Universal Exchange-Correlation Surface Asymptotics: Metal Slabs Versus Semi-infinite Metal Surfaces

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Density-functional theory is well known to rely on approximations to the *unknown* exchange-correlation xc) energy functional, which can be constructed from the satisfaction of a number of known properties. One of those properties is the asymptotic behavior of exchange and correlation in localized or extended many-electron systems. However, the actual asymptotics of the xc energy and potential in the vacuum region of a metal surface have remained elusive over the years. Here, we report what we consider to be a final word for the asymptotics of the xc energy per particle $\varepsilon_{xc}[n](z)$ and the xc Kohn-Sham potential $v_{xc}[n](z)$ in the vacuum side of both an *extended* semi-infinite metal and a *localized* metal slab, which are always *universal* i.e., electron-density independent), negative, and inversely proportional to the distance from the surface. We find that, contrary to previous conclusions by other authors, while for extended systems the asymptotics are dominated by a type of correlation, for metal slabs they are dominated by exchange, as in the case of systems that are finite in all directions, like atoms, molecules, and metal clusters.

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The asymptotics of the exchange-correlation xc) energy per particle $\varepsilon_{xc}[n](z)$ and xc Kohn-Sham KS) potential $v_{xc}[n](z)$ of density-functional theory DFT) at metal surfaces represent important ingredients for the development of DFT [1]: i) $\varepsilon_{xc}[n](\ )$ is the main ingredient of the so-called “enhancement factor” that is used to build many of the existing most popular DFT xc functionals and ii) the asymptotics of $v_{xc}[n](\ )$ are usually taken as a constraint for the development of those functionals. Nevertheless, the actual asymptotics of these two quantities have been the source of considerable controversy over the years [2,3].

Soon after the DFT formalism was published [4], a number of authors concluded that $\varepsilon_{xc}[n](z)$ and $v_{xc}[n](z)$ at large normal distances outside a metal surface are [5 9] i) of the form $\varepsilon_{xc}[n](z \quad \infty) = v_{xc}[n](z \quad \infty) = \quad e^2/4z$ and ii) fully originated from correlation, as the exchange contribution was claimed to decay as $1/z^2$ [7,8] or exponentially [9]. This result was, however, later questioned in view of rigorous exact-exchange calculations of these quantities, which for metal slabs and a semi-infinite SI) metal, were found to be [10 15]

$$2\varepsilon_x^{\mathrm{slab}}[n](z \quad \infty) = v_x^{\mathrm{slab}}[n](z \quad \infty) = \quad e^2/z, \tag{1}$$

$$\varepsilon_x^{\mathrm{SI}}[n](z \quad \infty) = \quad \alpha\, e^2/z, \tag{2}$$

and

$$v_x^{\mathrm{SI}}[n](z \quad \infty) = e^2 \ln(a k_F z)/(2 \quad az), \tag{3}$$

where α, a, and k_F represent material-dependent nonuniversal) constants, with k_F being the Fermi momentum of the electron system. Later on, Qian and Sahni [16] wrongly assumed that the exchange KS potential of a SI metal $v_x^{\mathrm{SI}}(z)$ coincides far away from the surface with the exchange energy per particle of Eq. 2) which for metallic densities is found to decay approximately as $\quad e^2/4z$) and employed the plasmon-pole approximation for the correlation part of the electron self-energy to conclude that $v_c^{\mathrm{SI}}[n](z \quad \infty) = \quad e^2/4z$ and $v_{xc}^{\mathrm{SI}}[n](z \quad \infty) \approx \quad e^2/2z$, i.e., approximately twice as large as the classical $\quad e^2/4z$. That the plasmon-pole correlation part of the electron self-energy is responsible for an image-potential asymptote of the form $\quad e^2/4z$ had already been reported by Sham [7]. Nonetheless, and as explained below, for the total xc energy per particle

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$\varepsilon_{xc}[n](z)$ and xc KS potential $v_{xc}[n](z)$ the plasmon-pole correlation should be added not to an exact-exchange contribution of the form of Eqs. 1) 3) but to a screened-exchange component containing both exact exchange and a form of correlation *not included* in a plasmon-pole approximation, which in the case of a SI metal decays indeed as $1/z^2$ or faster.

In this Letter, we report jellium self-consistent calculations of $\varepsilon_{xc}[n](z)$ that i) combine the adiabatic-connection fluctuation-dissipation ACFD) theorem [17,18] with time-dependent DFT TDDFT) [19] at the level of the random-phase approximation RPA) as in Refs. [20] and [21]) and ii) are exact in the vacuum region far outside the surface [22]. In this region, we find

$$\varepsilon_{xc}^{\mathrm{slab}}[n](z \quad \infty) = \varepsilon_{x}^{\mathrm{slab}}[n](z \quad \infty) = \quad e^2/2z \qquad (4)$$

and

$$\varepsilon_{xc}^{\mathrm{SI}}[n](z \quad \infty) = \quad e^2/4z \qquad (5)$$

We also find that, while for extended systems the asymptotics are dominated by a type of correlation, for metal slabs they are dominated by exchange [see Eq. 4)], as in the case of systems that are finite in all directions, like atoms, molecules, and metal clusters [23]. This is in contrast to the conclusion drawn by White *et al.* [24] who, in an attempt to reconcile previous calculations, stated that, while correlation gives the asymptotic image limit for slab geometries with the exchange part of the potential showing a $1/z^2$ dependence), exchange provides the limit in the case of a SI metal.

In DFT, the crucial magnitude that embodies all the Coulomb-mediated interactions of a many-electron system is the xc energy functional $E_{xc}[n]$, which in the case of an electron system that is invariant under translations in the xy plane can be expressed as follows:

$$E_{xc}[n] = A \quad {}_{\infty}^{\infty} dz\, n(z)\varepsilon_{xc}[n](z), \qquad (6)$$

with z being the coordinate normal to the surface located at $z = \ \ )$ of a SI metal or metal slab. A is a normalization area in the xy plane, $n(z)$ is the number) electron density, and $\varepsilon_{xc}[n](z)$ is the position-dependent xc energy per particle, which we obtain by the coupling-constant integration adiabatic connection) formula [3]

$$\varepsilon_{xc}[n](z) = \frac{e^2}{2} \quad dz \quad d^2\rho \frac{\bar{h}_{xc}(z;\rho,z\ )}{\sqrt{\rho^2 + (z \quad z\ )^2}}, \qquad (7)$$

where $\bar{h}_{xc}(z;\rho,z\ )$ represents the coupling constant averaged) xc hole fulfilling the all-important constraint

$$d^2\rho \quad dz\, h_x(z;\rho,z\ ) = \quad d^2\rho \quad dz\, \bar{h}_{xc}(z;\rho,z\ ) = \quad 1 \qquad (8)$$

and

$$d^2\rho \quad dz\, \bar{h}_c(z;\rho,z\ ) = \qquad (9)$$

for all values of z. ρ is the in-plane coordinate. Physically, $\bar{h}_{xc}(z;\rho,z\ )$ represents a region around one electron probe) located at z where the probability of finding a second electron test) located at $(\rho,z\ )$ is significantly reduced due to the Pauli exclusion principle exchange) and Coulomb repulsion correlation).

In the case of a metal slab, the exchange hole $h_x(z;\rho,z\ )$, the correlation hole $\bar{h}_c(z;\rho,z\ )$, and the xc hole $\bar{h}_{xc}(z;\rho,z\ ) = h_x(z;\rho,z\ ) + \bar{h}_c(z;\rho,z\ )$ are all expected to be localized test coordinates $\rho, z\ )$ in the xy plane and within the slab for values of the probe coordinate z well outside the surface, so using the sum rules of Eqs. 8) and 9) one easily finds Eq. 4), with no leading contribution from correlation [25]. In the case of a SI metal, however, the exchange hole is known to spread, for large values of z, far away inside the metal [26] and the xc hole is known to spread laterally within the xy plane [27], so Eq. 4) is not valid anymore; instead, we find Eq. 5), as explained below.

For a numerical analysis of the xc energy per particle $\varepsilon_{xc}[n](z)$, we use the fluctuation-dissipation theorem to obtain $\bar{h}_{xc}(z;\rho,z\ )$ from the knowledge of the density-response function $\chi(\ \ ,\ \ ;\omega)$, which we calculate, within a jellium model of the metal, in the framework of TDDFT at the level of the RPA [28], well known to be exact at large normal distances outside a metal surface [22].

Figure 1 exhibits the results that we obtain for $\varepsilon_{xc}[n](z)$ at various values of the electron-density parameter r_s and slab widths $d = \ \ .5$ blue lines) and $d = 15$ red lines), both $d = \ \ .5$ and $d = 15$) in units of the Fermi wavelength λ_F [29]. The narrow slab $d = \ \ .5$) allows us to look at the slab asymptotics at $d \ll z$, and the wide slab $d = 15$) allows us to look at the SI asymptotics at $\lambda_F \ll z \ll d$. The inset of Fig. 1 clearly shows that in the asymptotic limit $\varepsilon_{xc}^{\mathrm{slab}}[n](z)$ and $\varepsilon_{xc}^{\mathrm{SI}}[n](z)$ are *universal*, i.e., the same for all values of r_s. This is, in the case of the SI metal, in contrast with the exchange contribution of Eq. 2), which is material dependent. The inset of Fig. 1 also shows how, as we move away from the surface, $\varepsilon_{xc}^{\mathrm{slab}}[n](z)$ and $\varepsilon_{xc}^{\mathrm{SI}}[n](z)$ approach the asymptotics of Eqs. 4) and 5), respectively. In the SI case, the analytical and numerical results become very close, which allows us to conclude that the asymptotic behavior of $\varepsilon_{xc}^{\mathrm{SI}}[n](z)$ is indeed given by Eq. 5). In the case of metal slabs, $\varepsilon_{xc}^{\mathrm{slab}}[n](z)$ approaches more slowly the asymptotic limit of Eq. 4).

Whether the asymptotics of $\varepsilon_{xc}[n](z)$ that are visible in Fig. 1 are dominated by exchange or by correlation can be seen in Figs. 2 and 3 for the SI metal and the metal slab, respectively), where these contributions are exhibited separately. In the case of the SI metal Fig. 2), we see

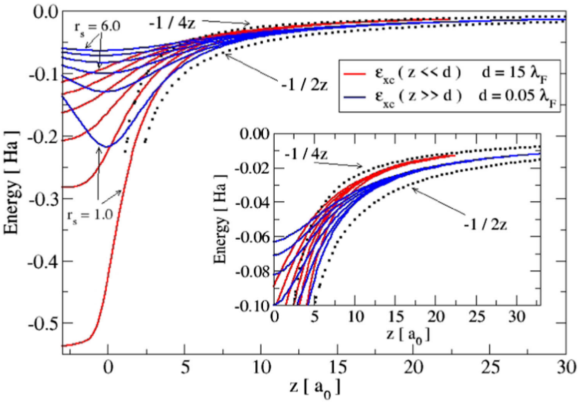

FIG. 1. Exchange-correlation energy per particle $\varepsilon_{xc}^{\rm slab}[n](z)$ blue lines) and $\varepsilon_{xc}^{\rm SI}[n](z)$ red lines) for slab widths $d = \ .5$ blue lines) and $d = 15$ red lines), both in units of the Fermi wavelength λ_F and various values of the electron-density parameter, from $r_s = 1$ lowest blue and red lines) to $r_s = 6$ highest blue and red lines). The metal-slab and SI asymptotics of Eqs. 4) and 5) are represented by black dotted lines. Here and in the following figures, the metal-vacuum interface is located at $z =$, with the vacuum corresponding to $z >$ [30]. Inset: Enhanced view of the asymptotic region. $r_s = r\ /a$, with r being the volume per electron and a the Bohr radius. $\lambda_F = 2\ /k_F = (32\ \ ^2/9)^{1/3} r_s a$ is the Fermi wavelength.

that, while the exchange asymptotics [dictated by Eq. 2)] and the correlation asymptotics are both clearly material dependent, the full $\varepsilon_{xc}[n](z \quad \infty)$ see the inset) is *universal*. At the light of the numerical results displayed in Fig. 2, we conclude that correlation has two distinct contributions: i) a nonuniversal part providing an exact cancellation to the order of $1/z$) with the nonuniversal exact-exchange asymptotics of Eq. 2) and ii) a universal surface-plasmon contribution as implemented by Sham [7] and by Qian and Sahni [16] for $v_{xc}[n](z)$. Indeed, this remaining surface-plasmon contribution dominates the asymptotics [dictated by Eq. 5)] that are visible in the inset of Fig. 2. To the sum of the exact-exchange contribution and the correlation contribution of point i) we call *screened* exchange, which in the case of a SI metal decays asymptotically as $1/z^2$ or faster. This screened exchange energy per particle may be considered as the result of the interaction between an electron at z and its *screened* exchange hole.

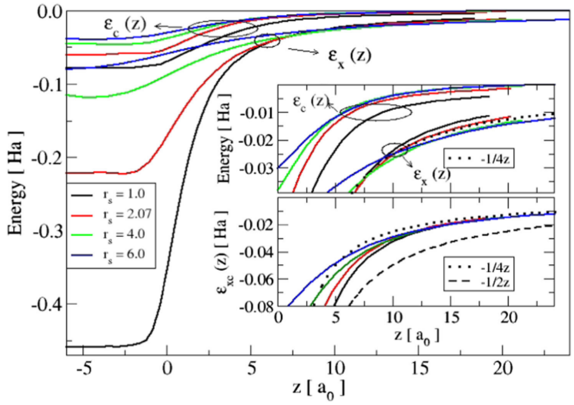

FIG. 2. Separate contributions $[\varepsilon_x^{\rm SI}[n](z)$ and $\varepsilon_c^{\rm SI}[n](z)]$ to the *xc* energy per particle of a SI metal $d = 15\lambda_F$) at various values of r_s, as in Fig. 1. An enhanced view of the asymptotic region is shown at the upper inset. The lower inset contains the total *xc* energy per particle $\varepsilon_{xc}^{\rm SI}[n](z)$, together with the asymptotics of Eqs. 4) and 5), represented by black dashed and dotted lines, respectively.

In the case of metal slabs see Fig. 3), one finds that $\varepsilon_c^{\rm slab}(z)$ decays rapidly to zero in vacuum and, therefore, does not contribute to the asymptotics of $\varepsilon_{xc}^{\rm slab}(z)$, as occurs in the case of systems that are finite in all directions [9,23] and in contrast with the case of a SI metal, where the asymptotics $\varepsilon_{xc}^{\rm SI}[n](z \quad \infty)$ are dominated by correlation. We conclude, therefore, that in the case of metal slabs both $\varepsilon_x^{\rm slab}[n](z)$ and $\varepsilon_{xc}^{\rm slab}[n](z)$ approach the asymptotics of Eq. 4). We note, however, that as in the case of $\varepsilon_x^{\rm slab}[n](z)$ see, e.g., Fig. 2 of Ref. [13]), $\varepsilon_{xc}^{\rm slab}[n](z)$ is not fully converged at the vacuum region under study in Figs. 1 and 3) due to the fact that second and third order corrections to Eq. 4) are still relevant in this region.

Now we focus on the *xc* KS potential $v_{xc}[n](z)$, which is the functional derivative of the *xc* energy functional $E_{xc}[n]$ with respect to the ground-state density $n(z)$:

$$v_{xc}[n](z) \coloneqq A^{\ 1} \frac{\delta E_{xc}[n]}{\delta n(z)} \tag{10}$$

In the case of metal slabs, the exchange asymptotics of Eq. 1) were found both analytically and numerically [12] by using the optimized effective potential OEP) formalism [32], thereby dispelling some doubts that, at the time, were present on this issue [10]. It was later demonstrated [13] that $v_x^{\rm slab}(z \quad \infty) = 2\varepsilon_x^{\rm slab}(z \quad \infty)$ [see Eq. 1)], which is a

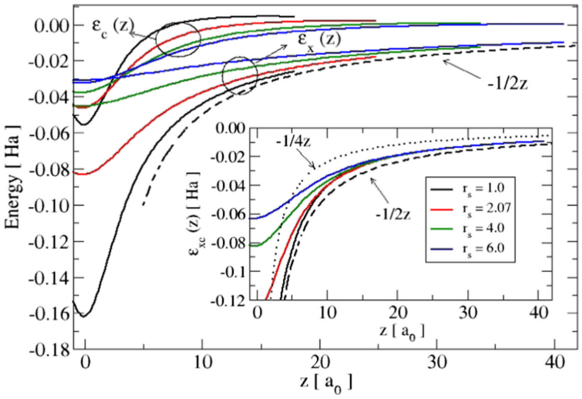

FIG. 3. As in Fig. 2, but now for a metal slab $d = \ .5\lambda_F$). In this case, the correlation energy per particle $\varepsilon_c^{\rm slab}[n](z)$ does not contribute to the asymptotics of the total *xc* energy per particle $\varepsilon_{xc}^{\rm slab}[n](z)$, which is represented at the inset together with the asymptotics of Eqs. 4) dashed line) and 5) dotted line).

hallmark of the exchange interaction for finite systems. This can be seen by introducing $E_x[n]$ from Eq. 6) into Eq. 10) and then exploiting the fact that far outside the surface the total electron density is dominated by the electron density $n_m(z)$ of the last occupied m) KS orbital. Using Eq. 24) of Ref. [13]

$$\begin{aligned} v_x^{\rm slab}(z \quad \infty) = & \quad \frac{2\ e^2}{(k_F^m)^2}\frac{\delta}{\delta n_m(z)} \\ & \times \Bigg[\quad dz_1\, dz_2\, n_m(z_1) n_m(z_2) \\ & \times \quad {}^{\infty} \frac{d\rho [J_1(k_F^m \rho)]^2}{\rho\sqrt{\rho^2 + (z_1 \quad z_2)^2}} \Bigg] \\ = & \quad 2e^2 \quad dz\, |\xi_m(z\ )|^2 \\ & \times \quad {}^{\infty} \frac{d\rho [J_1(k_F^m \rho)]^2}{\rho\sqrt{\rho^2 + (z \quad z\ )^2}} \overset{z \gg d}{\quad} \quad \frac{e^2}{z} \end{aligned} \tag{11}$$

The result in the last line is obtained by first performing the analytical evaluation of the integral over the in-plane coordinate ρ, then taking the limit $k_F^m z \gg 1$, and finally using the normalization constraint of $\xi_m(z)$ [13]. From here, it is clear that the asymptotic factor of 2 between $v_x^{\rm slab}(z)$ and $\varepsilon_x^{\rm slab}(z)$ comes from the intrinsic structure of $E_x^{\rm slab}[n]$, leading asymptotically to a quadratic Hartree-like) dependence on the electron density of the last occupied KS orbital whose variational derivative contributes twice), as expressed in the second line of Eq. 11).

In the case of a SI metal, the asymptotics of Eq. 3) were obtained [14] through a mixed analytical and numerical study of the exchange-only OEP equations, by considering from the very beginning the continuous feature of the electronic spectra. This result was then challenged by Qian [33], but later confirmed in Ref. [34]. As occurs in the case of the exchange energy per particle $\varepsilon_x[n](z)$, the asymptotics of the exchange KS potential $v_x[n](z)$ are found to be universal for metal slabs [see Eq. 1)] but material dependent for a SI metal, as in Eq. 3).

Now with correlation, the *xc* KS potential $v_{xc}[n](z)$ of Eq. 10) can be calculated from the knowledge of the electron self-energy, by solving the so-called Sham-Schlütter integral equation [35]. By examining the electron self-energy studied by Rudnick for a SI metal [36], Sham [7] concluded that the asymptotics of $v_{xc}[n](z)$ are dominated by a surface-plasmon correlation term $v_{c\quad {\rm sp}}[n](z \quad \infty)$, leading to the following result:

$$v_{c\quad {\rm sp}}^{\rm SI}[n](z \quad \infty) = \quad e^2/4z, \tag{12}$$

which exactly coincides with the asymptotics that we obtained [see Eq. 5) and Figs. 1 and 2] for the *xc* energy per particle $\varepsilon_{xc}[n](z)$:

$$v_{xc}^{\rm SI}[n](z \quad \infty) = \varepsilon_{xc}^{\rm SI}[n](z \quad \infty) = \quad e^2/4z \tag{13}$$

Here, there is no extra factor of 2 between $\varepsilon_{xc}[n](z)$ and $v_{xc}[n](z)$, as this extra factor only occurs for metal slabs) at the level of exchange, whose leading contribution to order $\sim 1/z$) is exactly canceled out by a form of correlation that goes beyond the surface-plasmon correlation of Eq. 12). Indeed, added to the exact-exchange term, this form of correlation leads to a screened exchange contribution to both $\varepsilon_{xc}^{\rm SI}[n]$ and $v_{xc}^{\rm SI}[n]$ that decays asymptotically as $1/z^2$ as concluded by Sham [7], although referring to exchange and not to screened exchange) or faster.

A plasmon-pole approximation to the electron self-energy was also used by Qian and Sahni [16] to obtain, again, the $e^2/4z$ asymptotics that had been previously reported by Sham [7] and coincide with the well-known asymptotics of the classical image potential $v_{\rm im}^{\rm SI}(z)$ of a recoiless charged particle outside a SI metal surface, defined as half the induced potential acting on the external charged particle itself.

Equation 13) shows that, as occurs in the case of the *xc* energy per particle $\varepsilon_{xc}[n](z)$, for a SI metal the asymptotics of $v_{xc}[n](z)$ are universal and dominated by correlation [see Eq. 12)]. For finite slabs, however, the correlation KS potential $v_c[n](z)$ is expected to decay at $z \gg d$) faster than $1/z$, as in the case of $\varepsilon_c[n](z)$ see Fig. 3) and also the classical image potential $v_{\rm im}^{\rm slab}(z)$ of a recoiless charged particle [37], so, as in the case of exchange [see Eq. 1)], one would simply write

$$2\varepsilon_{xc}^{\rm slab}[n](z \quad \infty) = v_{xc}^{\rm slab}[n](z \quad \infty) = \quad e^2/z \tag{14}$$

The results presented here for the asymptotics of the *xc* energy per particle $\varepsilon_{xc}[n](z)$ and the *xc* KS potential $v_{xc}[n](z)$ are summarized in Table I, together with the existing rigorous asymptotics of the exact-exchange quantities $\varepsilon_x[n](z)$ and $v_x[n](z)$ [Eqs. 1) 3)]. Also shown in Table I are the asymptotics of the classical image potential $v_{\rm im}(z)$ of a charged particle in a SI and slab geometry. After the validation by Engel of the exchange-only asymptotics for real metal slabs [15], the *universal xc* asymptotics given in Table I should be expected to be valid also for a real metal slab and SI metal, beyond the jellium approximation used here.

In the case of a SI metal, the asymptotics of the correlation-only energy per particle $\varepsilon_c[n](z)$ and the correlation-only KS potential $v_c[n](z)$ have two distinct contributions: i) a material-dependent correlation that exactly cancels to the order of $\sim 1/z$) the exact-exchange term and ii) a *universal* form of correlation that for the KS potential $v_c[n](z)$ Sham [7] and Qian and Sahni [16] found to be originated in the surface plasmon.

In retrospective, the ultimate physical reason for the difference between slabs and SI metals is that in the case of slabs electrons are confined in the direction perpendicular

TABLE I. Asymptotics of the xc energy per particle $\varepsilon_{xc}[n](z)$ and the xc KS potential $v_{xc}[n](z)$ in the vacuum side of both a metal slab middle column) and a SI metal right column). The works by Engel [15] are for nonjellium slabs.

	SLAB $d \ll z$) exchange dominated)	SI $\lambda_F \ll z \ll d$) correlation dominated)
$\varepsilon_x[n](z)$	$e^2/2z$ [13,15])	$\alpha e^2/z$ [10,11])
$\varepsilon_c[n](z)$	$O(1/z^2)$ This work)	$\alpha e^2/z \quad e^2/4z$ This work)
$\varepsilon_{xc}[n](z)$	$e^2/2z$ This work)	$e^2/4z$ This work, [21])
$v_x[n](z)$	e^2/z [12,15])	$e^2 \ln(ak_F z)/(2 \ az)$ [14,34])
$v_c[n](z)$	$O(1/z^2)$ This work)	$e^2 \ln(ak_F z)/(2 \ az)$ $e^2/4z$ This work)
$v_{xc}[n](z)$	e^2/z This work)	$e^2/4z$ This work, [7])
$v_{\mathrm{im}}(z)$	$O(1/z^2)$ This work)	$e^2/4z$

to the surface, leading to a partially discrete electronic spectrum that inhibits correlation from fully screening the electron-electron interaction.

In summary, we have presented ACFD jellium self-consistent calculations of the xc energy per particle $\varepsilon_{xc}[n](z)$ that are asymptotically exact in the vacuum side of both an *extended* SI metal and a *localized* metal slab. We find that $\varepsilon_{xc}[n](z \quad \infty)$ is always negative, inversely proportional to the distance from the surface, and *universal* i.e., electron-density independent), thanks to the cancellation in the case of a SI metal and to order $\sim 1/z$) between the material-dependent exact-exchange contribution $\varepsilon_x[n](z)$ and a form of correlation that goes beyond a surface-plasmon contribution, thus showing that this plasmon-pole correlation should be added not to the exact-exchange contribution but to a *screened* exchange; this should be taken into account for the construction of functionals. Similar results are obtained for the xc KS potential $v_{xc}[n](z)$, which i) in the case of metal slabs dominated by exchange) is simply asymptotically) twice as large as $\varepsilon_{xc}[n](z)$ and ii) in the case of a SI metal is dominated by a *universal* surface-plasmon correlation already reported by Sham [7] and by Qian and Sahni [16]) that coincides asymptotically) with $\varepsilon_{xc}[n](z)$. We consider this to be a final word for the asymptotics of the xc energy per particle and the xc KS potential at metal surfaces. This is important for all kinds of electronic structure calculations and, in particular, surface-sensitive phenomena like, e.g., image states. [38].

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Data availability The data that support the findings of this Letter are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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