Exact exchange plane-wave-pseudopotential calculations for slabs

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(Received 22 November 2013; accepted 13 January 2014; published online 31 January 2014)

The exact exchange of density functional theory is applied to both free-standing graphene and a Si(111) slab, using the plane-wave pseudopotential (PWPP) approach and a periodic repetition of the supercell containing the slab. It is shown that (i) PWPP calculations with exact exchange for slabs in supercell geometry are basically feasible, (ii) the width of the vacuum required for a decoupling of the slabs is only moderately larger than in the case of the local-density approximation, and (iii) the resulting exchange potential \(v_x\) shows an extended region, both far outside the surface of the slab and far from the middle of the vacuum region between the slabs, in which \(v_x\) behaves as \(-e^2/2z\), provided the width of the vacuum is chosen sufficiently large. This last result is corroborated by an analytical analysis of periodically repeated jellium slabs. The intermediate \(-e^2/2z\) behavior of \(v_x\) can be used for an absolute normalization of \(v_x\) and the total Kohn-Sham potential, which, in turn, allows the determination of the work function. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4863219]

I. INTRODUCTION

During the last years the exchange-correlation (xc) potential at metallic surfaces has attracted renewed interest.\(^{1-7}\) It has been shown\(^2\) that the exact exchange (EXX) potential \(v_x(z)\) of a jellium slab, for which the electrons are confined in the region \(-L < z < L\), behaves as \(-e^2/2L\) for \(z \gg L\), while developing a repulsive shoulder in the vacuum region close to the surface \((z \gtrsim L)\). Consistent with the asymptotic form of \(v_x\), the (suitably defined) exact exchange energy per particle \(\epsilon_x(z)\) falls off as \(-e^2/2z\).\(^3\) Moreover, substantial finite quantum size effects were observed in the EXX work function of jellium slabs.\(^4\) By contrast the \(\epsilon_x(z)\) of semi-infinite jellium, which should provide a more accurate description of real metallic surfaces, decays as\(^5,8\)

\[
\epsilon_x(z) \rightarrow -\frac{\pi + 2\alpha \ln(\alpha)}{2\pi(1 + \alpha^2)} \frac{e^2}{z},
\]

where \(\alpha\) is given in terms of the work function \(W\) and Fermi momentum \(\epsilon_F\) of semi-infinite jellium as \(\alpha^2 = \epsilon_F/W\). For large slab thickness \((L\) much larger than the Fermi wavelength) the semi-infinite behavior is expected to dominate close to the surface, while ultimately for \(z \gg L\) the slab behavior should come through.\(^4\) In the low density limit both asymptotic forms coincide anyway (\(\alpha\) approaches zero in the low density limit). The corresponding \(v_x\) of semi-infinite jellium was found to be\(^5\)

\[
v_x(z) \rightarrow -\frac{\ln(ak_Fz)}{2\pi\alpha z},
\]

with \(k_F\) denoting the Fermi wavevector of the 3D electron gas with the same uniform jellium/electron density \(n_0\), \(k_F = (3\pi^2n_0)^{1/3}\). So far, however, it is not fully clear how the slab result for \(v_x\) is reconciled with the semi-infinite form for increasing slab thickness. While the asymptotic behavior for slabs, \(v_x \sim -e^2/2z\), originates from the Slater component in the exact \(v_x\), the semi-infinite jellium asymptote is a consequence\(^5\) of the additional contributions to \(v_x\), obtained by rigorous evaluation of \(v_x = \delta E_x/\delta n\) via the optimized potential method (OPM) integral equation\(^9\) (for a detailed discussion of the difference between the OPM, requiring a multiplicative \(v_x\), and the Hartree-Fock treatment of the exact exchange, allowing for a nonlocal exchange potential, see Ref. 10).

The asymptotic behavior of \(v_x\) and \(\epsilon_x\) is in obvious contrast to the expected \(-e^2/4z\) decay of the complete xc-potential \(v_{xc}\).\(^{11,12}\) This expectation was triggered by the observation\(^13\) that the interaction energy of a small perturbing charge in front of the jellium surface with the induced density behaves like \(-e^2/[4(z - z_0)]\) (where \(z_0\) is the position of the effective image plane close to the surface). This result, in turn, is in line with the form of the classical image potential outside the metal surface, which is well established experimentally.\(^14\) Recently, it has been shown numerically\(^6\) that the random phase approximation (RPA) yields a net \(\epsilon_{xc}(z)\) which is quite close to \(-1/[4(z - z_0)]\) for large \(z\). Arguments for a \(-e^2/4z\) decay of the RPA correlation potential (within the plasmon-pole approximation) have been presented in Ref. 1, with, however, the resulting total \(v_{xc}\) being roughly proportional to \(-e^2/2z\). The complete asymptotic xc-potential was also examined\(^{11,12}\) on the basis of the Sham-Schlüter equation\(^15\) (which is equivalent to the OPM at least in the exchange-only limit\(^16\)). For the infinite barrier model of the surface (in which there is no electronic density outside the jellium surface) it was shown\(^11\) that the exact \(v_x\) decays as \(-e^2/4z\), while \(v_x\) is asymptotically proportional to \(-a/\alpha^2\). The same behavior was found\(^12\) by a numerical solution of the Sham-Schlüter equation for the finite barrier model (within the GW approximation for the self-energy operator\(^13\)), in obvious contradiction to the more recent results for \(v_x\). It thus seems that a final proof for the exact \(v_{xc}\) of the standard jellium model decaying like \(-e^2/4z\) is still missing. Also, no information on the asymptotic behavior seems to be available for \(v_{xc}\) at the surfaces of semiconductors and insulators, which implies breaking the translational...
inquivariance of jellium slabs or semi-infinite jellium in the x-y-directions.

In applications, bulk surfaces are often studied by combination of the plane-wave pseudopotential (PWPP) approach with the supercell technique, in which a slab of finite thickness is periodically repeated along one of the directions (see, e.g., Ref. 18). The supercell technique relies on a decoupling of neighboring slabs by a sufficiently large vacuum region between the slabs. While this decoupling is ensured by the exponentially decaying xc-potentials of the local-density approximation (LDA) and generalized gradient approximation (GGA) for quite moderate width of the vacuum, the question arises whether this technique can also be applied with an asymptotic \( v_{\alpha s} \) proportional to \( 1/z \). Moreover, slabs do not only serve as calculational tools for studying bulk surfaces, they are also interesting in themselves, free-standing graphene being the most prominent example.

In this work, PWPP supercell calculations for slabs with the exact exchange are reported. As model systems, graphene and a Si(111) slab consisting of 3 bilayers are considered. In order to prepare the analysis of the resulting \( v_{\alpha s} \), first the jellium slab of Ref. 2 is examined in supercell geometry, using an alternative strategy for extracting the leading \( -1/z^2 \) term. It is shown that there is an intermediate regime, with \( z \) being sufficiently far from both the surface and the middle of the vacuum region, in which \( v_{\alpha s}(z) \) decays like \( -1/z \). Utilizing the same arguments, it is also shown that the exact exchange energy density \( \epsilon_x \) of a single slab, which is periodic in the \( x-y \)-directions (but not fully translationally invariant), asymptotically falls off as

\[
\epsilon_x(r) \xrightarrow{z \to \infty} -\frac{e^2n(r)}{2z},
\]

with \( n(r) \) the electron density \( (\epsilon_x(r) = n(r)\epsilon_x(r)) \). This result applies to both metallic and insulating slabs.

On this basis the numerical results are studied. It is found that for both model systems the long-range potential between the slabs does not prevent their decoupling. However, for the EXX a somewhat larger slab separation is required than for the LDA or GGAs, in order to reach the same degree of decoupling. In addition, corrugation effects in \( v_{\alpha s} \) decay rapidly with increasing \( z \). Next, it is demonstrated that for graphene sheets separated by a moderate vacuum region (~14 bohrs) the Krieger-Li-Iafrate (KLI) approximation\(^{19}\) for \( v_{\alpha s} \) reproduces the full LDA solution rather well, thus justifying the use of the KLI potential for larger vacuum width (for which the full LDA is computationally too demanding). A larger slab separation is in particular required as soon as an absolute normalization of \( v_{\alpha s} \) is of interest, since the normalization necessarily has to be based on the asymptotic form of \( v_{\alpha s} \). In fact, in the case of graphene the width of the vacuum has to be beyond 30 bohrs in order to extract the predicted \( -1/z^2 \) behavior of \( v_{\alpha s} \) in some extended intermediate region.\(^{20}\) The properly normalized \( v_{\alpha s} \) and the corresponding total Kohn-Sham (KS) potential \( v_{\alpha} \) are finally used for a comparison with the LDA and an evaluation of the work function. For the slabs considered, the EXX/KLI potential wells are found to be deeper than the LDA potentials. Correspondingly, the EXX/KLI work function of graphene turns out to be much larger than both the LDA result and the experimental data, indicating that the correlation potential in the region near the surface has to be repulsive.

The paper is organized as follows. The analytical proofs for the (semi-)asymptotic behavior of \( v_{\alpha s} \) and \( \epsilon_x \) are given in Sec. II. The computational details of the supercell calculations are provided in Sec. III, followed by a comparison of the complete OPM solution with the KLI approximation in Sec. IV A. In Sec. IV B, the question of decoupling of neighboring slabs is addressed. Section IV C presents the procedure for absolute normalization of the supercell \( v_{\alpha s} \). A detailed comparison of EXX/KLI results for \( v_{\alpha s} \) and the resulting work functions with their LDA counterparts is given in Sec. IV D. Finally, Sec. V summarizes the findings. The Appendix shows how the approach of Ref. 3 can be combined with the present strategy to derive the asymptotic \( v_{\alpha s} \).

\[ \hat{h} = e = 1 \] is used throughout this work.

II. THEORY

A. States and density of single jellium slab

In Ref. 2, it has been shown that the exact \( v_{\alpha s} \) of jellium slabs behaves as \( -1/z \) for large \( z \) outside the slab. In this section, we first give an alternative proof of this property, which is (i) not based on the particular confining potential produced by a uniform positive background charge, and (ii) more easily extended to non-jellium like slabs. Let us therefore consider a system which is translationally invariant with respect to the \( x \)- and \( y \)-directions, while a potential confines the electrons to the finite range \(-L < z < L \) in \( z \)-direction. The corresponding KS equations with total potential \( v_\alpha(z) \) are separable, so that the KS states have the form

\[
\phi_{\alpha}(r) = \frac{\phi_{\alpha}(z)}{2\pi},
\]

with standard normalization

\[
\int_{-\infty}^{\infty} dz \phi_{\alpha}^*(z)\phi_{\alpha'}(z) = \delta_{\alpha\alpha'}.
\]

For simplicity, all \( \phi_{\alpha} \) are chosen to be real in the following. The KS eigenvalues corresponding to (1) are given by

\[
\epsilon_{k_\alpha} = \frac{k^2}{2m} + \epsilon_x.
\]

Since we are interested in simulating real surfaces, the confining potential is assumed to vanish far from the slab,

\[
v_{\alpha}(z) \xrightarrow{|z| \to \infty} 0.
\]

As a result, the normalizable solutions of (2) correspond to negative \( \epsilon_x \).
The density matrix of the system (which is assumed to be spin-saturated for simplicity) is given by
\[ \rho(r, r') = 2 \int \frac{d^2 k}{(2\pi)^2} \sum_a \Theta(\epsilon_F - \epsilon_{ka}) e^{i k \cdot (r - r')} \phi_a(z) \phi_a(z'), \]
with the Fermi level \( \epsilon_F \) defining the occupied part of the spectrum. The density matrix may be integrated out further (with the result (A1)), which is, however, not necessary for the present purpose. Correspondingly, the density is found to be
\[ n(r) \equiv n(z) = \frac{k_f^2}{2\pi} \Theta(\epsilon_F - \epsilon_a) \phi_a(z)^2, \]
with
\[ k_a := \sqrt{2m(\epsilon_F - \epsilon_a)}. \]
If one assumes the highest occupied state \( \alpha = h \) to be non-degenerate, the asymptotic form of the density for \( z \gg L \) is dominated by \( \phi_h \),
\[ n(z \gg L) = \frac{k_h^2}{2\pi} \phi_h(z)^2, \]
where the asymptotic form of the bound solutions of (2) is controlled by the eigenvalue of the state,
\[ \phi_a(z \gg L) \sim e^{-\sqrt{2m\epsilon_a} z}. \]

B. Exchange energy and potential of single jellium slab

The exchange energy per unit area of the spin-saturated system can be written as
\[ E_x = -\frac{1}{4} \int_{-\infty}^{\infty} dz \int d^3 r' \frac{\rho(r, r') \rho(r', r)}{|r - r'|}. \]
Insertion of (6) allows one to evaluate \( E_x \) to
\[ E_x = -\int \frac{d^2 k}{(2\pi)^2} \frac{d^2 k'}{(2\pi)^2} \sum_{a, a'} \Theta(\epsilon_F - \epsilon_{ka}) \Theta(\epsilon_F - \epsilon_{k'a'}) \]
\[ \times \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dz' \frac{2\pi e^{-|k' - k||z - z'|}}{|k' - k|} \]
\[ \times \phi_a(z) \phi_{a'}(z') \phi_{a'}(z') \phi_a(z'). \]
Functional differentiation with respect to the asymptotic density (9) following Ref. 21 then yields
\[ \frac{\delta E_x}{\delta n(z)} \xrightarrow{\gg L} \frac{4\pi}{k_h^4} \phi_h(z) \int \frac{d^2 k}{(2\pi)^2} \frac{d^2 k'}{(2\pi)^2} \]
\[ \times \sum_a \Theta(\epsilon_F - \epsilon_{ka}) \Theta(\epsilon_F - \epsilon_{k'a'}) \]
\[ \times \int_{-\infty}^{\infty} dz' \frac{2\pi e^{-|k' - k||z - z'|}}{|k' - k|} \]
\[ \times \phi_a(z') \phi_h(z') \phi_a(z). \]
For \( z \gg L \) the sum over \( a \) on the right-hand side is dominated by \( \phi_h(z) \),
\[ v_x(z) \xrightarrow{\gg L} -\frac{4\pi}{k_h^4} \int \frac{d^2 k}{(2\pi)^2} \frac{d^2 k'}{(2\pi)^2} \]
\[ \times \Theta(\epsilon_F - \epsilon_{kh}) \Theta(\epsilon_F - \epsilon_{k'h}) \]
\[ \times \int_{-\infty}^{\infty} dz' \frac{2\pi e^{-|k' - k||z - z'|}}{|k' - k|} \phi_h(z')^2. \]
Since \( \phi_h(z') \) decays exponentially for \( z' \gg L \), the \( z' \)-integration is effectively restricted to a range \(-L < z' < L\) with \( L = L + \Delta L \) (where \( \Delta L \) characterizes the range over which \( e^{-\sqrt{2m\epsilon_h} z} \) decays). Moreover, only the immediate neighborhood of \( k \) is relevant in the \( k' \)-integration for large \( z - z' \), so that the restriction of the \( k' \)-integration by \( \Theta(\epsilon_F - \epsilon_{k'h}) \) can be neglected for \( z \gg L \).
\[ v_x(z) \xrightarrow{\gg L} -\int_{-L}^{L} dz' \phi_h(z')^2 \frac{1}{|z - z'|}. \]
Finally, the denominator \( 1/|z - z'| \) can be expanded about some suitable point \( z_0 \) as soon as \( z \gg L \),
\[ v_x(z) \xrightarrow{\gg L} -\int_{-L}^{L} dz' \phi_h(z')^2 \frac{1}{|z - z'|}. \]
Here \( (z) \) denotes the expectation value of \( z \) with respect to \( \phi_h \),
\[ (z) = \int_{-L}^{L} dz \phi_h(z)^2. \]
One should note, however, that an additional power-law contribution proportional to \( 1/z^2 \) shows up in the asymptotic \( v_x \), as soon as the \( k' \)-integration is treated more accurately\(^2\) (see also the Appendix).

Equations (15) and (16) remain valid for arbitrarily large \( L \), as long as there is a non-degenerate highest occupied (surface) state \( \phi_h \) (compare Ref. 2). This implies that the exchange potential ultimately behaves like \(-1/z^2\) even for bulk-like slabs, if \( z - L \) is larger than the spatial extension of the density \( \phi_h^2 \). However, if \( \phi_h \) corresponds to a localized surface state with \( (z) \approx L \), a \(-1/z\)-behavior may even be found close to the surface.

Equations (15) and (16) can be directly extended to spin-polarized systems, due to the additivity of \( E_x \) with respect to spin. Moreover, direct application of the same arguments to the spatial exchange energy density \( e_x(z) \), i.e., the integrand of (11), leads to
\[ e_x(z) \xrightarrow{\gg L} -\frac{n(z)}{2(z - z_0)} = \frac{n(z)}{2} v_x(z). \]
This asymptotic form also remains true for more realistic slabs, for which the x-y- and z-directions are not decoupled (see Sec. II E).

C. States and density of jellium slab in supercell geometry

Let us now consider a potential \( v_s \) which is periodic in z-direction,

\[
v_s(z + a) = v_s(z),
\]

(19)
each period representing one copy of the slab of Sec. II A. For consistency with the discussion of Sec. II A, the center of one of the slabs is chosen to be at \( z = 0 \). The lattice constant \( a \) is assumed to be large compared to the thickness of the slab, \( 2L \), and the extension of all occupied states, \( 2\tilde{L} \). In the supercell approach to surfaces or actual slabs like graphene the supercell is designed to meet exactly this condition.

The corresponding Bloch states are given by

\[
\phi_{kq}(r) = \frac{e^{ik\cdot r}}{2\pi} e^{iq\cdot z} u_{q\alpha}(z),
\]

(20)
where \( u_{q\alpha} \) denotes the strictly periodic solutions of

\[
\left\{ \begin{array}{l}
\frac{1}{2m} \left( i \frac{\partial}{\partial z} - q \right)^2 + v_s(z) \right. \\
\left. u_{q\alpha}(z) = \epsilon_{q\alpha} u_{q\alpha}(z). \right.
\]

(21)
Using the Born-von Karman approach for quantization in a (large) cell of size \( Na \), the crystal momentum \( q \) in the 1st Brillouin zone is given by

\[
q = \frac{2\pi}{a} \frac{l}{N}, \quad -\frac{N}{2} \leq l < \frac{N}{2}
\]
and the states are normalized as

\[
\int_{-a/2}^{a/2} dz \ u_{q\alpha}^*(z) u_{q\alpha}(z) = \delta_{a,a'}
\]
(23)
(in accordance with (3)). The complete KS eigenvalues now read

\[
\epsilon_{kq\alpha} = \frac{k^2}{2m} + \epsilon_{q\alpha}.
\]
(24)
The density matrix of the periodic system is obtained after proper normalization of \( u_{q\alpha} \) in the quantization cell,

\[
\rho(r, r') = \frac{2}{N} \sum_{q \in \text{BZ}} \int \frac{d^2k}{(2\pi)^2} \sum_a \Theta(\epsilon_F - \epsilon_{kq\alpha})
\]
\[
\times e^{i(k(r-r')_1)} e^{i(q(z'-z))} u_{q\alpha}(z) u_{q\alpha}^*(z').
\]
(25)
In the case of the density, this expression reduces to

\[
n(r) = \frac{1}{2\pi N} \sum_{q \in \text{BZ}} \sum_a k^2 q_{q\alpha}^2 \Theta(\epsilon_F - \epsilon_{q\alpha}) |u_{q\alpha}(z)|^2,
\]
(26)
with

\[
k_{q\alpha} = \sqrt{2m(\epsilon_F - \epsilon_{q\alpha})}.
\]
(27)
If \( a \) is sufficiently large, there is an extended regime outside each slab in which all \( u_{q\alpha}(z) \) decay exponentially: only if one approaches the middle of the vacuum region between two slabs the behavior of \( u_{q\alpha}(z) \) starts to deviate from that of the states of a single slab. This is demonstrated explicitly in Fig. 1, which shows the density of the highest occupied band of repeated graphene sheets (integrated over the x- and y-directions of the unit cell, similar to Eq. (52)). The exponential decay of the density for \( 0 \ll z \ll a/2 \) is obvious. The range of this exponential decay depends on the lattice constant. Nevertheless, Fig. 1(b) shows that the density is quite insensitive to this choice in the range \( 0 \ll z \ll a/2 \). Consequently, there is one band, the (non-degenerate) highest occupied band \( h \), whose states decay most slowly in this exponential regime \( L \ll z \ll a/2 \),

\[
n(z) \rightarrow \frac{a/20 < z \ll L}{2\pi N} \sum_{q \in \text{BZ}} k^2 q_{q\alpha}^2 \Theta(\epsilon_F - \epsilon_{q\alpha}) |u_{q\alpha}(z)|^2.
\]
(28)
In addition, the widths of the bands \( \epsilon_{q\alpha} \) shrink to zero and \( u_{q\alpha}(z) \) becomes more and more independent of \( q \) with increasing \( a \). In fact, extremely flat bands are obtained already for moderately large \( a \), as Fig. 2 confirms for graphene: no dispersion is visible for the occupied bands, the bandwidth being below 1 \( \mu \)eV already for \( a = 5a_0 \) (where \( a_0 \) denotes the in-plane lattice constant of the honeycomb lattice). Even the bandwidth of the lowest unoccupied band is below 0.5 meV for \( a = 7a_0 \). If one assumes the highest occupied band (with

FIG. 1. x-y-integrated density of highest occupied band of graphene in supercell approach: (a) complete width of vacuum for \( a = 6a_0 \) \((a_0 = 2.461 \text{ Å})\); (b) half of vacuum for three different \( a \) (for technical details see Sec. III).
respects to \( q \) to be fully occupied, one can thus utilize the flatness of the band to replace \( u_{qh} \) by the state for a single \( k \)-point \( \bar{q} \),

\[
n(z) \rightarrow \frac{k_{qh}^2}{2\pi} |u_{\bar{q}h}(z)|^2.
\]

The most suitable \( k \)-points for the present purpose are \( \bar{q} = 0 \), for which \( u_{\bar{q}h} \) is real, and \( \bar{q} = \pi/a \), for which one has

\[
u_{\bar{q}a}(z) = e^{2\pi iz/a} u_{\bar{q}a}(z) \quad \left( \bar{q} = \frac{\pi}{a} \right).
\]

In fact, in actual applications the Brillouin zone summation in (26) necessarily has to be replaced by some finite sum, for which a single grid point \( \bar{q} \) is just the simplest variant. Obviously, the quality of this approximation depends on the size of \( a \).

**D. Exchange energy and potential of jellium slab in supercell geometry**

The exchange energy per surface area and unit cell in \( z \)-direction is given by insertion of Eq. (25) into the Fock integral,

\[
E_x = \int_{-a/2}^{a/2} dz \epsilon_x(z)
\]

\[
\epsilon_x(z) = \int_{-a/2}^{a/2} dz' \epsilon_x(z')
\]

\[
E_x(z) = -\frac{1}{N^2} \sum_{q,q',a,b} \int \frac{d^2k}{(2\pi)^2} \frac{d^2k'}{(2\pi)^2} \sum_{a,a'}
\times \Theta(\epsilon_F - \epsilon_{kqh}) \Theta(\epsilon_F - \epsilon_{k'q'a'})
\times \int_{-\infty}^{\infty} dz' \frac{2\pi}{|k-k'|} e^{-|k-k'||z-z'|} u_{q,a}^* \epsilon_{q,a}(z') u_{q',a'}(z')
\times P \left( \frac{z - z' - na}{a} \right) |u_{\bar{q}h}(z')|^2.
\]

Relying on the flatness of the bands, the states and band energies may now be approximated by their values at \( \bar{q} \), so that the Brillouin zone summations over \( q, q' \) can be performed independently,

\[
\epsilon_x(z) = -\int \frac{d^2k}{(2\pi)^2} \frac{d^2k'}{(2\pi)^2} \sum_{a,a'} \int_{-\infty}^{\infty} dz' \epsilon_x(z')
\times \Theta(\epsilon_F - \epsilon_{kqh}) \Theta(\epsilon_F - \epsilon_{k'q'a'})
\times 2\pi e^{-|k-k'||z-z'|} |k-k'| P \left( \frac{z - z' - na}{a} \right) |u_{\bar{q}h}(z')|^2.
\]

The Brillouin zone summation in Eq. (33) is, however, not as straightforward as in the case of the density (28), the reason being the long range of the Coulomb interaction. Due to this long range, the term \( q = q' \) in (34) eventually leads to a divergence, when taken directly. The role of this term becomes more clear when the Brillouin zone summations in (34) are evaluated exactly,

\[
P_z(\frac{z - z'}{a}) = \lim_{N \to \infty} \frac{1}{N^2} \sum_{q,q' \in BZ} e^{i(q-q')(z-z')}
\]

\[
= a^2 \int_{-\pi/a}^{\pi/a} dq dq' \epsilon_{q,a} \epsilon_{q',a'}
\times \left( \frac{\sin(\pi(z-z')/a)}{z - z'} \right)^2.
\]

For large \( z - z' \) this term contributes an additional \( 1/(z-z')^2 \) to the 2D Coulomb denominator proportional to \( 1/(z-z') \) inherent in (33) (see below).

If one chooses \( \bar{q} = 0 \), the (non-degenerate) highest occupied state \( u_{\bar{q}h} \) is real, which allows direct functional differentiation of (33) with respect to \( n(z) \) in the exponential regime, utilizing Eq. (29). Similarly, for \( \bar{q} = \pi/a \) the functional derivative can be performed by use of (30). In both cases the result is

\[
v_x(z) \rightarrow -2(2\pi)^2 \int_{-\infty}^{\infty} dz' \frac{d^2k}{k_{qh}^2} \frac{d^2k'}{(2\pi)^2} \sum_{a,a'}
\times \Theta(\epsilon_F - \epsilon_{kqh}) \Theta(\epsilon_F - \epsilon_{k'q'a'})
\times \int_{-\infty}^{\infty} dz' \frac{2\pi}{|k-k'|} e^{-|k-k'||z-z'|} u_{q,a}^* \epsilon_{q,a}(z') u_{q',a'}(z')
\times P \left( \frac{z - z' - na}{a} \right) |u_{\bar{q}h}(z')|^2.
\]

As for a single slab, the restriction of the \( k' \)-integration to the Fermi circle can be relaxed relying on the exponential localization of \( u_{\bar{q}h}(z') \),

\[
v_x(z) \rightarrow -\int_{-L}^{L} dz' \sum_{n=-\infty}^{\infty} |u_{\bar{q}h}(z')|^2
\times P \left( \frac{z - z' - na}{a} \right).
\]
One now explicitly recognizes the Coulomb divergence arising when both sums in (34) are performed by discrete summation: the term \( q = q' \) leads to a \( z \)-independent constant in \( P \), so that the summation over the complete crystal in (37) diverges. In applications the Coulomb singularity is therefore usually handled by performing an integration over \( q' \) for the interval covered by the grid point \( q \) (see, e.g., Refs. 23 and 24). In the present approach, utilizing a single \( k \)-point this amounts to

\[
P_1 \left( \frac{z - z'}{a} \right) = a \int_{1/\pi a}^{\pi/\alpha} \frac{dq}{\pi} e^{i(q - q')(z - z')} = \frac{a \sin(\pi(z - z')/a)}{\pi(z - z')}.
\]

Finally, expansion of (37) and (38) for \( \pi|z - z'| \ll a \) yields

\[
v_x(z) \frac{a^{2/3} \langle \beta \rangle \tilde{L}}{2} \int_{-L}^{L} dz' \left| u_{q_0}(z') \right|^2 \frac{1}{|z - z'|^2} + \ldots.
\]

The same procedure can be applied to the exchange energy density (32) with the result

\[
e_x(z) \frac{a^{2/3} \langle \beta \rangle \tilde{L}}{2} n(z) v_x(z).
\]

The behavior of the asymptotic exchange potential (36) is illustrated in Fig. 3, which shows the example of graphene for a very large sheet separation of \( a = 21a_0 \) (the actual density of the highest occupied state has again been averaged over the \( x \)- and \( y \)-directions in order to evaluate (36)). Over most of the asymptotic regime the potential (36) follows the asymptotic exchange potential (15) of a single slab with the same density \( u_{q_0} \). An obvious difference is observed in the middle of the vacuum region, where the potential (36) necessarily has to become flat. For moderate \( z \) minor differences (below 2 mHa) originate from the fact that the integral in (36) involves the orthonormality factor \( P(\pi|z - z'|/a) \) also for the slab with \( n = 0 \), unlike the integral in (15). The difference between the two potentials becomes more clearly visible, if their derivatives are compared (see Fig. 3(b)). Now one clearly identifies a range between 10 and 20 bohrs for which both potentials decay like \(-1/z\). This is the actual exponential regime \( L \ll z \ll a/2 \) for the present situation.

E. Exchange energy density of arbitrary slab

In realistic systems, such as graphene, the KS potential is periodic with respect to the \( x-y \)-plane, but not fully translationally invariant as assumed in Eq. (1). As a result, the \( x-y \)-directions do not decouple from the \( z \)-direction and the KS states have the form

\[
\phi_{k\alpha}(r) = e^{ikr_1} u_{k\alpha}(r)
\]

where \( k \) is the 2D crystal momentum resulting from the Born-von Karman boundary conditions in the \( x-y \)-directions,

\[
k = \sum_{j=1}^{2} \frac{l_j}{N_j} \mathbf{b}_j \quad \text{with} \quad -\frac{N_j}{2} \leq l_j < \frac{N_j}{2}.
\]

Here \( \mathbf{b}_j \) denotes the 2 primitive vectors of the 2D reciprocal lattice and the condition on the right-hand side restricts \( k \) to the 1 Brillouin zone (1BZ). Similarly, \( \mathbf{G} \) is a vector of the 2D reciprocal lattice,

\[
\mathbf{G} = \sum_{j=1}^{2} m_j \mathbf{b}_j \quad \text{with} \quad m_j \in \mathbb{Z}.
\]

The normalization is chosen so that \( u_{k\alpha} \) integrates up to 1 for a single unit cell of area \( A \),

\[
\delta_{\alpha,\alpha'} = \int_A d^2r_1 \int_{-\infty}^{\infty} dz u_{k\alpha}(r) u_{k'\alpha}(r) = \int_{-\infty}^{\infty} dz \sum_{\mathbf{G}} c_{k\alpha}(\mathbf{G}, z) c_{k'\alpha}(\mathbf{G}, z).
\]

The total density can be written as

\[
n(r) = 2 \int_{1BZ} \frac{d^2k}{(2\pi)^2} \sum_{\alpha} \Theta(\epsilon_f - \epsilon_{k\alpha}) \sum_{\mathbf{G}} e^{i\mathbf{G} \cdot r_1} \times \sum_{G'} c_{k\alpha}(\mathbf{G}', z) c_{k\alpha}(\mathbf{G} + \mathbf{G}', z).
\]

Insertion of (42) into the exchange energy density of Eq. (11) and use of the 2D Fourier transform of the Coulomb

![Figure 3: x-y averaged asymptotic exchange potential of graphene: supercell result (36) with k-point sampling function (38) for a = 21a_0 versus single slab potential (15) — (a) v_{k\alpha}(z); (b) z^2v_{k\alpha}(z) for technical details see Sec. III.](image-url)
interaction yields
\[ e_s(r) = -\int_{\text{BZ}} \frac{d^2k}{(2\pi)^2} \frac{d^2k'}{(2\pi)^2} \sum_{a,a'} \Theta(\varepsilon_F - \varepsilon_{k,a}) \Theta(\varepsilon_F - \varepsilon_{k',a'}) \]
\[ \times \sum_{G,G'} e^{i(G-G')r} \int_{-\infty}^{\infty} dz' \frac{2\pi e^{-|k-k'|z'}}{|k-k'|} \]
\[ \times \sum_{G''} c^*_{k,a}(G'',z)c_{k,a}(G'' + G,z) \]
\[ \times \sum_{G''} c^*_{k,a}(G'',z')c_{k,a}(G'' + G',z'). \] (48)

For large \( z \), one can now use the exponential localization of the \( u_{k,a} \) to neglect the \( z' \)-dependence in \( e^{-|k-k'+G||z-z'|} \). Moreover, for large \( z \) only \( k-k' + G' = 0 \) contributes sizably, so that the sum over \( G' \) reduces to the term with \( G' = 0 \) and \( k' \) can be approximated by \( k \) elsewhere in the integrand,

\[ e_s(r) \approx -\int_{\text{BZ}} \frac{d^2k}{(2\pi)^2} \frac{d^2k'}{(2\pi)^2} \sum_{a,a'} \Theta(\varepsilon_F - \varepsilon_{k,a}) \]
\[ \times \sum_{G} e^{iG r} \int_{-\infty}^{\infty} dz' \frac{2\pi e^{-|k-k'|z'}}{|k-k'|} \]
\[ \times \sum_{G''} c^*_{k,a}(G'',z)c_{k,a}(G'' + G,z) \]
\[ \times \sum_{G''} c^*_{k,a}(G'',z')c_{k,a}(G'' + G',z'). \] (49)

Utilizing the orthonormality (46), one arrives at

\[ e_s(r) \approx -\int_{\text{BZ}} \frac{d^2k}{(2\pi)^2} \frac{d^2k'}{(2\pi)^2} \sum_{a} \Theta(\varepsilon_F - \varepsilon_{k,a}) \]
\[ \times \sum_{G} e^{iG r} \frac{2\pi e^{-|k-k'|z'}}{|k-k'|} \]
\[ \times \sum_{G''} c^*_{k,a}(G'',z)c_{k,a}(G'' + G,z). \] (50)

Finally, one can argue as in Sec. II B in order to extend the \( k' \)-integration over the complete space and use Eq. (47),

\[ e_s(r) \approx -\frac{n(r)}{2z}. \] (51)

III. COMPUTATIONAL DETAILS

In the present work, the PWPP approach is combined with the supercell technique to study two prototype systems, free-standing graphene and a silicon slab with (111) surface, consisting of 3 bilayers (see Fig. 4). In both cases the experimental lattice constants are applied (\( a_0 = 2.46 \text{ Å for graphene}, \ a_0 = 5.43 \text{ Å for bulk Si} \), any reconstruction/relaxation of the Si (111) surface is neglected. In order to ensure a decoupling of neighboring slabs and to extract the \(-1/z\)-behavior of \( v_s \), a vacuum width of up to \( 7a_0 (\approx 32 \text{ bohrs}) \) is utilized for graphene, of up to \( 8a_0/\sqrt{3} (\approx 47 \text{ bohrs}) \) for the Si slab (for a discussion see Sec. IV B).

PWPP supercell calculations with the exact exchange suffer from the high scaling of the computational cost with the size of the unit cell and the cut-off energy (for details on the PWPP-EXX approach see Refs. 25 and 26). The same time, the most interesting property of the EXX potential, its \(-1/z\)-decay into the vacuum, is only clearly visible, if the separation of the slabs is sufficiently large. In addition, the EXX potential is much more sensitive to the asymptotic form of the KS states than the LDA potential. In order to illustrate the challenge posed by the EXX, Fig. 5 shows the exponential decay of the atomic 2s state of Carbon, comparing the exact (numerical) radial orbital with Fourier representations truncated at different cut-off energies \( E_{\text{cut}} \) of the plane-wave expansion. While the (conservative) standard value of \( E_{\text{cut}} = 80 \text{ Ry} \) covers already a good part of the exponential decay, any increase...
of the range for which the Fourier representation is supposed to give an accurate account of the true orbital requires extremely high cut-off energies. For instance, an $E_{\text{cut}}$ beyond 2000 Ry is necessary to obtain a clean Fourier representation for $r \approx 15$ bohrs, which is about half of the minimum sheet separation required for graphene (see below). For this reason most PWPP-EXX calculations of this work rely on the KLI approximation\(^{19}\) for which these huge cut-off energies can be handled (a comparison of KLI and OPM solutions is given in Sec. IV A).

In all EXX calculations correlation has been omitted for this conceptual study, LDA results always include correlation in the Vosko-Wilk-Nusair (VWN) form\(^{27}\) (if not stated otherwise). In the case of the largest slab separations, an energy cut-off of 2000–4000 Ry has been applied for graphene, 1000 Ry for the Si slab. For $k$-point sampling the Monkhorst-Pack scheme\(^{28}\) has been utilized. Tests showed that for graphene the $8 \times 8 \times 1$ $k$-point grid (or $8 \times 8 \times 2$) is sufficient for EXX calculations. For the Si slab the more moderate $6 \times 6 \times 1$-sampling (and also $6 \times 6 \times 2$) has been used, since the exact exchange scales quadratically with the number of $k$-points and the number of occupied states. For the LDA and GGA calculations of this work larger $k$-point grids ($10 \times 10 \times 2$ and more) but smaller cut-off energies ($320–640$ Ry) were employed. The EXX pseudopotentials have been constructed with the iterative scheme of Ref. 29, all LDA and GGA pseudopotentials are based on the standard Troullier-Martins procedure.\(^{30}\)

IV. RESULTS

A. Comparison of full OPM solution with KLI approximation

The KLI approximation is known to reproduce the asymptotic behavior of the exchange potential of atoms and molecules extremely well, due to its asymptotic $-1/r$-behavior.\(^{19}\) Moreover, Eqs. (18), (40), and (51) show the close relationship between the exact $v_\Omega$ and the KLI potential in the asymptotic regime of slabs. The KLI potential has quite generally been found to be fairly accurate both for atoms and diatomic molecules.\(^{31}\) Similarly moderate differences between the KLI and OPM potentials have been observed for jellium slabs.\(^{2,3}\) However, the KLI approximation often yields inaccurate bandgaps and misses spatial fine-structure in $v_\Omega$ (see, e.g., Ref. 10). As a result of the latter, it does not reproduce the OPM ground state in the case of transition metal oxides.\(^{32}\)

In order to analyze the quality of the KLI approximation in the case of slabs, we compare the KLI result for graphene with the full OPM solution\(^{9,26}\) for a sheet separation of $3a_0$ (which is close to the stacking of $a \approx 2.7a_0$ in graphite) — PWPP-OPM calculations for larger separation turned out to be computationally prohibitive. For this vacuum width, a cut-off energy of 240 Ry for the KS states is sufficient. However, in order to limit the size of the KS response function in the OPM integral equation, a reduced cut-off energy of 200 Ry has been applied for the OPM exchange potential (the response function is nevertheless calculated from the complete KS spectrum, involving more than 16 000 states). Since $v_\Omega$ is usually smoother than the pseudopotential, this reduced Fourier representation is often sufficient (compare Ref. 33).

Figure 6 displays the resulting band structure. The maximum deviation of the KLI energies from the exact OPM values is found for the valence band at the $\Gamma$-point (3.37 eV versus 3.74 eV below $\epsilon_F$). Still, the errors involved seem acceptable: the ordering of all bands is identical, only small shifts of parts of the bands are observed. In particular, the valence and conduction bands around the Dirac points agree very well.

The corresponding total KS potentials are shown in Fig. 7. In order to extract more clearly the well depth of the KLI potential, the full $v_\Omega(r)$ has been averaged over the $x$- and $y$-directions as in Eq. (52). Both potentials are normalized such that their spatial average in the 3D unit cell vanishes. Figure 7 demonstrates that the KLI potential follows the full OPM reference rather closely (the small oscillations of the OPM potential in the middle of the vacuum region are a consequence of the reduced cut-off energy applied to $v_\Omega$, i.e., a numerical artefact). In particular, the net well depth of the KLI potential does not differ from the correct OPM depth. Correspondingly, one finds only minor differences between the total ground and exchange energies per atom (0.5 mHa for

---

**FIG. 6.** EXX band structure of graphene with sheet separation of $3a_0$: KLI approximation versus full OPM.

**FIG. 7.** $x$-$z$-averaged total KS potential of graphene with vacuum of $3a_0$: KLI approximation versus full OPM. $z = 6.97$ bohrs corresponds to the middle of the vacuum.
$E_{\text{tot}}$, 5 mHa for $E_{\chi}$, quite similar to the situation for atoms. These results suggest that the error of the KLI approximation is of limited importance for the systems considered in this work. All subsequent EXX results have been produced with the KLI approximation.

**B. Decoupling of slabs**

The next question to be addressed is that of the interaction between neighboring slabs. In the case of the LDA or GGA typically a slab separation of 15–30 bohrs is sufficient for a decoupling of the slabs. Figure 8 demonstrates that the situation is basically similar for EXX calculations. The occupied bands of graphene obtained with a vacuum width of $3a_0 \approx 14$ bohrs cannot be visually distinguished from those resulting from a width of $7a_0 \approx 32$ bohrs: the corresponding eigenvalues differ by less than 8 meV (measured relative to the corresponding $\epsilon_F$). The differences reduce to less than 1.5 meV, when comparing the eigenvalues from a width of $5a_0 \approx 23$ bohrs with those from $7a_0$. These differences are, however, somewhat larger than their LDA counterparts: the LDA eigenvalues only change by less than 2 meV, when going from $3a_0$ to $7a_0$, and by less than 0.01 meV, when increasing the width from $5a_0$ to $7a_0$. Depending on the desired degree of decoupling, EXX calculations therefore require a larger vacuum region than LDA or GGA calculations.

**C. Normalization of total and exchange potential**

As a prototype EXX result obtained with the supercell approach, Fig. 9 shows the exchange potential of graphene in two different planes including the $z$-axis. Two features are worth noting at this point: (i) the potential approaches a non-vanishing constant in the middle of the vacuum between the graphene sheets; (ii) the corrugation of the potential dies out rapidly with increasing $z$. For very large $z$ the detailed structure of the density in the slab becomes irrelevant, so that the true $v_\chi$ is well characterized by the exchange potential obtained for the 2D translationally invariant slab of Sec. II.

The non-vanishing potential in the middle of the vacuum is a consequence of the overall normalization of the average exchange potential to zero. Similarly, the total KS potential approaches a constant in this regime, the precise value depending on the computational details. On the other hand, the absolute scale of the total KS potential becomes relevant as soon as, e.g., the work function or electron scattering at the surface is considered. One thus has to address the question of how to normalize the exchange and the total potential. While this normalization is simple in the case of the LDA or GGA (due to the “exponentially” decaying xc-potentials in the vacuum), the same is no longer true for the long-range $1/z$-potential of the EXX approach.

In the first step of the normalization procedure, one considers the derivatives of both the exchange and the total KS potential, since any ambiguity related to normalization drops out in $v'$. In order to compare the numerical potentials with the asymptotic limit (16) an average over the directions parallel to the slab is used,

$$v_{av}(z) = \frac{1}{A} \int_A d^2 r \parallel v(r)$$

$$= \sum_{G_\perp} e^{iG_\perp z} v(G_1 = 0, G_\perp).$$

Here $A$ denotes the area of the 2D in-plane unit cell of the slab, $\int_A d^2 r \parallel$ indicates an integration over this cell, and $G_1$ and $G_\perp$ are the reciprocal lattice vectors parallel and perpendicular to
the slab. As indicated before, $v_{av}(z)$ is very close to the local $v(r)$ for large $z$ (the index $av$ is dropped in the following).

Figure 10 shows the quantity $z^2 v'(z)$ for graphene. Ultimately, the exact $z^2 v'(z)$ must approach $+1$ in the case of a single slab for both $v_z$ and $v_s$ (assuming the slab to be neutral). As discussed in Sec. II D, the results of supercell calculations can be close to this limit only in the exponential regime $L \ll z \ll a/2$, while the derivatives of both $v_z$ and $v_s$ necessarily have to vanish in the middle of the vacuum region (compare Fig. 3; note that $z^2 v'(z)$ is an extremely sensitive measure of the numerical quality of $v(z)$ in regions in which $v(z)$ is almost constant, which manifests itself in the numerical noise visible for $7a_0$ — the derivative of $v_z$ shown in Fig. 10 has been calculated from the potential displayed in Fig. 9). Figure 10 demonstrates that one actually has such an exponential regime for a sheet separation of $7a_0$: the derivatives of both $v_z$ and $v_s$ are very close to $1/z^2$ for 6 bohrs $\lesssim z \lesssim 9$ bohrs. The more refined treatment of the Coulomb singularity in a 3D supercell calculation — as compared to the complete decoupling of the $k_y$-sampling from the $q$-sampling in Eq. (33) — lets $v_z$ approach its semi-asymptotic form much more rapidly than observed in Fig. 3. In fact, the minimum separation for which a small exponential regime is observed is $6a_0$, while a vacuum width of only $5a_0$ does not allow $v_s$ to approach its asymptotic form for a sizable range of $z$. A measure of the uncertainty in this normalization is obtained by comparison with the asymptotic exchange potential (15), evaluated with the $x$-$y$-averaged density of the highest occupied band: at $z = 8$ bohrs this potential differs by 4 mHa from $-1/z$.

Moreover, Fig. 10 confirms that $v'_z$ and $v'_s$ and thus the properly normalized $v_z$ and $v_s$ are identical beyond $z = 6$ bohrs: at this point the total electrostatic potential has already approached its constant vacuum value. Consequently, the normalization of $v_z$ can also serve as normalization of $v_s$. According to Fig. 10, the optimum point for normalization should be between 7 and 8 bohrs.

The result of a normalization of the numerical $v_z$ to $-1/z$ at $z = 8$ bohrs is plotted in Fig. 11. One observes the deviation of the supercell $v_z$ from $-1/z$ when $z$ approaches the middle of the vacuum region. However, both $v_z$ and $v_s$ follow $-1/z$ over a substantial range of $z$. In fact, $v_s$ remains close to $-1/z$ even for comparatively small $z$, as Fig. 12 demonstrates.

In principle, the normalization proceeds in exactly the same way for the Si(111) slab. However, as Fig. 13 illustrates, complete convergence of the total and exchange potential to $-1/z$ in the exponential regime has not been achieved, due to the limited width of the vacuum for which numerically stable calculations were possible. Figure 13 nevertheless confirms the identity of the total potential with the exchange potential outside the surface regime. Moreover, the result obtained for $a = 8a_0/\sqrt{3}$ shows at least some indication of convergence to $-1/z$ in the intermediate regime $L \ll z \ll a/2$. The point $z = L = 18$ bohrs ($z = 24.8$ bohrs), for which the numerical $v'_z(z)$ is equal to $1/z^2$, suggests itself for normalization. It seems worthwhile to note that a 20% error at this point amounts to an error in normalization of only 8 mHa.

D. Comparison of EXX and LDA results

Figures 11 and 12 also provide the starting point for a comparison of the EXX results with their LDA counterparts.
One first of all recognizes the exponential decay of \( v_{z}^{\text{LDA}} \) for large \( z \) with its obvious consequences for surface states. In fact, Fig. 11 clearly shows that the uncertainty in the normalization of \( v_{z}^{\text{EXX}} \) is irrelevant when comparing EXX with LDA or GGA results.

One next observes that part of the additional depth of the asymptotic EXX potential is transferred to the well depth in the interior of the graphene sheet. As a result, the unoccupied EXX bands are slightly less dense than the LDA bands, which is most obvious for the lowest unoccupied bands around the \( \Gamma \)-point (see Fig. 14).

The increased well depth is even more remarkable, since the LDA potential and bands of Figs. 12 and 14, respectively, include correlation. The effect of the correlation potential is most obvious in the work function, obtained from the KS Fermi energy of the slab relative to the electrostatic potential in the middle of the vacuum region. Table I lists the LDA and GGA work functions, both including and without correlation (for the GGA the PBEsol form has been applied). The LDA and GGA values are in good agreement with the literature, given the dependence of the work function on \( \alpha \) and the various other technical parameters. Similar to the situation for atomic ionization potentials, the LDA underestimates the EXX values by roughly a factor of 2, and the same is true for GGAs. Unlike for atomic ionization potentials, however, the EXX work function differs from the experimental value much more than the LDA and GGA data. The difference of 3.5 eV is clearly beyond the uncertainty in the normalization of the EXX potential, which should be of the order of 0.1–0.2 eV. Moreover, there appears to be no length scale available for graphene which could induce some additional structure in \( v_{z} \) for \( z > 10 \) bohrs, which would not have been resolved in this work due to the limited width of the vacuum. In view of the results of Sec. IV A, it is also unlikely that the KLI approximation is responsible for the large EXX work function. One thus concludes that the correlation potential has to come up for the substantial difference between EXX and experiment (note that a repulsive \( v_{c} \) has also been found for several atoms). It remains to be checked whether the large EXX value for \( W \) is a manifestation of the large finite size effects observed for jellium slabs in Ref. 3.

As a second example we consider the Si(111) slab. For this conceptual study of the EXX potential relaxation of the atomic positions has been ignored—all atoms remain at their bulk positions. The corresponding EXX exchange potential (after normalization as discussed in Sec. IV C) is plotted in Fig. 15. The Si(111) potential shows even less corrugation than its graphene counterpart, thus corroborating the normalization procedure of Sec. IV C. Moreover, similar to atomic and bulk exchange potentials, the EXX potential exhibits a somewhat more pronounced spatial structure than the LDA (compare Figs. 15 and 16). Unlike predicted for the full OPM potential of metallic slabs, the KLI results for Si(111) do not show any shoulder in \( v_{c} \) outside the surface of the slab, consistent with the origin of the shoulder.

In order to provide a clearer account of the well depth inside the slab, the EXX potential is directly compared with the LDA exchange and its asymptotic form in Fig. 17, using the average (52). The EXX exchange potential is about 60 mHa more attractive than the LDA exchange, which is quite close to the difference of 54 mHa obtained between the EXX and x-only LDA work functions (see Table I).

### Table I. Work function of graphene as well as Si(111) slabs (without relaxation): EXX-only (in KLI approximation) versus LDA and PBEsol-GGA results with and without correlation. The uncertainties given for the EXX values have been estimated by variation of the normalization point, the width of the vacuum and the \( k \)-point sampling. The experimental value for graphene is also listed (all energies in eV).

<table>
<thead>
<tr>
<th>Method</th>
<th>Graphene</th>
<th>Si(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expt.</td>
<td>4.6</td>
<td>5.05</td>
</tr>
<tr>
<td>LDA/VWN</td>
<td>4.55</td>
<td>4.69</td>
</tr>
<tr>
<td>PBEsol</td>
<td>4.25</td>
<td>3.98</td>
</tr>
<tr>
<td>LDA x-only</td>
<td>3.21</td>
<td>3.98</td>
</tr>
<tr>
<td>PBEsol x-only</td>
<td>2.89</td>
<td>3.66</td>
</tr>
<tr>
<td>EXX x-only</td>
<td>8.13 ± 0.15</td>
<td>5.45 ± 0.2</td>
</tr>
</tbody>
</table>

FIG. 13. Derivative of \( x-y \)-averaged potential \( (52) \) for Si(111) slab with 3 bilayers: total EXX/KLI KS potential for different width of the vacuum \( (6a_{0}/\sqrt{3} \) and \( 8a_{0}/\sqrt{3} \) \) and two different \( k \)-point samplings \( (6 \times 6 \times 1 \) and \( 6 \times 6 \times 2 \) \) versus EXX/KLI exchange potential for vacuum width of \( 6a_{0}/\sqrt{3} \) as well as asymptotic exchange potential (15) (evaluated with the \( x-y \)-averaged density of the highest occupied band) and \(-1/\gamma\).

FIG. 14. Band structure of graphene with sheet separation of \( 7a_{0} \). EXX/KLI versus LDA (including VWN correlation). The right-hand scale shows the energies relative to the EXX/KLI vacuum limit.
The latter potential corresponds to the expansion point $-L$ in Eq. (16) and represents a potential which decays like $-1/z$ relative to the surface of the slab, rather than relative to the middle of the slab. It is obvious that the true exchange potential is much closer to the pure $-1/z$ behavior, which reflects the fact that $(z)$ vanishes for the highest occupied state of the Si(111) slab.

In fact, as soon as the highest occupied state is a delocalized bulk state, $(z)$ will always be (close to) zero. As a consequence, the regime in which the exchange potential dominates the total KS potential moves further and further away from the surface with increasing thickness $L$ of the slab until the $-1/z$ behavior ultimately becomes invisible in the limit $L \rightarrow \infty$.

The width $2L$ of the slab sets the scale for the truly asymptotic regime. This subtle limiting behavior could explain why the $-1/z$ behavior is not seen in experiments at metal surfaces.

Figure 17 also shows two variants of the asymptotic potential (16): a pure $-1/z$ behavior is compared with $-1/(z-L)$ (with $L$ denoting the position of the outermost atomic layer). The latter potential corresponds to the expansion point $z_0 = L$ in Eq. (16) and represents a potential which decays like $-1/z$ relative to the surface of the slab, rather than relative to the middle of the slab. It is obvious that the true exchange potential is much closer to the pure $-1/z$ behavior, which reflects the fact that $(z)$ vanishes for the highest occupied state of the Si(111) slab.

In fact, as soon as the highest occupied state is a delocalized bulk state, $(z)$ will always be (close to) zero. As a consequence, the regime in which the exchange potential dominates the total KS potential moves further and further away from the surface with increasing thickness $L$ of the slab until the $-1/z$ behavior ultimately becomes invisible in the limit $L \rightarrow \infty$.

The width $2L$ of the slab sets the scale for the truly asymptotic regime. This subtle limiting behavior could explain why the $-1/z$ behavior is not seen in experiments at metal surfaces.

V. SUMMARY

In this work, it has been demonstrated that (i) standard PWPP calculations with the exact exchange are viable for slab geometries, and (ii) the resulting exchange potential shows an extended range where it behaves as $-1/z$, if the width of the vacuum is chosen sufficiently large. However, due to the high cut-off energies required for an accurate representation of the exponentially decaying KS states outside the surface, such EXX calculations are extremely expensive. Unlike for the LDA or GGA, for which an inaccurate density in the middle of the vacuum region does not really affect calculations, the correct asymptotic form of the KS states is important for the stability of EXX calculations, both in the KLI and the OPM form.

Full OPM calculations were therefore only possible for rather limited separation of the slabs, more realistic vacuum widths could only be handled with the KLI approximation. For the case considered, however, the KLI approximation gives a fairly accurate account of the full OPM potential. It remains to be examined, though, whether the same is true more generally.

A physical decoupling of the slabs requires a somewhat larger vacuum region in the case of the EXX than necessary for the LDA or GGA. Moreover, an absolute normalization of the EXX exchange (and thus of the total potential) is only possible if $v_{\text{ks}}$ has reached its asymptotic limit. It turns out that an extremely large vacuum region has to be used to approach this limit: already for the Si(111) slab of only 3 bilayers a vacuum width of more than 45 bohrs is required for an accurate normalization. In fact, the asymptotic EXX potential of a Si(111) slab with 6 bilayers and a vacuum width of only 35 bohrs (not shown in this paper) has little in common with the expected asymptotic form. Quite generally, the distance between the range in which $v_{\text{ks}}$ starts to behave like $-1/z$ and the surface increases with the slab thickness. A determination of the EXX work function is therefore difficult, if not impossible for realistic slabs with 10–20 atomic layers, as long as a plane-wave basis is utilized.
So far, a normalization is only possible for thin slabs like graphene. For this material the EXX work function (in the KLI approximation) was found to be much larger than its LDA counterpart and the experimental work function. Given the accuracy of the KLI approximation for limited separation of the graphene sheets, this result suggests that the correlation potential is always attractive and GGA correlation potentials are known to be unreliable for atoms.\(^4\) It remains to be seen whether any of the orbital-dependent correlation functionals\(^5\) can account for the substantial difference between EXX and experiment.

ACKNOWLEDGMENTS

Very helpful discussions with J. Braun, D. Ködderitzsch, J. Minar, and T. Stroucken are gratefully acknowledged. The calculations for this work have been performed on the computer cluster of the LOEWE Center for Scientific Computing of J. W. Goethe University Frankfurt am Main.

APPENDIX: COMPLETE ASYMPTOTIC EXCHANGE POTENTIAL OF JELLIUM SLAB

We start again with Eq. (11). However, rather than performing the \(r_s\)-integration first, we follow Ref. 3 and integrate out the density matrix completely,

\[
\rho(r, r') = \sum_a \frac{k_a}{\pi} \Theta(\epsilon_F - \epsilon_a) \left| J_1(k_a |r - r'|) \right|^2 \times \varphi_a(z) \varphi_a(z')
\]  

(A1)

\((\varphi_n)_{\text{denotes the Bessel functions of first kind}}\). Insertion into the exchange energy (11) yields

\[
E_x = -\frac{1}{2\pi} \int_0^\infty dz \int_0^\infty dz' \int_0^\infty du \frac{u}{|r - r'|} \sum_{a,a'} k_a k_{a'} \times \Theta(\epsilon_F - \epsilon_a) \Theta(\epsilon_F - \epsilon_{a'}) J_1(k_a u) J_1(k_{a'} u) \times \varphi_a(z) \varphi_{a'}(z') \varphi_a(z') \varphi_{a'}(z') \left[ \frac{u^2 + (z - z')^2}{|u|^2} \right]^{1/2}.
\]  

(A2)

Functional differentiation of this result with respect to the asymptotic \(n(z)\) (following Ref. 21) gives

\[
\frac{\delta E_x}{\delta n(z)} \xrightarrow{z \gg L} -\frac{2}{k_h \varphi_h(z)} \int_0^\infty dz' \int_0^\infty du \sum_a k_a \times \Theta(\epsilon_F - \epsilon_a) J_1(k_a u) J_1(k_{h} u) \times \varphi_a(z) \varphi_h(z') \varphi_h(z') \frac{u^2 + (z - z')^2}{|u|^2}^{1/2}.
\]  

(A3)

However, due to the exponential decay of \(\varphi_a\), the highest occupied \(\varphi_a\) dominates for \(z \gg L\),

\[
\frac{\delta E_x}{\delta n(z)} \xrightarrow{z \gg L} -2 \int_0^\infty dz' \int_0^\infty du \left( \frac{u}{|u|^2} \right) J_1(k_{h} u)^2 \times \frac{\varphi_h(z')^2}{\left[ |u|^2 + (z - z')^2 \right]^{1/2}}.
\]  

(A4)

At this point, one can finally use the integral (A1) of Ref. 4 to arrive at the complete asymptotic \(v_\alpha\) of Ref. 3,

\[
v_\alpha(z) \xrightarrow{z \gg L} -\int_0^\infty dz' \frac{\varphi_h(z')^2}{|z - z'|} \times \left[ 1 - \frac{I_1(2k_h |z - z'|)}{k_h |z - z'|} \right] + \frac{I_1(2k_h |z - z'|)}{k_h |z - z'|}.
\]  

(A5)

Here \(I_1\) and \(L_1\) denote the modified Bessel and Struve functions, respectively. Equation (A5) includes all power-law corrections to the asymptotic \(v_\alpha\). Its accuracy depends, however, quite sensitively on the difference between the eigenvalues of the two most weakly decaying states.

20. Note that the KLI potential is determined by \(2\epsilon_n(r)/n(r)\) for exponentially decaying \(n(r)\), so that Eq. (51) proves that the KLI potential asymptotically falls off as \(-e^{-r}/r\).
22. In Eq. (36) the periodicity of \(\varphi_{\alpha u}\) has been taken into account in the functional derivative,
In the case of the EXX the normalization procedure of Sec. IV C has to be used to extract the work function $W$. One first realizes that inside the slab and in the exponential regime far from the middle of the vacuum region the true $v_e$ for a single slab differs from the actual $v_e^{sc}$ of the supercell calculation by a constant,

$$v_e^{sc}(z) = v_e(z) + \alpha \quad \text{for } z \ll a/2.$$ 

The same is thus true for the corresponding Fermi energies,

$$\varepsilon_F^{sc} = \varepsilon_F + \alpha.$$

The difference between $v_e^{sc}$ and $v_e$ can be determined in the exponential regime $L \ll z \ll a/2$, in which the electrostatic potential $v_e^{sc}\text{elec}$ has already approached its vacuum limit. Choosing the normalization so that $v_e^{sc}\text{elec} = v_{elec}$, $v_e^{sc} - v_e$ is determined by the exchange potential,

$$\alpha = v_e^{sc}(z_0) + \frac{1}{z_0}$$

for $L \ll z \ll a/2$. $W$ is then obtained as

$$W = v_{elec} \left( \frac{a}{2} \right) - \varepsilon_F^{sc} + v_e^{sc}(z_0) + \frac{1}{z_0}$$

$$\approx v_e^{sc}(z_0) + \frac{1}{z_0} - \varepsilon_F^{sc}.$$ 

$z_0 = 8$ bohrs has been used for graphene, as discussed in Sec. IV C.

The shoulder in the exchange potential of jellium slabs observed in Ref. 2 is due to the non-KLI component of the exact OPM potential, which is not present in the $v_e$ of Secs. IV B–IV D. However, the argument of the missing length scale in the case of graphene also applies to the full OPM potential.

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