Simple exchange-correlation potential with a proper long-range behavior for low-dimensional nanostructures

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(Dated: September 1, 2010)

The exchange-correlation potentials stemming from the local-density approximation and several generalized-gradient approximations are known to have incorrect asymptotic decay. This failure is independent of the dimensionality, but so far the problem has been corrected – within the mentioned approximations – only in three dimensions. Here we provide a cured exchange-correlation potential in two dimensions, where the applications have a continuously increasing range in, e.g., semiconductor physics. The given potential is a generalized-gradient approximation, which is as easy to apply as the local-density approximation. We demonstrate that the corrected potential agrees very well with the analytic result of a two-electron quantum dot in the asymptotic regime, and yields plausible exchange-correlation potentials for larger two-dimensional systems.

PACS numbers: 71.15.Mb, 31.15.E-, 73.21.La

I. INTRODUCTION

Developments in density-functional theory (DFT), particularly in the derivation of functionals for exchange-correlation (xc) energies and potentials, can often be characterized by a compromise between accuracy and efficiency. In quantum chemistry and condensed matter physics, applications of generalized-gradient approximations (GGAs) are still among the most popular choices to evaluate the xc terms in the Kohn-Sham (KS) scheme. Even the local-density approximation (LDA) has well preserved its popularity due to the several beneficial properties, e.g., the computational efficiency, the natural compatibility between the exchange and correlation, satisfaction of the sum rule of the xc hole etc.

One of the most prominent problems in the LDA and in many GGAs is the wrong asymptotic behavior of the xc potential. Essentially, this is due to the fact that these approximations depend in a oversimplified fashion on the (exponentially decaying) electron density, leading to the wrong exponential decay of the approximate xc potential. A simple and efficient cure for this problem was put forward by van Leeuwen and Baerends\textsuperscript{9}. They provided a GGA for the xc potential with the proper asymptotic behavior, commonly known as the LB94 functional (or potential). The LB94 potential is very accurate for, e.g., ionization energies and electron affinities, and it has received considerable popularity in quantum chemistry.

The three-dimensional (3D) LDA and GGAs are not applicable for systems having suppressed dimensionality, such as the well-known two-dimensional (2D) examples, e.g., semiconductor quantum dots (QDs), rings, slabs, and quantum Hall systems. Instead, the 2D LDA\textsuperscript{7,8} and – to the best of our knowledge – the only 2D GGA\textsuperscript{9} are suitable, in principle, to deal with those systems. However, these functionals suffer from the same deficiencies as their 3D counterparts, most importantly, the wrong asymptotic behavior. Motivated by this fact, we derive here a xc potential which corrects the asymptotic decay and remains computationally efficient due to its simple GGA form. In the derivation we essentially follow the steps of Ref.\textsuperscript{9}. Finally we demonstrate the usefulness of the model potential by considering a few typical 2D applications: two semiconductor QDs and two quantum rings.

II. CORRECTED LONG-RANGE BEHAVIOR

Following Ref.\textsuperscript{9} we start by expressing the total xc potential in the KS scheme as

\[ v_{xc} = v_{xc}^{\text{LDA}} + \rho^{1/2} F(x) \]  

where

\[ x = \frac{\left| \nabla \rho \right|}{\rho^{3/2}}. \]  

In Eq. (1), \( F(x) \) together with \( x \) can be considered as a quantity evaluating the relevance of the density gradient as well as its asymptotic behavior. We remind that \( x \) has been introduced already for the 2D GGA in Ref.\textsuperscript{9}. We observe that the term \( \rho^{1/2} F(x) \) scales linearly under homogeneously scaling. As it is well known, the linear scaling applies to \( v_x \) exactly, but this may not be the case for \( v_c \). Nevertheless, in the spirit of LB94 we treat \( v_c \) together with \( v_x \). This may be justified considering that for \( r \to \infty \) the leading contribution to the asymptotics of \( v_{xc} = v_x + v_c \) is due to \( v_x \); in other words, \( v_c \) decays faster.\textsuperscript{9} It should be noted, however, that the present correction has effect also elsewhere, i.e., not only in the asymptotic limit.

For the function \( F(x) \) in Eq. (1) we require \( F(0) = 0 \), so that the total \( v_{xc} \) will be given by the LDA whenever \( \nabla \rho = 0 \). In this way, the result for the homogeneous electron gas is \textit{exactly} recovered. This property is useful
also when considering inhomogeneous systems, in view of
the success of the LDA.
To the leading order, the model should fulfill\textsuperscript{11,12}

\[ v_{xc} \sim -\frac{1}{r}, \]  \hspace{1cm} (3)

in contrast to the exponential decay of the LDA potential.\textsuperscript{13} This requirement translates into the following condition

\[ F(x) \sim -\frac{1}{r} \beta^{-1/2}. \]  \hspace{1cm} (4)

We remind that far away from the central region of QDs,\textsuperscript{14}

\[ \rho \sim e^{-\alpha r^2}, \quad \alpha > 0 \]  \hspace{1cm} (5)

and thus, using Eq. (5) in Eq. (2) we find

\[ x \sim 2\alpha r \rho^{-1/2}. \]  \hspace{1cm} (6)

Equations (1) and (6) lead to

\[ F(x) \sim -\frac{1}{2\alpha r^2}. \]  \hspace{1cm} (7)

Moreover, since

\[ \ln x \sim \frac{\alpha r^2}{2}, \]  \hspace{1cm} (8)

we may re-write Eq. (1) as follows:

\[ F(x) \sim -\frac{1}{4\ln x}. \]  \hspace{1cm} (9)

The desired behavior is given by a function

\[ F(x) = -\beta \frac{x^2}{1 + 4\beta x \sinh^{-1}(x)}, \]  \hspace{1cm} (10)

where

\[ \sinh^{-1}(x) = \ln(x + \sqrt{1 + x^2}). \]  \hspace{1cm} (11)

The parameter $\beta$ can be determined, for example, by fitting the model potential against the exact xc potential in a soluble test system. We consider the effects of $\beta$ below.

Apart from the factor of four in the denominator of Eq. (6), and the 2D definition of $x$, the resulting model is very similar to the 3D case.\textsuperscript{12} Moreover, as for the 3D case, the exact constraints for the exchange-correlation potential resulting from the translational and rotational invariance are satisfied.

Finally we point out that it is straightforward to obtain a spin-dependent model potential by simply adding a spin index to all the quantities but $\beta$.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{(Color online) Exchange-correlation potentials of a parabolic ($\omega = 1$) two-electron quantum dot calculated from the analytic density. The result from the present model (solid line) has been calculated with $\beta = 0.01$ in Eq. (10). The chosen value is kept fixed in the following examples. The inset shows the relative deviation of the integrated model potential from the exact result as a function of $\beta$ (note the logarithmic scale).}
\end{figure}

\section{III. Further Analysis and Applications}

Next we test our model for the xc potential in a 2D two-electron QD defined by a radial external potential $v_{ext}(r) = \omega^2 r^2/2$ with $\omega = 1$ (see Ref. \textsuperscript{19} for information about the units). The ground-state (singlet) density has an exact analytic expression\textsuperscript{20,21}

\[ \rho(r) = \frac{4}{\pi(\sqrt{2} + 3)} \left\{ e^{r^2}(1 + r^2/2) + \frac{1}{2} \sqrt{\pi} e^{r^2/2} \times \right. \]

\[ \left. \times \left[ I_0(r^2/2) + r I_0(r^2/2) + r^2 I_1(r^2/2) \right] \right\}, \]  \hspace{1cm} (12)

where $I_0(x)$ is the zeroth-order modified Bessel function of the first kind. The exact KS orbital is given simply by $\varphi(r) = \sqrt{\rho(r)/\beta}$, and the KS equation can be inverted to obtain the exact KS potential from

\[ v_{KS}(r) = \epsilon_{KS} + \frac{\nabla^2 \varphi(r)}{2\varphi(r)}. \]  \hspace{1cm} (13)

where $\epsilon_{KS} = 2$ is the KS eigenvalue.\textsuperscript{10,20} The exact xc potential is then given by

\[ v_{xc}^{\text{exact}}(r) = v_{KS}(r) - v_{ext}(r) - v_H(r), \]  \hspace{1cm} (14)

where $v_H$ is the Hartree potential, which is in fact the only term having no analytic expression for the given analytic density. However, it can be solved numerically with a good precision.

In Fig. 1 we compare the exact xc potential with the LDA potential and with our model, i.e., Eqs. (1) and (10) with $\beta = 0.01$. Whereas the LDA potential decays exponentially, the model potential has the correct asymptotic
behavior in an excellent agreement with the exact result. At $r = 0$ the density gradient is zero and hence the model agrees with the LDA as required.

To analyze the effect of the parameter $\beta$ in Eq. (10) on the xc potential, we consider the relative difference in the integrated xc potential weighted by the density, i.e.,

$$\Delta I = \frac{\int d^2r \rho(r) |v_{xc}^{\text{exact}}(r) - v_{xc}(r)|}{\int d^2r \rho(r)v_{xc}^{\text{exact}}(r)}.$$  \hspace{1cm} (15)

This quantity is plotted as a function of $\beta$ in the inset of Fig. [1] We find that the deviation is overall very insensitive to $\beta$ (note the logarithmic x-axis). We have chosen the value $\beta = 0.01$ (dashed line) that yields a “reasonable” shape for the xc potential and a relatively small deviation in $\Delta I$ for this test case. The chosen value is kept fixed in the following examples.

Figure [2] shows the xc potentials for a significantly larger parabolic QD with 42 electrons. The confinement strength is now $\omega = 0.5$ (Ref. [19]). Here we have performed a self-consistent LDA calculation using the octopus code\textsuperscript{[22]} and use the LDA density as an input for the model potential. Again the correct asymptotic limit seems to be recovered by the model potential, although the tail cannot be followed as far as in the exact two-electron case in Fig. [1]. This is due to the numerical instability in the implementation of the LDA correlation in the regime where the density is very small ($\lesssim 10^{-16}$). Nevertheless, Fig. [2] confirms the improvement of the model potential over the LDA for a large QD system.

Finally, we consider quantum rings defined by an external potential $v_{\text{ext}}(r) = \omega^2(r - r_0)^2/2$, where $\omega = 0.5$ and the ring radius $r_0 = 3$. The obtained potentials for two-electron and ten-electron rings are shown in Figs. [3] and [4] respectively. Similarly to the previous test cases, the correct asymptotic behavior ($-1/r$) is obtained with the model potential for both quantum rings. At the ring radius where the density gradient is zero, the model agrees with the LDA in a smooth fashion.

It is noteworthy that the present model for the xc potential sets specific constraints on the external potential. In particular, infinite potentials (at finite positions) – leading to situations where both the density and its gradient are zero – may result in divergence of $F(x)$. A typical example would be a quantum ring studied in Ref. [12]. In this respect, the present potential needs to be applied with special care, or alternative models should be considered, when studying 2D structures represented by such external potentials. Nevertheless, the presented scheme opens up a path to design of a more general GGA approach.
IV. SUMMARY

In summary, we have derived a generalized-gradient approximation for the exchange-correlation potential with a proper asymptotic decay for two-dimensional nanostructures. The expression has a proper asymptotic decay and thus corrects one of the most significant errors in the commonly used two-dimensional local-density approximation. The validity of the model potential is confirmed in quantum dots and rings with different number of electrons. We believe that the presented approach gives promising prospects in two-dimensional many-body physics, first and foremost for systems where the correct decay of the exchange-correlation potential is of great importance, for example, quantum-dot molecules and chains, coupled quantum rings, and periodic electron lattices such as the artificial graphene.23

Acknowledgments

We thank Robert van Leeuwen for useful discussions. This work has been supported by DOE grant DE-FG02-05ER46203 (S.P.) and by the Academy of Finland (E.R.).

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