Two-dimensional limit of exchange-correlation energy functional approximations in density functional theory

Yong-Hoon Kim, In-Ho Lee, Satyadev Nagaraja, Jean-Pierre Leburton, Randolph Q. Hood, and Richard M. Martin

1 Department of Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801
2 Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801
3 Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, United Kingdom

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Abstract

We investigate the behavior of three-dimensional (3D) exchange-correlation energy functional approximations of density functional theory in anisotropic systems with two-dimensional (2D) character. Using two simple models, quasi-2D electron gas and two-electron quantum dot, we show a fundamental limitation of the local density approximation (LDA), and its semi-local extensions, generalized gradient approximation (GGA) and meta-GGA (MGGA), the most widely used forms of which are worse than the LDA in the strong 2D limit. The origin of these shortcomings is in the inability of the local (LDA) and semi-local (GGA/MGGA) approximations to describe systems with 2D character in which the nature of the exchange-correlation hole is very non-local. Nonlocal functionals provide an alternative approach, and explicitly the average density approximation (ADA) is shown to be remarkably accurate for the quasi-2D electron gas system. Our study is not only relevant for understanding of the functionals but also practical applications to semiconductor quantum structures and materials such as graphite and metal surfaces. We also comment on the implication of our findings to the practical device simulations based on the (semi-)local density functional method.

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I. INTRODUCTION

In the Kohn-Sham (KS) density functional theory (DFT), significant efforts have been devoted to improve the local density approximation (LDA). One approach, the generalized gradient approximation (GGA), has been successively improved for the last two decades and now is approaching chemical accuracy (atomization energy errors of order 1 kcal/mol = 0.0434 eV) with further refinements in the so-called meta-GGA (MGGA). The (M)GGA is desirable in that it leads to better physical quantities for various systems of interest, while it is still computationally cheap due to its semi-local nature. It is clear, however, that any local or semi-local approximation cannot fully reproduce the behavior of the exact nonlocal exchange-correlation energy functional, so one needs to be aware of the limitations of these approximation schemes and the situations where they can break down.

In this article, we discuss one situation where the local and semi-local approximations of the exchange-correlation energy functional inherently break down: systems with two-dimensional (2D) characteristics, which is relevant to DFT computations of semiconductor devices or other physical systems with 2D character. The original motivation of the current work is recent developments in semiconductor nanotechnology that have achieved quantum dots, which offer enormous technological prospects and allow the study of novel physical phenomena due to dimensionality and electronic correlation effects. Quantum dots can be achieved by confining a 2D electron gas with patterned gates. Semiconductor quantum devices in general involve large ranges of electron densities and density gradients, and the effect of electron-electron interactions can be important, so they provide ideal test cases of the approximate functionals commonly used in DFT. However, although DFT has been already extensively applied to the study of these systems, the validity of conventional approximation schemes in these systems has not been fully addressed. Hence, we investigate the robustness of various density-based three-dimensional (3D) local and semi-local exchange and correlation energy functional approximations, LDA, GGA, and MGGA, in the 2D-limit using the idealized quasi-2D electron gas and quantum dot systems. We show that there are inherent limitations resulting from the local or semi-local nature of the exchange-correlation hole in these approximations. Especially, we point out that within the restricted form of the GGA it is very difficult to incorporate the necessary requirement for the 2D limit while at the same time maintaining desirable features of present functionals. We contrast the limitation of these local and semi-local approximations with the nonlocal average density approximation (ADA), and explicitly show the improvement by employing the ADA for the quasi-2D electron gas system.

The organization of the paper is as follows. In Sec. II, we review the features of the LDA, GGA, MGGA, and ADA necessary for our later discussions. In particular, we emphasize that the approximations in these functionals are essentially approximations to the exchange-correlation hole. In Sec. III, we first establish the limitation of the local and semi-local approximations by considering the nature of the approximations to the exchange-correlation holes in the 2D limit, and contrast them with the nonlocal approximation (Sec. III A). In Sec. III B we explicitly show this in the 2D homogeneous electron gas with finite thickness: compared with the exact exchange energy which is finite in the 2D limit, the 3D LDA, GGA, and MGGA exchange energies incorrectly diverge to negative infinity. Especially, we point out that the direction of the GGA and MGGA correction to the LDA should be opposite to
that of the current forms. This is contrasted with the nonlocal ADA approximation which has a finite 2D-limit. In Sec. III C, we investigate an idealized quantum dot system. By varying the confinement strength along one direction, the system changes its character from 3D to 2D. We show that, while the LDA, GGA, and MGGA give satisfactory descriptions of the isotropic limit, they again fail in the 2D-limit. Present (M)GGA’s are better than the LDA in the isotropic 3D-limit, but they are again worse than the LDA in the 2D-limit. In addition, we comment on the validity of 2D and 3D DFT calculations of quantum dots at the experimentally realistic range of anisotropy. In Sec. III D, we discuss density functional calculations of two physical systems with 2D characters, jellium surface and the graphite. We conclude this paper by summarizing the current work in Sec. IV.

II. EXCHANGE-CORRELATION ENERGY FUNCTIONALS

The exchange-correlation energy may be written as the interaction energy between the electron density \( n(r) = \sum_{\sigma=\uparrow,\downarrow} n_{\sigma}(r) \) and the coupling-constant integrated exchange-correlation hole:\[ E_{xc}\{n_{\sigma}\} = \frac{1}{2} \int d^3 r \int d^3 r' \frac{n(r) \bar{\rho}_{xc}\{\{n_{\sigma}\}; r, r'\}}{|r - r'|}, \]

where \( \bar{\rho}_{xc}\{\{n_{\sigma}\}; r, r'\} = n(r') \int_0^1 d\lambda \left[ g^\Lambda([\{n_{\sigma}\}; r, r']) - 1 \right] \equiv n(r') [g([\{n_{\sigma}\}; r, r']) - 1], \)

where \( g^\Lambda([\{n_{\sigma}\}; r, r']) \) is the pair-correlation function. We adopt atomic units throughout the paper with \( \hbar = e = m_e = 1 \). The exact exchange and correlation hole have several important physical conditions that should be also observed by approximations such as the negativity of the exchange hole:

\[ \bar{\rho}_x\{\{n_{\sigma}\}; r, r'\} < 0, \]

and sum rules of the exchange and correlation holes:\[ \int d^3 r' \bar{\rho}_x\{\{n_{\sigma}\}; r, r'\} = -1, \]
\[ \int d^3 r' \bar{\rho}_c\{\{n_{\sigma}\}; r, r'\} = 0. \]

Various approximation schemes based on density-derived variables are attempts to approximate the exchange-correlation energy functional

\[ E_{xc}\{n_{\sigma}\} = \int d^3 r \ n(r) \ \epsilon_{xc}\{\{n_{\sigma}\}; r\}, \]

or exchange-correlation energy density functional

\[ \epsilon_{xc}\{\{n_{\sigma}\}; r\} = \frac{1}{2} \int d^3 r' \frac{\bar{\rho}_{xc}\{\{n_{\sigma}\]; r, r'\}}{|r - r'|}. \]
in terms of a function of density and/or other density related variables. In the standard LDA, the exchange-correlation energy density is replaced by that of the homogeneous electron gas at each point $r$

$$\epsilon_{xc}([\{n_\sigma\}; r]) \approx \epsilon_{xc}^{LDA}([\{n_\sigma(r)\})] = \epsilon_{xc}^{hom}([\{n_\sigma(r)\})], \quad (7)$$

which can be interpreted as an approximation to the exchange-correlation hole

$$\bar{\rho}_{xc}^{LDA}([\{n_\sigma\}; r, r']) = n(r) [\bar{g}^{hom}([\{n_\sigma\}; |r - r'|) - 1]. \quad (8)$$

It is important to notice that the local replacement of density prefactor $n(r')$ by $n(r)$ in Eq. (8) leads to the LDA exchange-correlation hole being spherical and centered on the electron, while the exact one is centered at the another point (such as at the nucleus position in an atom or molecule) and very asymmetric. Thus we might expect the LDA hole to be a reasonable approximation when the exact exchange-correlation hole is close to the electron. Since only the spherical average of the exchange-correlation hole

$$\bar{\rho}_{xc}^{SA}(r, R) = \frac{1}{4\pi} \int_{\Omega} dr' \bar{\rho}_{xc}(r, r'), \quad \Omega : |r - r'| = R \quad (9)$$

influences the exchange-correlation energy, the spherically symmetric nature of the LDA hole does not necessarily represent a poor approximation. In addition, it is known that the LDA is a surprisingly robust approximation scheme, which may be understood from the fact that its exchange-correlation hole satisfies the hole conditions Eqs. (3) and (4).

In the following sections, we examine important features of other approximations, including the GGA, MGGA, and ADA, which are relevant for our discussions in later sections.

**A. Generalized Gradient Approximation**

Although the idea of utilizing density gradient information as a way to improve the LDA was proposed in the original papers of Kohn and Sham, it is only in the last decade or so in which successful GGA functionals have appeared. This suggests that some of the correct physics of the exchange-correlation effects, which were missing in the original naive gradient expansion approximation (GEA), have been incorporated in recent developments of the GGA. The most important step in the development of the GGA was the recognition by Perdew and coworkers that the exchange-correlation hole in the GEA does not correspond to a physical hole, nor does it satisfy the negativity condition of the exchange hole [Eq. (3)] and normalization conditions of the exchange and correlation holes [Eq. (4)]. Following their argument, the GGA can be understood as an approximation of the exchange-correlation hole in which the spurious long-range part of the second-order GEA exchange-correlation GEA hole has been cut-off in the real space to satisfy the conditions of Eq. (3) and Eq. (4). One should note that the GGA is based on the modification of the LDA exchange-correlation hole, so its hole is local and it tends to be an improvement over the LDA when the LDA is a good first-order approximation.

Different GGA approaches can be compared by writing the GGA exchange-correlation energy density in terms of the reference LDA exchange energy density multiplied by the factor $F_{xc}$.
\[ \epsilon_{xc}(\{n_\sigma\}; r) \approx \epsilon_{xc}^{GGA}(\{n_\sigma(r), |\nabla n_\sigma(r)|\}) \equiv \epsilon_{xc}^{LDA}(n(r)) \ F_{xc}^{GGA}(\{n_\sigma(r), |\nabla n_\sigma(r)|\}), \] (10)

where \( \epsilon_{xc}^{LDA}(n(r)) = -3(3\pi^2 n(r))^{1/3} / (4\pi) \). \( F_{xc}^{GGA} \), can be naturally divided into two parts, exchange \( F_{x}^{GGA} \) and correlation \( F_{c}^{GGA} \). For exchange, because of the spin-scaling relation,

\[ E_{x}(\{n_\sigma\}) = \frac{1}{2} E_{x}[2n_\uparrow] + \frac{1}{2} E_{x}[2n_\downarrow], \] (11)

we only need to consider the spin-unpolarized case \( F_{x}^{GGA}(n, |\nabla n|) \), which is in terms of the dimensionless reduced density gradient

\[ s = \frac{|\nabla n|}{2(3\pi^2)^{1/3} n^{4/3}}, \] (12)

is \( F_{x}^{GGA}(s) \). Numerous gradient approximations for the exchange have been proposed, and in this work we consider the three most successful and popular ones by Becke (B88), Perdew and Wang (PW91), and Perdew, Burke, and Enzerhof (PBE). In Fig. we compare the \( F_{x}^{GGA} \)'s of these three approximations. Most other \( F_{x}^{GGA} \)'s fall between B88-GGA and PBE-GGA, so the qualitative results obtained by employing other functionals can be interpolated from the behavior of the B88-GGA and PBE-GGA.

As shown in Fig. one can divide the GGA into two regions, (i) small \( s \) \((0 \lesssim s \lesssim 3)\) and (ii) large \( s \) \((s \gtrsim 3)\) regions. In region (i), which is relevant for most physical applications, different \( F_{x}^{GGA} \)'s have nearly identical shapes, which explains why different GGA's give similar improvement for many conventional systems with small density gradient contributions.

Most importantly, \( F_{x}^{GGA} \geq 1 \), so all the GGA’s leads to exchange energy lower than the LDA. Typically there are more rapidly varying density regions in atoms than condensed system, so this will lead to the lowering of the exchange energy in atoms more than molecules and solids. This results in the reduction of binding energy, correcting the LDA overbinding and improving agreement with experiment, which is one of the most important characteristics of present GGA’s.

In region (ii), the different limiting behaviors of \( F_{x}^{GGA} \)'s result from choosing different physical conditions for \( s \to \infty \). In B88-GGA, \( F_{x}^{B88-GGA}(s) \sim s/\ln(s) \) was chosen to give the correct exchange energy density \( (\epsilon_{x} \to -1/2r) \). In PW91-GGA, choosing \( F_{x}^{PW91-GGA}(s) \sim s^{-1/2} \) satisfies the Lieb-Oxford bound and the non-uniform scaling condition. In PBE-GGA, the non-uniform scaling condition was dropped in favor of a simplified parameterization with \( F_{x}^{PBE-GGA}(s) \sim const. \) The fact that different physical conditions lead to very different behaviors of \( F_{x}^{GGA} \)'s in region (ii) not only reflects the lack of knowledge of the large density gradient regions but also an inherent difficulty of the density gradient expansion in this region: even if one GGA form somehow gives the correct result for a certain physical property while others fail, it is not guaranteed that the form is superior for other properties in which different physical conditions prevail.

Correlation is more difficult to include, but its contribution to the total energy is typically much smaller than the exchange, especially for systems with large density gradients. Hence, the main qualitative results of this work, which is concerned with the strong anisotropic 2D-limit, are determined at the exchange level. For correlations, we employed PW91- and PBE-GGA which are almost identical and designed to be turned off for large density gradient region as shown in Fig. (b) for the PBE-GGA correlation part enhancement factor.
The fact that correlation decreases with increasing gradients can be qualitatively understood in that systems with large gradients have strong confining potentials that increase level spacings and reduce the effect of correlations.

### B. Meta-Generalized Gradient Approximation

One natural extension of the GGA is to employ the next higher order gradient expansion variables, the Laplacian of the density $\nabla^2 n_\sigma (r)$ and the orbital kinetic energy density $\tau_\sigma (r)$, in addition to the density $n_\sigma (r)$ and density gradient $\nabla n_\sigma (r)$. Several forms of this so-called meta-GGA (MGGA) have been suggested, and here we only consider the recent work of Perdew and his coworkers (PKZB) based on the PBE-GGA. They removed the dependence on the Laplacian of the density by introducing a new variable

$$\bar{q} = \frac{3\tau}{2(3\pi^2)^{2/3} n^{5/3}} - \frac{9}{20} - \frac{s^2}{12},$$

which reduces to the dimensionless Laplacian of the density $q = \nabla^2 n/(4(3\pi^2)^{2/3} n^{5/3})$ in the slowly varying limit but remains finite at a nucleus where $q$ diverges. Hence we can write PKZB-MGGA as,

$$\epsilon_{xc}([\{n_\sigma\}; r]) \approx \epsilon_{xc}^{MGGA}([n_\sigma (r), |\nabla n_\sigma (r)|, \tau_\sigma]) \equiv \epsilon_{x}^{LDA} (n(r)) F_{xc}^{MGGA} ([n_\sigma (r), |\nabla n_\sigma (r)|, \tau_\sigma]),$$

similar to Eq. (10). The enhancement factor $F_{xc}^{PKZB-MGGA}$ for the exchange is shown in Fig. 2 as a function of $s$ and $\bar{q}$. Unlike PBE-GGA, PKZB-MGGA exchange energy functional satisfies both the correct gradient expansion and the linear response limit for the exchange, and its correlation energy functional is self-interaction free for a single electron. However, the relevant feature of the $F_{xc}^{PKZB-MGGA}$ for the current discussion is that it (or its exchange-correlation hole) is still semi-local and $F_{xc}^{PKZB-MGGA}$ is always larger than or equal to 1 since it is based on the PBE-GGA (see Fig. 2 along the $s$-axis). So the qualitative feature of the PKZB-MGGA is similar to that of the PBE-GGA, and its exchange energy is always lower than the LDA exchange energy.

### C. Average Density Approximation

Two decades ago, Gunnarsson et al. criticized the earlier gradient expansion approaches because of their failure to satisfy the sum rule [Eq. (4)], and proposed two completely non-local approximation schemes, the average density approximation (ADA) and the weighted density approximation (WDA). In the ADA, which has been utilized in this work, the exchange-correlation hole [Eq. (13)] is approximated by

$$\tilde{\rho}_{xc}^{ADA} ([\{\tilde{n}_\sigma (r)\}; r, r']) = \tilde{n}(r) [\tilde{g}^{hom} (\{\tilde{n}_\sigma (r)\}; |r - r'|) - 1],$$

6
leading to

\[ \epsilon_{xc}(\{n_\sigma\}; \mathbf{r}) \approx \epsilon_{xc}^{ADA}(\{\bar{n}_\sigma(\mathbf{r})\}) = \epsilon_{xc}^{hom}(\{\bar{n}_\sigma(\mathbf{r})\}), \]

where

\[ \bar{n}(\mathbf{r}) = \int d^3 \mathbf{r}' w(\bar{n}(\mathbf{r}); \mathbf{r} - \mathbf{r}') n(\mathbf{r}') , \]

is a non-local functional of the density. The important point is the nonlocal nature of the ADA exchange-correlation hole whose extent depends not only upon the density at the observation point but upon a weighted average around \( \mathbf{r} \). The weight function \( w \) could be chosen in several ways. Gunnarsson et al. originally proposed a form based on the information of the linear response limit of the homogeneous electron gas. We follow their suggestion and use the weight function \( w \) tabulated in their paper [14] with the Eq. (18) evaluated by the method based on fast Fourier transforms.

III. INHERENT LIMITATION OF THE LOCAL AND SEMI-LOCAL APPROXIMATIONS IN THE ANISOTROPIC 2D-LIMIT

A. Basic issues

We first outline the underlying physics by considering the behavior of the exchange-correlation hole of 3D electrons in the 2D-limit. The 2D-limit of a 3D density can be written as

\[ n(\mathbf{r}) \to n^{2D}(r^{2D}) \delta(z). \]

If we employ the exact exchange-correlation hole [Eq. (3)], the exchange-correlation energy density [Eq. (6)] in the 2D-limit is

\[ \epsilon_{xc}([n_\sigma]; \mathbf{r}) \to \frac{1}{2} \int d^2 \mathbf{r}' n^{2D}(r'^{2D}) \frac{[\bar{g}([n_\sigma]); r'^{2D}, r^{2D}] - 1}{|r^{2D} - r'^{2D}|} \]

which is finite. Note that the Dirac delta function has been removed through the integration along the z-direction. On the other hand, when we employ the local LDA or the semi-local GGA/MGGA, density prefactor \( n(\mathbf{r}') \) in the exact exchange-correlation hole expression [Eq. (3)] is replaced by \( n(\mathbf{r}) \). In these cases the Dirac delta function in Eq. (19) will not be removed through the integration in the evaluation of the exchange-correlation energy density as in Eq. (20) which results in the divergence

\[ \epsilon_{xc}^{LDA, \text{(M)GGA}}(\{n_\sigma(\mathbf{r})\}) \to -\infty. \]

In conclusion, we can expect the incorrect divergence of the (semi-)local approximations due to the approximation of the exchange-correlation hole as being (semi-)local.

Now, we contrast this with a nonlocal approximation. Specifically, we employ the ADA, which has been described in Sec. II C and will be used in the next subsection. In the ADA, the prefactor \( n(\mathbf{r}') \) is replaced by \( \bar{n}(\mathbf{r}) \) as in Eq. (18), which is finite in the 2D-limit:
\[ \bar{n}(\mathbf{r}) \to \bar{n}(\mathbf{r}^{2D}) = \int d^2\mathbf{r}^{2D} \, w(\bar{n}(\mathbf{r}^{2D});\mathbf{r}^{2D} - \mathbf{r}^{2D}) \, n(\mathbf{r}^{2D}). \]  

(22)

So, we expect the exchange-correlation hole and especially the exchange-correlation energy density in the ADA will correctly have a finite 2D limiting value:

\[ \epsilon_{xc}^{ADA}(\{\bar{n}_\sigma(\mathbf{r})\}) \to \frac{\bar{n}(\mathbf{r}^{2D})}{2} \int d^2\mathbf{r}^{2D} \left[ \frac{\partial^{\text{hom}} \{\bar{n}_\sigma(\mathbf{r}^{2D});\mathbf{r}^{2D} - \mathbf{r}^{2D}\}}{|\mathbf{r}^{2D} - \mathbf{r}^{2D}|} - 1 \right]. \]  

(23)

B. Quasi-2D electron gas

The 2D electron gas is experimentally realizable, for example, in the silicon metal-oxide-semiconductor field-effect transistor (MOSFET) inversion layer and in GaAs/Al\textsubscript{x}Ga\textsubscript{1-x}As heterostructures.\textsuperscript{22} Although the LDA in DFT formalism has been typically employed for the study of many-body effect in these device systems since the 1970’s,\textsuperscript{22} the limitations of the LDA has not been fully resolved.\textsuperscript{22,23} In this section we investigate the accuracy of the LDA, GGA, and MGGA for the quasi-2D homogeneous electron gas, which is an idealized model of a quantum well. For carrier with an isotropic effective mass \( m^* \), such as electrons in GaAs/Al\textsubscript{x}Ga\textsubscript{1-x}As, interacting with Coulomb interactions screened by a dielectric constant \( \epsilon \), the hamiltonian is the same as for electrons in free space if one adopts scaled units of length

\[ \tilde{\mathbf{r}} = \alpha \mathbf{r}; \, \alpha = \frac{m^*}{\epsilon}; \]  

(24)

and energy

\[ \tilde{E} = \beta E; \, \beta = \frac{\epsilon^2}{m^*}. \]  

(25)

For GaAs, \( m^* = 0.067 \, m_e \) and \( \epsilon = 13.2 \), hence the effective unit of energy is \( 1 \, \tilde{H}a = 10.46 \) meV and length is \( 1 \, \tilde{a}_0 = 104.22 \, \text{rA} \). However, in the following, we drop the tilde symbol for simplicity, unless explicitly stated otherwise.

A strict 2D electron gas can be characterized by one dimensionless parameter, \( r_s^{2D} = 1/\sqrt{\pi n_A} \) or \( k_F^{2D} = 2\pi/r_s^{2D} \), where \( n_A \) is the areal electron number density, which ranges \( 10^{11} \sim 10^{13} \, \text{cm}^{-2} \) for typical GaAs/Al\textsubscript{x}Ga\textsubscript{1-x}As heterostructures. However, since we are primarily interested in how various 3D DFT exchange-correlation energy approximations perform in the 2D-limit, we incorporate the finite thickness by including an envelope wavefunction \( \zeta_0(z) \), with the \( z \)-direction taken to be perpendicular to the 2D homogeneous electron gas layer. Here, we assume that only the lowest single 2D subband is populated. Then, within the effective mass approximation, the layer electrons can be characterized, by wavefunctions of the form

\[ \psi(\mathbf{r}) = \frac{1}{\sqrt{A}} \exp(i\mathbf{k}^{2D} \cdot \mathbf{r}^{2D}) \, \zeta_0(z), \]  

(26)

where \( \mathbf{r}^{2D} \) is the 2D radius vector and \( \mathbf{k}^{2D} \) is the 2D wavevector. It is normalized to area \( A \), and \( \zeta_0(z) \) is also assumed to be normalized. We take the quantum well potential along the confinement \( z \)-direction to be parabolic, with the envelope wavefunction \( \zeta_0(z) \) of the form
\[ \zeta_0(z) = \left(\frac{b^2}{\pi}\right)^{1/4} e^{-b^2z^2/2}. \]  

(27)

In Eq. (27) 1/b characterizes the spatial extension of wavefunctions along the \( z \)-direction, so we choose the dimensionless ratio \( b/k_F^{2D} \) as a measure of the finite thickness effect. Defining the average thickness as \( l_0 = \sqrt{2}/b \), which ranges from 20 to 100 r.A in experiments, the physically relevant range of \( b/k_F^{2D} = r_s^{2D}/l_0 \) will be approximately between 1 and 5.

Assuming that the wavefunction has the form in Eq. (27), Fig. 3-(a) and (b) show the comparison of the ratios of the exchange and exchange-correlation energy per electron obtained from 3D exact exchange (Hartree-Fock) method and various local/semi-local DFT approximation schemes over the absolute value of the 2D exact exchange energy. The quantity plotted is the ratio of the energy to the absolute value of the exchange energy in the 2D (large \( b \)) limit, \( \epsilon_x^{\text{exact},2D} = -(4\sqrt{2})/(3\pi r_s^{2D}) \). The finite thickness of the wavefunction gives the correction \( Y(b/k_F^{2D}) \)

\[ \epsilon_x^{\text{exact},2D} = \frac{-4\sqrt{2}}{3\pi r_s^{2D}} Y\left(\frac{b}{k_F^{2D}}\right). \]  

(28)

The finite thickness correction \( Y(b/k_F^{2D}) \) in Eq. (28) has been calculated with the envelope-wavefunction Eq. (26) in a similar manner to Ref. 24 where the Fang-Howard envelope-wavefunction was used. Physically, this finite thickness correction makes the effective interaction softer than \( 1/r \) Coulomb interaction for distances small compared to the extension in the \( z \) direction of the charge distribution, which leads to a significant correction to the 2D exchange energy for \( b/k_F^{2D} \leq 10 \).

The very weak confinement regime \( (b/k_F^{2D} < 1) \) in Fig. 3-(a) reveals that the LDA, GGA’s, and MGGA exchange are very close to the exact exchange values. However, as we increase the confinement strength they all go to the wrong limit: LDA, PBE-GGA, B88-GGA, and PKZB-MGGA diverge to \(-\infty \). Although PW91-GGA approaches a finite value at large \( b/k_F^{2D} \) (due to the fact that \( F_x^{\text{PW91-GGA}}(s) \sim s^{-1/2} \) for \( s \to \infty \)), the magnitude of the converged value is much too large. Note that the LDA is better than the GGA or MGGA for the physically relevant intermediate confinement strength regime, and the direction of GGA/MGGA correction should be opposite to that of current forms, i.e., the factor \( F_x^{\text{GGA}}/F_x^{\text{MGGA}} \) should be less than 1 to reduce the error in the LDA exchange. This feature is closely related with the nonuniform scaling relation, and the PW91-GGA has this property built in, but only for large-s region. In order to describe quasi-2D quantum nanostructures, one needs \( F_x \leq 1 \) for the small s region, but this will apparently worsen the (M)GGA for other systems such as spherical atoms. This shows that it is difficult use the restricted (M)GGA form to improve both 2D and conventional systems.

The total exchange-correlation energy for \( r_s = 1.7 \bar{a}_0 \) \((n_A = 10^{11} \text{cm}^{-2})\) is shown in Fig. 3-(b), together with the quasi-exact 2D-limit value obtained from the quantum Monte Carlo calculations. The contribution of correlation energy is smaller than the exchange energy in the physically relevant areal density regimes \( (5 \sim 25 \% \text{ for } n_A = 10^{13} \sim 10^{11} \text{cm}^{-2}) \), so the above qualitative conclusions at the exchange level will not be changed with the inclusion of the correlation energy. One noticeable difference between the LDA and (M)GGA correlation energy functionals is that the magnitude of the LDA correlation energy increases with increasing confinement strength, while that of the (M)GGA decreases due the nature of their correlation form as described in Sec. [IA]
Now, we explicitly show the different behavior of the nonlocal approximation which was expected in Sec. III A, by performing the 3D ADA calculations on the quasi-2D electron gas model. The ratio of the ADA exchange-correlation energy and the 2D exact exchange energy is shown in Fig. 3-(c) together with 2D LDA, and 3D exact exchange, LDA, and PBE-GGA results. The ADA not only correctly reduces to a finite value but also the limit value itself is surprisingly close to the exact 2D-limit. This correct limiting behavior of the ADA clearly differentiate it from local or semi-local approximations, and confirms our statements in Sec. III A. Recently, the ADA has been also shown to give improved descriptions of the exchange-correlation energy density over the LDA for the conventional bulk silicon system, but its applications are scarce in the literature due to the difficulty of its implementation.

C. Quantum Dot

The second physical system with 2D character we discuss is a GaAs quantum dot. Because the orthogonal dot-growth direction confinement is usually much stronger than the in-plane confinement, the electron distribution in a quantum dot has a pancake-like spheroidal shape. For realistic potential shapes of actual quantum dots, we refer the reader to Fig. 2 and 5 of Ref. 10.

We take the simplest model of quantum dot systems with the external potential an anisotropic harmonic oscillator potential, as employed in our previous investigation, \[ V_{\text{ext}}(r) = \frac{1}{2} \omega^2 (x^2 + y^2) + \frac{1}{2} \omega_z^2 z^2. \] (29)

Here \( z \) is the dot-growth direction, and we will examine \( \omega_z \geq \omega \). We consider only two interacting electrons in this potential. The exact exchange energy for this two-electron system is equal to one half the Hartree energy. In the isotropic potential limit \( \omega = \omega_z \), this model can be solved analytically for a discontinuous but infinite set of oscillator frequencies and a comparative study of the exact KS, LDA, and GGA schemes has been reported recently. These results were used as a check of our calculation method described below.

We performed self-consistent LDA, PBE-GGA, and exact exchange (EXX) calculations for \( \omega_z/\omega \leq 20 \), and PW91-GGA and PKZB-MGGA energy have been evaluated by PBE-GGA density and wave functions. Technical details of our self-consistent EXX calculations based on the finite-difference grid scheme have been presented in Ref. 30. For \( \omega_z/\omega > 20 \), we used a simple variational EXX approach to generate approximate solutions: Taking the variational trial wavefunction as

\[ \psi(r) = \left( \frac{\omega'}{\pi} \right)^{1/2} e^{-\omega'(x^2+y^2)/2} \left( \frac{\omega'_z}{\pi} \right)^{1/4} e^{-\omega'_z z^2/2} \] (30)

with two variational parameters \( \omega' \) and \( \omega'_z \) for a given external potential characterized by \( \omega \) and \( \omega_z \), we minimize the EXX total energy of the system, and use the variationally optimal wavefunctions and the corresponding density to evaluate various 3D exchange (and correlation) energy. The self-consistent and variational EXX exchange energy obtained through this procedure shows the agreement of respectively 99.8 and 99.4 % with the exact KS value for the isotropic case. In addition to the 3D DFT calculations, we also performed 2D LDA calculations with the 2D density
\[ n^{2D}(r^{2D}) = 2 \left( \frac{\omega''}{\pi} \right) e^{-\omega''(x^2+y^2)}, \tag{31} \]

that has been obtained in a 2D EXX variational minimization procedure as in the large-confinement 3D case with a single variational parameter \( \omega'' \).

The exchange and exchange-correlation energies for \( \omega = 2 \text{ meV} = 0.1912 \, \tilde{\text{Ha}} \) are shown in Fig. 4-(a) and 4-(b) respectively. The EXX exchange values in Fig. 4-(a) reveal that the system approach the 2D limit at \( \omega_z/\omega \sim 20 - 30 \), and also the 2D LDA exchange value is quite close to the EXX value in that limit. Now we compare the 3D LDA, (M)GGA exchange energies with the EXX exchange energy. First, at the isotropic limit \( \omega_z/\omega = 1 \), we can see that the (M)GGA improves the 3D LDA, since the magnitude of the exact exchange energy is larger than that of the 3D LDA exchange energy at \( \omega_z/\omega = 1 \). On the other hand, as we go to the more anisotropic limit (larger \( \omega_z/\omega \) regime), the 3D LDA and GGA exchange energies become much larger in magnitude than the exact EXX values, and the GGA’s worsen the agreement with EXX, as in the 2D electron gas considered in the previous subsection. The required directions of correction to the LDA value have been indicated by upward/downward arrows, which shows that we need corrections of of opposite signs at the isotropic and very anisotropic limits; however, the (M)GGA correction always has the same sign, which clearly shows the inherent difficulty in constructing (M)GGA's that can satisfy all limits.

The qualitative results at the exchange level are not changed with the inclusion of the correlation energy as shown in Fig. 4-(b), except that, for small \( \omega_z/\omega \), the differences between the 3D LDA and (M)GGA exchange-correlation energies are smaller than the exchange case alone, which shows that the 3D LDA is a good approximation with the exchange and correlation together rather than separately.

Before closing this section, we comment on realistic experimental situations for quantum dots. Using a value of \( \omega_z = 20 - 50 \text{ meV} \), estimated by the vertical extent of quantum dots (approximately 100\( r_A \)), one finds the realistic range of \( \omega_z/\omega \) is about 10 - 25, which is not the extreme 2D-limit where we observed the breakdown of 3D local/semilocal DFT approximations. Hence 3D LDA or (M)GGA quantum dot simulation results should be reliable for such experimentally realistic problems. Further Fig. 4-(b) suggests that 3D and 2D functionals are about equally applicable in this range although 3D functionals are definitely better for \( \omega_z/\omega < 10 \).

In addition, by comparing our 3D and 2D EXX models, we can study the effect of employing strict-2D quantum dot simulations as have been adopted in many theoretical studies. In Fig. 5, we compare the lateral components of 3D total kinetic energy \( \langle K_{||} \rangle \), total external potential energy \( \langle V_{\text{ext}} \rangle \), and Hartree + exchange energy \( \langle V_{\text{ex}} \rangle \), with the corresponding 2D values. Physically, the electron-electron interaction makes the electrons more extended than the noninteracting counterparts, which decreases the kinetic energy and increases the potential energy. On the other hand, the finite thickness of the 2D electron layer has the effect of softening the Coulomb interaction as discussed in Sec. 113. This effect is pronounced up to \( \omega_z/\omega \sim 20 \), and we expect this feature will be missing in the strict-2D calculations. One more noticeable point is that the anisotropy of the potential induces bigger change in the Hartree + exchange energy (+1.20 meV) than those in the kinetic energy (-0.38 meV) and potential energy (+0.80 meV) from the values.
of the isotropic limit.

D. Other systems

In this subsection, we consider two physical systems with 2D character to which our study might have relevance. First example is jellium surfaces, which have recently drawn renewed interest due to the discrepancies between results from different schemes. Although we believe quantum Monte Carlo calculation results are the most accurate, it is not our intention here to address this question. Rather, the relevant point we would like to emphasize is that the conclusions of the present study are consistent with those of Rasolt and Geldart on the gradient corrections in the jellium surface: to support their first gradient correction coefficient having a different sign from that found in the atomic systems, they emphasized the difference between the localized and extended system and argued that their form is the proper one to use especially for jellium surfaces. Actually, they further brought caution on forcing a “universal” gradient approximation form where none exists, which is a warning we feel has been largely ignored. We believe our study supports the argument of Rasolt and Geldart, and especially our second model system, quantum dot, is a dramatic example showing the nonexistence of a universal GGA form.

The second system we examine is graphite. Graphite and intercalated graphite constitute another large family of materials with quasi-2D electronic properties. Interestingly, in our previous investigations, we observed that the LDA gives a better description of the energy difference between the diamond and hexagonal graphite structures of C than the PW91- or PBE-GGA both at the theoretical and experimental lattice constants. Since the LDA and GGA descriptions of the diamond C are both satisfactory, we can conclude that the GGA descriptions of the graphite is the origin of the problem. To trace the specific source of the error, we decomposed the self-consistent total energies at the experimental lattice constants from LDA, PW91-GGA, and PBE-GGA calculations into kinetic, potential, and exchange-correlation energies. The kinetic + potential energy differences between the diamond and graphite structures from the LDA/PBE-GGA calculations were -820/-865 meV, while the exchange-correlation energy differences between the two structures were 231/386 meV. The fact that the magnitude of the kinetic + potential energy is more than two times bigger than the exchange-correlation energy, while the energy difference in the exchange-correlation part is three times bigger than the kinetic + potential part indicates that the description of the graphite in the PBE-GGA functional is the main source of the deficiencies. This is closely related with our findings in the present work, that the GGA gives poorer descriptions of 2D systems than the LDA. In hexagonal graphite, there are eight electrons per unit cell, and two of them in the \( \pi \)-like state can be considered as 2D electrons, which corresponds to \( r_s = 3.54 \tilde{a}_0 \) or \( l_F^{2D} = 0.41 \tilde{a}_0^{-1} \). The valence-electron charge density distribution is known experimentally so one can estimate the thickness of the electron layer \( l_0 \) as \( \approx 2.33 \tilde{a}_0 \) or \( b = \sqrt{2}/l_0 = 0.61 \tilde{a}_0^{-1} \). This correspond to \( b/k_F^{2D} = 1.5 \) in Fig. 3, suggesting that the GGA’s poorer description of the energy difference between the hexagonal graphite and diamond can be explained by our findings in this work.
IV. SUMMARY AND DISCUSSIONS

The purpose of this work was to show the fundamental limitation of the 3D local/semi-local exchange-correlation energy functional approximations of DFT by considering systems with 2D characteristics. We traced the source of the failure of the LDA, GGA, and MGGA in 2D systems to the (semi-)local nature of their approximate exchange-correlation holes. These local/semi-local approximations have been contrasted with a nonlocal approximation such as the ADA, and the difference has been explicitly demonstrated in our first model, quasi-2D electron gas, in which the ADA reproduced the correct limiting behavior. The 2D-limit can be considered as a constraint on approximate functionals. This condition is not built in most of the (M)GGA’s, and we emphasized that its form is inherently too restricted to incorporate this requirement while keeping the necessary property to improve the LDA for other conventional systems. Our second example, an anisotropic quantum dot in which we need different signs of the (M)GGA corrections to the LDA at 3D- and 2D-limits, explicitly shows the danger of expecting a universal gradient approximation form as pointed out by Rasolt and Geldart. Two other realistic systems, jellium surface and graphite have been discussed as relevant examples. For practical device simulations, however, we pointed out that the LDA and (M)GGA results should be qualitatively correct, as long as experimentally realistic situations are considered.

Note After completion of the present work, we were informed that Pollack and Perdew have also studied the quasi-2D electron gas results using a different quantum well model, finding results in agreement with ours presented in Sec.III B. They have employed a scaling argument more extensively, and also made a connection to the liquid drop model.

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* Present address: School of Physics, Korea Institute for Advanced Study, Cheongryangri-dong, Dongdaemun-gu, Seoul 130-012, Korea
† Present address: Lawrence Livermore National Laboratory, Livermore, CA 94550.
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FIGURES

FIG. 1. The enhancement factor over the LDA exchange energy density for (a) B88-, PW91-,
and PBE-GGA exchange $F_x^{\text{GGA}}$ and (b) PBE-GGA correlation $F_c^{\text{PBE-GGA}}$ in terms of the dimensionless reduced density gradient $s = |\nabla n|/(2k_F n)$.

FIG. 2. The exchange part of PKZB-MGGA enhancement factor over the LDA exchange energy
density $F_x^{\text{PKZB-MGGA}}$ in terms of the dimensionless reduced density gradient $s = |\nabla n|/(2k_F n)$ and $\bar{q}$ defined in the text.

FIG. 3. The ratio of 3D exact, LDA, GGA’s and MGGA (a) exchange energy and (b) exchange-correlation energy per electron over the absolute value of the 2D exact exchange energy for the quasi-2D jellium model versus $b/k_F^{2D}$. (c) The ratio of the 3D ADA exchange-correlation energy per electron over the absolute value of the 2D exact exchange energy for the same system. This ratio is independent of the areal electron number density at the exchange-only level (a), and $r_s = 1.7 \tilde{a}_0 (n_A = 10^{11} \text{ cm}^{-2})$ case has been shown in (b) and (c). The experimentally realistic range of $b/k_F^{2D}$ is about $1 - 5$. For (c), the exact exchange, LDA and PBE-GGA exchange-correlation energies given in (b) are reproduced for comparison. Note that the ADA reduces very closely to the exact 2D exchange-correlation limit.

FIG. 4. (a) Exchange energy and (b) exchange-correlation energy of 2 electrons confined in a
quantum dot modeled by an anisotropic harmonic oscillator potential as functions of $\omega_z/\omega$. For
a fixed lateral-direction external potential $\omega = 2 \text{ meV}$, the dot-growth direction potential $\omega_z$ has
been varied from 2 to 2000 meV. The realistic value of $\omega_z$ is about $20 - 50 \text{ meV}$, or $\omega_z/\omega \approx 10 - 25$.

The upward/downward arrows in (a) indicate the direction of correction to the LDA exchange energy. Note that (M)GGA correction is always downward, hence improves the LDA at the isotropic limit, but worsens at the anisotropic limit.

FIG. 5. The lateral components of 3D total kinetic energy $\langle K || \rangle$, total external potential energy
$\langle V_{\text{ext}} \rangle$, and Hartree + exchange energy $\langle V_{\text{ee}} \rangle$, and the corresponding 2D values $\langle K^{2D} \rangle$, $\langle V_{\text{ext}}^{2D} \rangle$, and $\langle V_{\text{ee}}^{2D} \rangle$ obtained from variational EXX calculations. For a fixed lateral-direction confinement
potential $\omega = 2 \text{ meV}$, the dot-growth direction potential has been varied from 2 to 200 meV.
Fig. 1 (a)

Fig. 1 (b)
\[ \frac{\varepsilon_X + \varepsilon_C}{|\varepsilon_X^{2D}|} \]

- exact 2D limit
- exact exchange
- LDA
- PW91–GGA
- PBE–GGA
- PKZB–MGGA

Fig. 3 (b)

\[ \frac{\varepsilon_X + \varepsilon_C}{|\varepsilon_X^{2D}|} \]

- exact 2D limit
- exact exchange
- LDA
- PBE–GGA
- ADA

Fig. 3 (c)
Fig. 4 (a)

Fig. 4 (b)
Energy (meV)

\[ \frac{\omega_z}{\omega} \]

Fig. 5