mathbf{r})$ defined as

$$V_x^{\mathrm{shift}}(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})}\sum_i^{\mathrm{occ}} [\phi_i^*(\mathbf{r})\,\nabla^2\,\psi_i(\mathbf{r}) - \psi_i(\mathbf{r})\,\nabla^2\,\phi_i^*(\mathbf{r})], \quad (71)$$

is sacrificed for the purpose of less calculation labor. [For convenience, the same symbols $V_x^{\triangle}(\mathbf{r})$ and $V_x^{\mathrm{shift}}(\mathbf{r})$ in Ref. 12 are adopted here.]

We first make a digression to comment on some bulk properties of $\psi_k(z)$ and $V_x^{\mathrm{KLI}}(z)$. The expression for $V_x^{\mathrm{shift}}(z)$ at the metal surface is

$$V_x^{\mathrm{shift}}(z) = \frac{1}{2\pi^2\rho(z)}\int_0^{k_F} dk\lambda^2 \times \left[\phi_k^*(z)\frac{\partial^2}{\partial z^2}\psi_k(z) - \psi_k(z)\frac{\partial^2}{\partial z^2}\phi_k(z)\right]. \quad (72)$$

On the other hand, in view of Eq. (31), one has

$$v_x(z=-\infty) = D_k^a = -\frac{k_F}{\pi} \quad (73)$$

and

$$u_{xk}(z=-\infty) = D_k^b. \quad (74)$$

It follows that the right-hand side of Eq. (27) vanishes. With the understanding that the homogeneous solution of $\psi_k(z)$ in Eq. (27) is excluded, one thus has

$$\psi_k(z) = 0 \quad \text{for} \quad z = -\infty. \quad (75)$$

Therefore $V_x^{\mathrm{shift}}(z)$, according to Eq. (72), vanishes in the metal bulk:

$$V_x^{\mathrm{shift}}(z) = 0 \quad \text{for} \quad z = -\infty, \quad (76)$$

and, consequently, $V_x^{\mathrm{KLI}}(z)$, according to Eq. (70), has the merit of possessing the same bulk limit as $v_x(z)$:

$$V_x^{\mathrm{KLI}}(z) = -\frac{k_F}{\pi} \quad \text{for} \quad z = -\infty. \quad (77)$$

We next return to the issue of the asymptotic behavior of $V_x^{\mathrm{KLI}}(z)$ in the classically forbidden region. $V_x^{\mathrm{KLI}}(z)$ is shown below to deviate strongly from $v_x(z)$ at large distance from the metal surface. To this end, we first write the expression for $V_x^{\triangle}(z)$:

$$V_x^{\triangle}(z) = \frac{1}{\pi^2\rho(z)}\int_0^{k_F} dk\lambda^2|\phi_k(z)|^2 D_k. \quad (78)$$

For limiting large z, $V_x^{\triangle}(z)$ turns out to have the form:

$$V_x^{\triangle}(z\to\infty) = \frac{\sqrt{\beta^2-1}}{2\pi}\frac{1}{z}\left[\ln\left(\frac{k_F z}{\sqrt{\beta^2-1}}\right) + C + 2\ln 2 - 1\right], \quad (79)$$

with $C = 0.577215$ the Euler constant. In obtaining Eq. (79), the following fact

$$D_k = \frac{1}{4\pi}(k_F-k)\left[1 - 2\ln\frac{k_F-k}{2k_F}\right] + o(k_F-k), \quad (80)$$

for small $k_F - k$, [which follows from Eq. (30)], has been employed. Equation (79) had also been reported in Ref. 12. Finally, Eq. (68), together with Eqs. (3) and (79), yields

$$V_x^{\mathrm{KLI}}(z\to\infty) = \frac{\sqrt{\beta^2-1}}{2\pi}\frac{1}{z}\left[\ln\left(\frac{k_F z}{\sqrt{\beta^2-1}}\right) + C + 2\ln 2 - 1\right] - 2\alpha_x\frac{1}{z}, \quad (81)$$

which has the leading form of $O(\ln z/z)$, and hence deviates from $v_x(z)$.

The HS potential $W_x(\mathbf{r})$[20] is defined as the work done in the Pauli field $\mathcal{E}_x(\mathbf{r})$ [$W_x(\mathbf{r})$ hence also known as the Pauli potential in the quantal density functional theory (Q-DFT)]:[29]

$$W_x(\mathbf{r}) = -\int_\infty^{\mathbf{r}} \mathcal{E}_x(\mathbf{r}')\cdot d\mathbf{l}' \quad (82)$$

and

$$\mathcal{E}_x(\mathbf{r}) = -\int \rho_x(\mathbf{r},\mathbf{r}')\bigtriangledown\frac{1}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'. \quad (83)$$

The asymptotic structure of $W_x(z)$ has been extensively investigated in Ref. 21, and one of the main results is

$$W_x(z) = -\alpha_W\frac{1}{z}, \quad (84)$$

where

$$\alpha_W = \frac{\beta^2-1}{\beta^2}\left\{\frac{\beta^2-2}{\beta^2} + \frac{2}{\pi\sqrt{\beta^2-1}} \times\left[1 - \frac{(\beta^2-1)\ln(\beta^2-1)}{\beta^2}\right]\right\}. \quad (85)$$

It might be helpful to mention the relation between $W_x(\mathbf{r})$ and $v_x(\mathbf{r})$:[30]

$$v_x(\mathbf{r}) = W_x(\mathbf{r}) - W_{tc}^{(1)}(\mathbf{r}), \quad (86)$$

where $W_{tc}^{(1)}(\mathbf{r})$ is the lowest-order correlation-kinetic component of $v_x(\mathbf{r})$. $W_x(\mathbf{r})$ has been well recognized as the component of $v_x(\mathbf{r})$ which arises purely from the exchange hole $\rho_x(\mathbf{r},\mathbf{r}')$.[20,30] Clearly, $W_{tc}^{(1)}(z)$ must also be long-ranged at the metal surface. This is in sharp contrast to its behavior in finite systems such as atoms and molecules in which $W_{tc}^{(1)}(\mathbf{r})$ decays in a rather short-ranged form of $\sim 1/r^5$.[26] We wish to further mention that it was shown in Ref. 21 that $W_x(z)$ deviates from $v_x(z)$ also in the metal bulk due to the contribution from $W_{tc}^{(1)}(z)$. Only in the LDA, $W_x(z)$ has the same bulk value of $-k_F/\pi$ as $v_x(z)$, as shown in Ref. 31. In this connection, we list the long-known fact for $V_x^S(z)$:

$$V_x^S(z) = -\frac{3k_F}{2\pi} \quad \text{for} \quad z = -\infty. \quad (87)$$

Therefore, strictly speaking, $V_x^{\mathrm{KLI}}(z)$ only, among all the approximate exchange potentials considered here, has the remarkable property with the same bulk value as that of $v_x(z)$.

Finally, we would make several comments on the results reported in Ref. 12. The large-distance structure of $v_x(z)$ was attributed solely to $V_x^{\triangle}(z)$ in Ref. 12, and, consequently, the conclusion $v_x(z)\sim \ln z/z$ was reached. On the other side, $V_x^{\mathrm{shift}}(z)$ was claimed to decay as $\sim\ln z/z^2$, and hence make no leading order contribution to $v_x(z)$.[12] On the contrary, we find that in fact,

$$V_x^{\mathrm{shift}}(z\to\infty) = -\frac{\sqrt{\beta^2-1}}{2\pi}\frac{1}{z}\left[\ln\left(\frac{k_F z}{\sqrt{\beta^2-1}}\right) + C + 2\ln 2 - 1\right] + \alpha_x\frac{1}{z}. \quad (88)$$

The leading order of $O(\ln z/z)$ therefore exactly cancels out in $v_x(z)$, resulting in a faster decay of $O(1/z)$. The discrepancy of $V_x^{\mathrm{KLI}}(z)$ from $v_x(z)$ in the classically forbidden region is also due to the ignored contribution [cf. Eq. (70)] from $V_x^{\mathrm{shift}}(z)$.

VI. ASYMPTOTIC STRUCTURES OF $v_x(z)$, $V_x^S(z)$, $V_x^{\mathrm{KLI}}(z)$, AND $W_x(z)$ AT THE SLAB SURFACE

So far, we have considered only the metal surface with the semi-infinite geometry. A great deal of work of the electronic structure at the metal surface has been carried out on a jellium slab instead. We shall consider the slab case in this section. To this end, we first mention two studies in which the asymptote of the xc potential in the classically forbidden region was addressed as one of the key issues. One was reported in Ref. 11, mentioned previously in Introduction in which it was claimed that $v_x(z\to\infty) = -1/z$ asymptotically. Numerical calculation in Ref. 32 based on the GW approximation to the electron exchange-correlation self-energy Σ_{xc}, however, yielded the different result: $v_x(z)\sim -1/z^2$ and $v_c(z)\sim -1/(4z)$. Both studies were performed on the slab surface. Part of our effort in this section will be devoted to shedding some light on these results. In fact, it is found that the asymptotic behavior of $v_x(z)$, $V_x^S(z)$, $V_x^{\mathrm{KLI}}(z)$, and $W_x(z)$ depends critically on the width of the slab.

We consider a metal slab with a typical width not exceedingly larger than λ_F or, in other words, comparable to or smaller than λ_F, where λ_F is the bulk Fermi wavelength. In this case, the discreteness of the eigenenergies of the electron in the slab must be taken into account. The system can be regarded virtually as a finite one, and the well-known conclusion for the finite system that $v_x(\mathbf{r})\sim -1/r$ mentioned in Sec. III therefore holds. As a matter of fact, this already explains the result in Eq. (4). More explicitly, the Dirac density matrix has the following well-known asymptotic form:

$$\gamma_s(\mathbf{r},\mathbf{r}') = 2\phi_m(\mathbf{r})\phi_m^*(\mathbf{r}') \quad \text{for} \quad z\to\infty. \quad (89)$$

From Eq. (20), by the use of multipole expansion argument for the Coulomb interaction, which evidently is applicable here, one immediately has

$$u_{xm}(z\to\infty) = -\frac{1}{z}. \quad (90)$$

The notation m clearly has the same meaning as k_F but is used instead to emphasize the discreteness of the eigenenergies. Equation (4) then follows from Eq. (42).

Additional care is needed in the above discussion for $v_x(z)$ in that it is not fully rigorous since actually $D_{k_F}\neq 0$ in the case of the slab metal surface. Equation (42) therefore is not valid and we in effect must resort to Eq. (41) instead. This point will get further refined near the end of this section [cf. Eq. (103) below].

In any way, the fact that the planar freedom remains extending to infinity is essentially irrelevant in the present discussion. The key point is the dominant behavior of the highest occupied orbital and localization of the exchange hole near the finite system. The slab clearly fails to catch the continuity feature of the electron eigenenergies, which is essential to the semi-infinite metal surface. Equation (4) thus has limitation in that it is valid only for the slab surface and can not be naively extrapolated for the semi-infinite surface. Nevertheless, a numerical demonstration of Eq. (4) for the slab surface like that in Ref. 11 is still quite valuable.

The effects of the delocalization of the exchange hole are negligible in the case of the slab surface. $V_x^S(z)$ consequently has the same asymptotic form as $v_x(z)$:

$$V_x^S(z \to \infty) = -\frac{1}{z} \tag{91}$$

at limiting large z. Correspondingly, $\epsilon_x(z \to \infty) = -\rho(z)/2z$. On the other hand, $\rho(z)$ has the following asymptotic form:

$$\rho(z \to \infty) = 2|\phi_{k_F}(z)|^2. \tag{92}$$

The reader is referred to Eq. (51) for comparison. Equation (91) can be readily obtained from Eq. (48) via keeping the leading-order term in the multipole expansion for the Coulomb interaction. It is basically just another illustration of the well-known result $V_x^S(\mathbf{r} \to \infty) = -1/r$ for a finite system. Indeed, it follows from Eqs. (14) and (89) that, for $z \to \infty$,

$$\rho_x(\mathbf{r},\mathbf{r}') = |\phi_m(\mathbf{r}')|^2. \tag{93}$$

Equation (91) immediately follows from Eqs. (48) and (93). Similarly, Eq. (83) together with Eq. (93) yields

$$\mathcal{E}_x(\mathbf{r}) = -\frac{1}{z^2}\mathbf{e}_z, \tag{94}$$

and it then follows from Eq. (82) that

$$W_x(z) = -\frac{1}{z}. \tag{95}$$

$V_x^{\mathrm{KLI}}(z)$ possesses the same asymptotic form [but see also Eq. (101)]. Only in this case, $V_x^{\mathrm{shift}}(z)$, which now decays exponentially at large z, is much smaller than $v_x^{\triangle}(z)$, which in contrast approaches a nonzero constant

$$v_x^{\triangle}(z) = D_m \quad \text{for} \quad z \to \infty. \tag{96}$$

We note once again that k_F has the same meaning as m. The fact that $D_{\mathbf{k}}|_{|\mathbf{k}|=k_F} = D_{k_F}$ guarantees no ambiguity in the meaning of D_m.

In summary, Eq. (90) [or Eq. (91)] can be obtained for the slab case via the argument for the multipole expansion of the Coulomb interaction. The metal-surface feature of the slab plays no crucial role at this point. Therefore it is not necessary to resort to detailed derivations based on Eq. (46) [or Eq. (49)]. [Equations (46) and (49) hold for both the cases of the semi-infinite and the slab metal surfaces.] Nevertheless, such derivations turn out to be amazingly simple (due of course also to the feature of the finiteness of the system). In the meanwhile, they could be fairly illuminating. We therefore include one in the following mainly for the purpose of illustration. To this end, we first copy Eq. (46) below with appropriate modifications in the form for the slab case:

$$u_{xk_F}(z) = -\frac{2}{L\phi_{k_F}(z)}\sum_k^{\mathrm{occ}} \lambda\phi_k(z)\int_{-L}^{0} dz'\phi_k^*(z')\phi_{k_F}(z') \times \int_0^{\infty} dr'_{\parallel}\frac{1}{\sqrt{(z-z')^2+r_{\parallel}'^2}}J_1(\lambda r'_{\parallel}). \tag{97}$$

Only the main domain ($-L \leqslant z' \leqslant 0$) has been taken into account for the integral over z', which is clearly justified. Since $z \gg z'$, the denominator $\sqrt{(z-z')^2+r_{\parallel}'^2}$ can be readily replaced by $\sqrt{z^2+r_{\parallel}'^2}$. The dominant contribution to the integration over k arises from the region of $k_F - k \sim 1/z$, and accordingly $\lambda \gg k_F - k$. On the other hand, the dominant contribution to the integration over $r'_{\parallel}$ arises from the region of $0 \leqslant r'_{\parallel} \lesssim O(\lambda^{-1})$ since $J_1(\infty) = 0$. Correspondingly, $r'_{\parallel} \ll z$ and hence $\sqrt{z^2+r_{\parallel}'^2}$ can be further replaced by z. The integration over $r'_{\parallel}$ then turns out simply to be

$$\int_0^{\infty} dr'_{\parallel}J_1(\lambda r'_{\parallel}) = \frac{1}{\lambda}. \tag{98}$$

Equation (97) as a consequence, becomes

$$u_{xk_F}(z \to \infty) = -\frac{2}{zL\phi_{k_F}(z)}\sum_k^{\mathrm{occ}}\phi_k(z)\int_{-L}^{0} dz'\phi_k^*(z')\phi_{k_F}(z'). \tag{99}$$

One then employs the following equation:

$$\int_{-L}^{0} dz'\phi_k^*(z')\phi_{k_F}(z') = \frac{L}{2}\delta_{k,k_F}. \tag{100}$$

Equation (90) follows (with m equivalent to k_F). Equation (91) can be obtained from Eq. (49) in a similar manner.

Notice that, strictly speaking,

$$V_x^{\mathrm{KLI}}(z \to \infty) = D_m - \frac{1}{z}, \tag{101}$$

where the term of the constant D_m arises from the $V_x^{\triangle}(z)$ component on the right-hand side of Eq. (68), as shown in Eq. (96). Furthermore, in accordance to the claims made for finite systems in Ref. 15, such type of constant might also possibly occur in $v_x(z)$, since as mentioned above the slab can be regarded essentially as a finite system. Indeed, since $D_{k_F} \neq 0$ for the slab surface, one should resort to Eq. (41) instead of Eq. (42). Equation (41) in fact can be understood as one of the special cases of the following general result:

$$v_x(\mathbf{r}) = u_{xm}(\mathbf{r}) + D_m, \tag{102}$$

proposed for the finite system in Ref. 15. In the light of Eq. (90), we consequently have

$$v_x(z \to \infty) = D_m - 1/z, \tag{103}$$

instead of Eq. (4). Therefore, strictly speaking, $v_x(\infty) \neq 0$ now [see also the discussions in the next paragraph.] Equation (103) can be alternatively obtained from Eq. (70) and Eq. (101) together with the fact that $V_x^{\mathrm{shift}}(z \to \infty)$ vanishes exponentially.

Finally, we remark that $V_x^S(\infty) = 0$ in any case. On the other hand, Eq. (82) automatically guarantees $W_x(\infty) = 0$. Furthermore, D_m can be made to vanish so that $v_x(\infty) = 0$ by shifting $v_x(\mathbf{r})$ in the finite system[15] or the slab of the present case. It is exactly in this sense that we justify the result in Eq. (4). However, we wish also to mention that it remains unclear whether $v_x(\infty)$ can always be simultaneously shifted to be zero in the exact (full) KS scheme in which one has already adopted $v_{\rm xc}(\infty) = 0$. The remarkable fact is that D_m in Eq. (103) evolves into $D_{\mathbf{k}}$ at $|\mathbf{k}| = k_F$ of Eq. (35) and vanishes for the semi-infinite metal surface. Thus for the semi-infinite metal surface one has definitely $v_{\rm xc}(\infty) = 0$ and $v_x(\infty) = 0$.

VII. CONCLUSIONS

By the use of the OEP method, we have established an identity between the planar-momentum averaged orbital-dependent exchange potential $u_{xk_F}(z)$ and the KS exchange potential $v_x(z)$ in the classically forbidden region of the metal surface. Based on it, the asymptotic form of $v_x(z)$ at large distance from the metal surface has been investigated. The result is $v_x(z \to \infty) = -\alpha_x/z$, which resolves the controversy raised recently in the literature. The point that $v_{\rm xc}(\infty) = 0$ and $v_x(\infty) = 0$ hold simultaneously gets emphasized and carefully elucidated. The asymptotic form of the Slater exchange potential $V_x^S(z \to \infty) = -2\alpha_x/z$ is also verified. The result for $v_x(z)$ and that for $V_x^S(z)$ were initially proposed in Ref. 8, and the former was verified subsequently in Ref. 10. The further confirmation in the present work indicates beyond doubt that they are correct and the issue is finally settled. Furthermore, the structure of the exchange hole has been examined, and especially the delocalization nature of it for an electron far outside the metal surface has been demonstrated. It is exactly such delocalization that gives rise to the quite nontrivial asymptotic behavior of $v_x(z)$. In addition, the asymptotic structure of the approximate KLI exchange potential $V_x^{\rm KLI}(z)$ and HS exchange potential $W_x(z)$ at large z has also been surveyed, which are of the forms $V_x^{\rm KLI}(z \to \infty) \sim \ln z/z$ and $W_x(z \to \infty) \sim -\alpha_W/z$, respectively.

As mentioned in Introduction, common wisdom favors the belief that the full Kohn-Sham exchange-correlation potential $v_{\rm xc}(z)$ decays like the classical image potential at large distance from the metal surface. Doubt, however, has been cast on it in Ref. 10 in which the asymptote of $v_c(z)$ was also studied. It was shown in Ref. 10 that the asymptotic form of $v_{\rm xc}(z)$ is not the same as the classical image potential. Recent progress on the asymptote of $v_c(z)$ has also been made in Ref. 33. Unfortunately, approximations have been employed in the calculations for $v_c(z)$ in both of Refs. 10 and 33 and it is not clear whether they are fully justified. The subject of the asymptote of $v_{\rm xc}(z)$ thus remains not fully settled.

The asymptotic behavior of the exchange potential at the metal slab surface has also been investigated. It is shown that asymptotically $v_x(z)$ as well as $V_x^S(z)$, $V_x^{\rm KLI}(z)$, and $W_x(z)$ depends critically on the width of the slab. In particular, if the width is comparable to or smaller than λ_F, the slab can be essentially regarded as a finite system and asymptotically $v_x(z) = -1/z$. $V_x^S(z)$, $V_x^{\rm KLI}(z)$, and $W_x(z)$ all have this same form. The exchange energy density $\epsilon_x(z)$ correspondingly approaches asymptotically $-\rho(z)/2z$. All these facts are inherently due to the localization of the exchange hole in the finite system. While by definition $V_x^S(z)$ and $W_x(z)$ vanish in the classically forbidden region of both the semi-infinite and the slab metal surfaces, a careful analysis reveals that the $-1/z$ term commences only to the second-order contribution to $v_x(z)$ and $V_x^{\rm KLI}(z)$ and, actually, both $v_x(z \to \infty)$ and $V_x^{\rm KLI}(z \to \infty)$ approach a nonzero constant, i.e., $v_x(\infty) = V_x^{\rm KLI}(\infty) = D_m \neq 0$. The constant D_m however can always be made to vanish in th exchange-only self-consistent calculations by shifting $v_x(z)$. It is precisely in this sense that one has the result of Eq. (4).

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APPENDIX A: PROOF FOR EQ. (24)

We substitute Eq. (12), together with Eq. (6), into Eq. (20). This results in

$$u_{x\mathbf{k}}(\mathbf{r}) = -\frac{1}{\pi^2\phi_{\mathbf{k}}(\mathbf{r})}\sqrt{\frac{2}{AL}}\int_0^{k_F} dk'\lambda'\phi_{k'}(z) \times \int_{-\infty}^{\infty} dz'\phi_{k'}^*(z')\phi_k(z') \times \int d\mathbf{x}'_\parallel e^{i\mathbf{k}_\parallel\cdot\mathbf{x}'_\parallel}\frac{J_1(\lambda'|\mathbf{x}_\parallel - \mathbf{x}'_\parallel|)}{|\mathbf{r} - \mathbf{r}'||\mathbf{x}_\parallel - \mathbf{x}'_\parallel|}. \quad \text{(A1)}$$

Making the transform $\mathbf{r}'_\parallel = \mathbf{x}_\parallel - \mathbf{x}'_\parallel$ in the above equation and making the use of Eq. (6) once again, we establish Eq. (24) explicitly with the following expression:

$$u_{x\mathbf{k}}(z) = -\frac{1}{\pi^2\phi_k(z)}\int_0^{k_F} dk'\lambda'\phi_{k'}(z)\int_{-\infty}^{\infty} dz'\phi_{k'}^*(z')\phi_k(z') \times \int d\mathbf{r}'_\parallel e^{i\mathbf{k}_\parallel\cdot\mathbf{r}'_\parallel}\frac{J_1(\lambda' r'_\parallel)}{r'_\parallel\sqrt{(z-z')^2 + r'^2_\parallel}}. \quad \text{(A2)}$$

Further algebra then yields

$$u_{x\mathbf{k}}(z) = -\frac{2}{\pi\phi_k(z)}\int_0^{k_F} dk'\lambda'\phi_{k'}(z)\int_{-\infty}^{\infty} dz'\phi_{k'}^*(z')\phi_k(z') \times \int_0^{\infty} dr'_\parallel \frac{J_0(k_\parallel r'_\parallel)J_1(\lambda' r'_\parallel)}{\sqrt{(z-z')^2 + r'^2_\parallel}}. \quad \text{(A3)}$$

APPENDIX B: DERIVATION FOR EQ. (47)

It is not difficult to see that, for limiting large z, the leading contribution to the integral over k on the right-hand side of Eq. (46) arises from the region $k_F - k \sim 1/z$, and that to the integral over z', on the other side, from the region of the metal bulk. Accordingly, $\lambda \gg (k_F - k)$ and hence $|z - z'| \gg 1/\lambda$. Since $J_1(\infty) = 0$ and accordingly the dominant contribution to the integral over $r'_\parallel$ arises from the region of $0 \leqslant r'_\parallel \lesssim O(\lambda^{-1})$, one has $|z - z'| \gg r'_\parallel$ in the integral over $r'_\parallel$ in Eq. (46). Thus

it follows that

$$\int_0^\infty dr'_\parallel \frac{1}{\sqrt{(z-z')^2+r'^2_\parallel}} J_1(\lambda r'_\parallel) = \frac{1}{|z-z'|}\int_0^\infty dr'_\parallel J_1(\lambda r'_\parallel) = \frac{1}{\lambda|z-z'|}. \quad \text{(B1)}$$

Correspondingly,

$$u_{xk_F}(z\to\infty) = -\frac{2}{\pi\phi_{k_F}(z)}\int_0^{k_F} dk\phi_k(z) \times \int_{-\infty}^{\infty} dz' \frac{1}{|z-z'|}\phi^*_k(z')\phi_{k_F}(z'). \quad \text{(B2)}$$

We next define

$$\Theta_{k,k'}(z) = 2\int_{-\infty}^{\infty} dz' \frac{1}{|z-z'|}\phi^*_{k'}(z')\phi_k(z'). \quad \text{(B3)}$$

Since, as just mentioned, the integral over z' arises mainly from the bulk region, one can make the use of Eq. (8a) for the orbitals in the above expression and it follows that

$$\Theta_{k,k'}(z) = \int_{-\infty}^{-d} \frac{dz'}{z-z'} \ [\cos(k_- z' + \delta_-) - \cos(k_+ z' + \delta_+)], \quad \text{(B4)}$$

where $k_\pm = k \pm k'$, $\delta_\pm = \delta(k) \pm \delta(k')$, and $-d$ stands for a negative position near the surface whose exact value is irrelevant for $z \gg d$. Indeed,

$$\Theta_{k,k'}(z) = \int_{-\infty}^{z+d} \frac{dz'}{z'}\{\cos[k_-(z-z')+\delta_-)] - \cos[(k_+(z-z')+\delta_+)]\}, \quad \text{(B5)}$$

and the upper limit of the integral, $z+d$, can be readily replaced by z. Thus one has

$$\begin{aligned}\Theta_{k,k'}(z) = {} & \cos(k_- z+\delta_-)\int_z^\infty \frac{dz'}{z'}\cos(k_- z') \\ & + \sin(k_- z+\delta_-)\int_z^\infty \frac{dz'}{z'}\sin(k_- z') \\ & - \cos(k_+ z+\delta_+)\int_z^\infty \frac{dz'}{z'}\cos(k_+ z') \\ & - \sin(k_+ z+\delta_+)\int_z^\infty \frac{dz'}{z'}\sin(k_+ z') \end{aligned} \quad \text{(B6)}$$

or

$$\begin{aligned}\Theta_{k,k'}(z) = {} & -\cos(k_- z+\delta_-)ci(k_- z) - \sin(k_- z+\delta_-)si(k_- z) \\ & + \cos(k_+ z+\delta_+)ci(k_+ z) + \sin(k_+ z+\delta_+)si(k_+ z), \end{aligned} \quad \text{(B7)}$$

where si and ci are the sine integral and cosine integral, respectively,[28]

$$si(x) = -\int_x^\infty \frac{dt}{t}\sin t, \quad \text{(B8)}$$

$$ci(x) = -\int_x^\infty \frac{dt}{t}\cos t. \quad \text{(B9)}$$

For $z\to\infty$, the third and fourth terms on the right-hand side of Eq. (B7) will be demonstrated at the end of this appendix to make only higher-order contribution to $u_{xk_F}(z)$. Consequently, these terms can be ignored. Hence one comes to

$$\Theta_{k,k'}(z\to\infty) = -\cos(k_- z+\delta_-)ci(k_- z) - \sin(k_- z+\delta_-)si(k_- z). \quad \text{(B10)}$$

We now substitute Eqs. (B3) and (B10) (with k replaced by k_F and k' by k) into Eq. (B2), and obtain

$$u_{xk_F}(z\to\infty) = \frac{1}{\pi\phi_{k_F}(z)}\int_0^{k_F} dk\phi_k(z)[\cos(a+\tilde\delta_-)ci(a) + \sin(a+\tilde\delta_-)si(a)], \quad \text{(B11)}$$

where $\tilde\delta_- = \delta(k_F) - \delta(k)$ and $a = (k_F - k)z$. Again, as mentioned above, for large z, the dominant contribution to the integral in the above equation arises from the region $k_F - k \sim 1/z$. Correspondingly, $\tilde\delta_- \to 0$ and $\phi_k(z) = \phi_{k_F}(z)\, e^{-ca}$, where $c = 1/\sqrt{\beta^2-1}$. Therefore we finally obtain Eq. (47) with

$$\alpha_x = -\frac{1}{\pi}\int_0^\infty da e^{-ca}[ci(a)\cos a + si(a)\sin a]. \quad \text{(B12)}$$

The value of α_x given in Eq. (2) may be obtained via carrying out the integral in Eq. (B12):[28]

$$\int_0^\infty da e^{-ca}[ci(a)\cos a + si(a)\sin a] = -\frac{\pi + 2c\ln c}{2(1+c^2)}. \quad \text{(B13)}$$

Solely to draw a connection with the calculations performed in an alternate approach in Ref. 10, we mention the following identity:[28]

$$\int_0^\infty du \frac{u}{u^2+a^2}e^{-u} = -ci(a)\cos a - si(a)\sin a. \quad \text{(B14)}$$

Were the third and fourth terms in Eq. (B7) taken into account, they would have made the following contribution to $u_{xk_F}(z)$:

$$-\frac{1}{c\pi z}\{\cos[2k_F z + \delta(k_F)]ci(2k_F z) + \sin[2k_F z + \delta(k_F)]si(2k_F z)\}. \quad \text{(B15)}$$

Since $ci(2k_F z) \to 0$ and $si(2k_F z) \to 0$ as $z\to\infty$, this contribution is therefore of the order $o(1/z)$ and the neglect of these terms in Eq. (B7) is thus justified.

APPENDIX C: VERIFICATION OF EQ. (3)

The $\phi_k(z)$ is in fact real, and hence the integrals over k and k' in Eq. (49) are clearly symmetric. Accordingly, we change

the domain of the k' integration in Eq. (49) to $\int_0^k dk'$ combined with a corresponding double. Similar arguments to those at the beginning of Appendix B then lead, for $z \to \infty$, to

$$\int_0^\infty dr'_\parallel \frac{1}{r'_\parallel \sqrt{(z-z')^2 + r'^2_\parallel}} J_1(\lambda r'_\parallel) J_1(\lambda' r'_\parallel) = \frac{1}{|z-z'|} \int_0^\infty dt \frac{1}{t} J_1(t) J_1(\lambda' t/\lambda) = \frac{\lambda}{2\lambda'|z-z'|}. \tag{C1}$$

Thus it follows from Eq. (49) that, for $z \to \infty$,

$$V_x^S(z) = -\frac{4}{\pi^3 \rho(z)} \int_0^{k_F} dk \phi_k(z) \lambda^2 \int_0^k dk' \phi^*_{k'}(z) \times \int_{-\infty}^\infty dz' \frac{1}{|z-z'|} \phi^*_{k'}(z') \phi_k(z'). \tag{C2}$$

Making the use of Eq. (B3) in the preceding equation yields, for $z \to \infty$, further

$$V_x^S(z) = -\frac{2}{\pi^3 \rho(z)} \int_0^{k_F} dk \phi_k(z) \lambda^2 \int_0^k dk' \phi^*_{k'}(z) \Theta_{k',k}(z). \tag{C3}$$

Clearly, the third and fourth terms in Eq. (B7) for $\Theta_{k',k}(z)$ can be ignored once again. Accordingly, Eq. (B10) for $\Theta_{k',k}(z)$ is substituted into Eq. (C3) instead. We make further the transform of the integral variable $k' = k - b/z$. It follows then that, for $z \to \infty$,

$$V_x^S(z) = \frac{2}{\pi^3 \rho(z)} \int_0^{k_F} dk |\phi_k(z)|^2 \lambda^2 \times \int_0^\infty db e^{-cb} [ci(b) \cos b + si(b) \sin b]. \tag{C4}$$

We next compare the above equation with Eq. (B12) to obtain Eq. (3). In doing so, the expression (13) for $\rho(z)$ has also been employed.

APPENDIX D: DERIVATIONS FOR EQS. (55), (62), AND (66)

For limiting large z, the leading-order contribution to the integral over k' on the right-hand side of Eq. (54) arises from the region of $k' \to k$, and hence we have

$$\rho_x(z,z') = -\frac{4}{\pi^3 z \rho(z)} \int_0^{k_F} dk \lambda^2 \frac{\kappa}{k} \phi^*_k(z) \phi_k(z') \phi_k(z) \phi^*_k(z'). \tag{D1}$$

Similarly, the contribution to the integral over k arises from the region of $k \to k_F$. Therefore

$$\rho_x(z,z') = -\frac{4}{\pi^3 z \rho(z)} \frac{1}{c} |\phi_{k_F}(z')|^2 \int_0^{k_F} dk \lambda^2 |\phi_k(z)|^2. \tag{D2}$$

We then make the use of the expression (13) for $\rho(z)$. Equation (55) follows.

We next present the derivation leading to Eqs. (62) and (66). The explicit expression for $F(q)$ has been reported in Refs. 8 and 10 as

$$F(q) = \pi \lambda_<^2 \theta(\lambda_> - \lambda_< - q) + \theta(\lambda_> + \lambda_< - q) \times \theta(q - \lambda_> + \lambda_<) \{\pi \lambda_<^2 \theta[(\lambda_>^2 - \lambda_<^2)^{1/2} - q] + S_{\lambda_>}(q) + S_{\lambda_<}(q)\}, \tag{D3}$$

where $\lambda_>$ ($\lambda_<$) is the larger (smaller) one of λ and λ', respectively. In Eq. (D3),

$$S_\lambda(q) = \lambda^2 \tan^{-1} \frac{(\lambda^2 - X_\lambda^2)^{1/2}}{X_\lambda} - X_\lambda (\lambda^2 - X_\lambda^2)^{1/2}, \tag{D4}$$

$$S_{\lambda'}(q) = S_\lambda(q)|_{\lambda \to \lambda'}, \tag{D5}$$

and

$$X_\lambda(q) = \frac{1}{2} \left(q + \frac{\lambda^2 - \lambda'^2}{q^2} \right), \tag{D6}$$

$$X_{\lambda'}(q) = \frac{1}{2} \left(q - \frac{\lambda^2 - \lambda'^2}{q^2} \right). \tag{D7}$$

The fact that the integral $\int_0^\infty dq F(q)$ can be carried out analytically is the key point in obtaining the neat final expressions (62) and (66) for $b_x(z,z')$. To this end, we write it as

$$\int_0^\infty dq F(q) = \int_0^{\sqrt{\lambda_>^2 - \lambda_<^2}} dq \pi \lambda_<^2 + \int_{\lambda_> - \lambda_<}^{\lambda_> + \lambda_<} dq [S_{\lambda_>}(q) + S_{\lambda_<}(q)]. \tag{D8}$$

The first integral on the right-hand side of the above equation is trivial. After performing a partial integration over q in the second one, we come to

$$\int_0^\infty dq F(q) = -\int_{\lambda_> - \lambda_<}^{\lambda_> + \lambda_<} dq \frac{\partial}{\partial q} [S_{\lambda_>}(q) + S_{\lambda_<}(q)]. \tag{D9}$$

We caution the reader that the function $S_{\lambda_>}(q) + S_{\lambda_<}(q)$ has a discontinuity at $q = \sqrt{\lambda_>^2 - \lambda_<^2}$:

$$S_{\lambda_>}(\sqrt{\lambda_>^2 - \lambda_<^2}_-) + S_{\lambda_<}(\sqrt{\lambda_>^2 - \lambda_<^2}_-) = -\frac{\pi}{2} \lambda_<^2, \tag{D10}$$

$$S_{\lambda_>}(\sqrt{\lambda_>^2 - \lambda_<^2}_+) + S_{\lambda_<}(\sqrt{\lambda_>^2 - \lambda_<^2}_+) = \frac{\pi}{2} \lambda_<^2. \tag{D11}$$

Care therefore is needed in obtaining Eq. (D9). We next list the following properties:

$$\lambda_>^2 - X_{\lambda_>}^2 = \lambda_<^2 - X_{\lambda_<}^2 \tag{D12}$$

and

$$\frac{\partial}{\partial q} S_{\lambda_>}(q) = \frac{\partial}{\partial q} S_{\lambda_<}(q) = -\sqrt{\lambda_<^2 - X_{\lambda_<}^2}. \tag{D13}$$

They are found to be useful in our further simplifying Eq. (D9) to

$$\int_0^\infty dq F(q) = 2 \int_{\lambda_> - \lambda_<}^{\lambda_> + \lambda_<} dq q (\lambda_<^2 - X_{\lambda_<}^2)^{1/2}. \tag{D14}$$

Equation (D14) is rewritten trivially as

$$\int_0^\infty dqF(q) = 2\int_{\lambda_>-\lambda_<}^{\sqrt{\lambda_>^2-\lambda_<^2}} dqq\left(\lambda_<^2 - X_{\lambda_<}^2\right)^{1/2} + 2\int_{\sqrt{\lambda_>^2-\lambda_<^2}}^{\lambda_>+\lambda_<} dqq\left(\lambda_<^2 - X_{\lambda_<}^2\right)^{1/2}. \quad \text{(D15)}$$

The right-hand side of Eq. (D15) can be further simplified via the following transform in the integrals:

$$x = \frac{1}{\lambda_<}\left(\lambda_<^2 - X_{\lambda_<}^2\right)^{1/2}. \quad \text{(D16)}$$

Under this transform,

$$\begin{aligned} X_{\lambda_<} &= -\lambda_<\sqrt{1-x^2}, \\ q &= \sqrt{\lambda_>^2 - \lambda_<^2 x^2} - \lambda_<\sqrt{1-x^2} \end{aligned} \quad \text{(D17)}$$

in the first integral on the right-hand side of Eq. (D15), but

$$\begin{aligned} X_{\lambda_<} &= \lambda_<\sqrt{1-x^2}, \\ q &= \sqrt{\lambda_>^2 - \lambda_<^2 x^2} + \lambda_<\sqrt{1-x^2} \end{aligned} \quad \text{(D18)}$$

in the second one. The resultant expression is

$$\int_0^\infty dqF(q) = 4\lambda_<^2\int_0^1 dxx^2\frac{\lambda_>^2 + \lambda_<^2(1-2x^2)}{\sqrt{(\lambda_>^2 - \lambda_<^2x^2)(1-x^2)}}. \quad \text{(D19)}$$

The preceding integral could be efficiently evaluated numerically. We here prefer to express it in terms of complete elliptic integrals. To this end, we cite the following relations ($t \geqslant 1$):[28]

$$\begin{aligned} \int_0^1 dxx^2\frac{1}{\sqrt{(t^2-x^2)(1-x^2)}} &= t\left[F\left(\frac{\pi}{2},\frac{1}{t}\right) - E\left(\frac{\pi}{2},\frac{1}{t}\right)\right] \\ &= t\left[\mathbf{K}\left(\frac{1}{t}\right) - \mathbf{E}\left(\frac{1}{t}\right)\right] \end{aligned} \quad \text{(D20)}$$

and

$$\begin{aligned} &\int_0^1 dxx^4\frac{1}{\sqrt{(t^2-x^2)(1-x^2)}} \\ &= \frac{1}{3}t\left[(2t^2+1)F\left(\frac{\pi}{2},\frac{1}{t}\right) - 2(t^2+1)E\left(\frac{\pi}{2},\frac{1}{t}\right)\right] \\ &= \frac{1}{3}t\left[(2t^2+1)\mathbf{K}\left(\frac{1}{t}\right) - 2(t^2+1)\mathbf{E}\left(\frac{1}{t}\right)\right], \end{aligned} \quad \text{(D21)}$$

where F and E are the elliptic integrals of the first and the second kinds, respectively. Substituting these relations into Eq. (D19), one has

$$\int_0^\infty dqF(q) = \frac{4\lambda_>}{3}\left[\mathbf{K}\left(\frac{\lambda_<}{\lambda_>}\right)(\lambda_<^2 - \lambda_>^2) + \mathbf{E}\left(\frac{\lambda_<}{\lambda_>}\right)(\lambda_<^2 + \lambda_>^2)\right]. \quad \text{(D22)}$$

Further substitution of Eq. (D22) into Eq. (61) then leads to

$$\begin{aligned} b_x(z,z') = &-\frac{4}{3\pi^5\rho(z)}\int_0^{k_F} dk\int_k^{k_F} dk' \\ &\times[\Phi_{k,k'}(z,z') + \Phi_{k',k}(z,z')] \\ &\times\lambda\left[\mathbf{K}\left(\frac{\lambda'}{\lambda}\right)(\lambda'^2 - \lambda^2) + \mathbf{E}\left(\frac{\lambda'}{\lambda}\right)(\lambda^2 + \lambda'^2)\right]. \end{aligned} \quad \text{(D23)}$$

Equation (62) follows from the symmetry property $\Phi_{k,k'}(z,z') = \Phi_{k',k}(z',z)$.

We next make the variable transform $y = \lambda'^2/\lambda^2$ in Eq. (63) to obtain, for $z \to \infty$,

$$\begin{aligned} G(z,z') = \phi_{k_F}(z)|\phi_{k_F}(z')|^2\int_0^{k_F} dk\lambda^5\phi_k^*(z) \\ \times\int_0^1\frac{dy}{2\sqrt{k_F^2 - \lambda^2 y}}e^{-c(k_F - \sqrt{k_F^2-\lambda^2 y})z} \\ \times[\mathbf{K}(\sqrt{y})(y-1) + \mathbf{E}(\sqrt{y})(y+1)]. \end{aligned} \quad \text{(D24)}$$

Further transform $x = (k_F - k)z$ then yields

$$G(z\to\infty,z') = \frac{3\pi^3}{16}k_F^{3/2}\gamma(cz)^{-7/2}\left|\phi_{k_F}(z)\right|^2\left|\phi_{k_F}(z')\right|^2, \quad \text{(D25)}$$

where

$$\begin{aligned} \gamma = \frac{32\sqrt{2}}{3\pi^3}c^{7/2}\int_0^\infty dx\int_0^1 dye^{-cx(y+1)}x^{5/2} \\ \times[\mathbf{K}(\sqrt{y})(y-1) + \mathbf{E}(\sqrt{y})(y+1)]. \end{aligned} \quad \text{(D26)}$$

Finally, we substitute Eq. (D25) into Eq. (62) and apply the identity

$$\int_0^\infty dxx^{5/2}e^{-c(y+1)x} = \frac{15}{8}\sqrt{\pi}[c(y+1)]^{-7/2} \quad \text{(D27)}$$

to Eq. (D26). The result is the expressions of (66) and (67). In doing so, we have also made the use of Eq. (51).

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