PHYSICAL REVIEW A **82**, 012505 (2010)

Colle-Salvetti-type local density functional for the exchange-correlation energy in two dimensions

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(Received 14 April 2010; published 8 July 2010)

We derive an approximate local density functional for the exchange-correlation energy to be used in density-functional calculations of two-dimensional systems. In the derivation we employ the Colle-Salvetti wave function within the scheme of Salvetti and Montagnani [Phys. Rev. A **63**, 052109 (2001)] to satisfy the sum rule for the exchange-correlation hole. We apply the functional to the two-dimensional homogeneous electron gas as well as to a set of quantum dots and find a very good agreement with exact reference data.

DOI: 10.1103/PhysRevA.82.012505 PACS number(s): 31.15.E−, 71.15.Mb, 73.21.La

I. INTRODUCTION

Development in modern technology has enabled the fabrication of nanoscale electronic devices with a large variety of low-dimensional systems. Two-dimensional (2D) quantum dots (QDs) are particularly interesting examples due to the tunability in their size and shape, and number of confined electrons [1,2]. From the theoretical point of view, QDs constitute an ideal platform to study the many-particle problem, electronic correlations, and the role of the dimensionality.

In density-functional theory [3] (DFT) particle-particle interactions beyond the classical (Hartree) term are captured through the exchange-correlation (xc) functional, which is approximated in practice. The development of xc functionals of varying portions of simplicity and accuracy has a long and successful history [4]. The Colle-Salvetti (CS) scheme [5,6] and its variants [7] have had an important role in the development, especially in terms of the electronic correlation. However, these efforts have focused almost solely on three dimensions (3D), apart from orbital functionals where the aspect of dimensionality is inbuilt through the Kohn-Sham orbitals. Only very recently, several local [8,9] and semilocal [10–16] functionals have been developed in 2D, and in many test cases involving, for example, different QDs, they have outperformed the commonly used 2D local density approximation based on the exact exchange and correlation of the homogeneous 2D electron gas (2DEG) [17,18].

In Ref. [8] a 2D local density functional for the correlation energy was derived using the CS framework with a Gaussian summation for the pair density [19]. Despite the good performance of this functional for the correlation, a compatible approximation for the exchange energy is needed in view of, for example, total-energy calculations. In fact, a combination with the 2D generalized-gradient approximation for the exchange [12] leads to a reasonable accuracy in the total energy [20]. However, this combined functional is still semilocal, that is, it depends on the density gradients, which reduces the numerical efficiency.

In this work we employ the CS framework to derive a 2D *local* functional for the xc energy, so that both the exchange and correlation are treated on the same footing. In the derivation we follow the 3D scheme of Salvetti and Montagnani [21] for the second-order density matrix to satisfy the sum rule of the xc hole, which is used to obtain a local density functional of a simple polynomial form. We optimize two remaining parameters of the functional by fitting against exact results for six-electron QDs. The obtained parameters show universality in the sense that a good accuracy and consistency is found when the functional is tested for QDs with varying electron numbers as well as for the 2DEG.

II. DERIVATION OF THE FUNCTIONAL

The electron-electron interaction energy can be *formally* expressed (in Hartree atomic units) as

$$E_{ee} = \langle \Psi | \hat{V}_{ee} | \Psi \rangle = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\rho_2(\mathbf{r}_1,\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (1)$$

where

$$\rho_2(\mathbf{r}_1,\mathbf{r}_2) = \frac{N(N-1)}{2} \sum_{\sigma_1,\sigma_2} \int d3, \ldots, \int dN \times |\Psi(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2,3,\ldots,N)|^2. \quad (2)$$

is the diagonal element of the spinless second-order density matrix describing the distribution density of electron pairs. Here $\int dN$ denotes the spatial integration and spin summation over the Nth spatial and spin coordinates $\mathbf{r}_N\sigma_N$, and $\Psi(1,2,\ldots,N)$ is the ground-state many-body wave function. The element $\rho_2(\mathbf{r}_1,\mathbf{r}_2)$ satisfies the normalization

$$\frac{N(N-1)}{2} = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \rho_2(\mathbf{r}_1,\mathbf{r}_2), \quad (3)$$

and it is related to the electron density, that is, the diagonal term of the first-order density matrix, through

$$\rho(\mathbf{r}_1) = \frac{2}{N-1} \int d\mathbf{r}_2\, \rho_2(\mathbf{r}_1,\mathbf{r}_2). \quad (4)$$

Next, the introduction of a symmetric function accounting for all nonclassical effects called the *pair correlation function* $h(\mathbf{r}_1,\mathbf{r}_2)$ suggests that we write [23]

$$\rho_2(\mathbf{r}_1,\mathbf{r}_2) = \tfrac{1}{2}\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)[1 + h(\mathbf{r}_1,\mathbf{r}_2)]. \quad (5)$$

The important sum rule for the xc hole can be expressed in terms of the pair correlation function as

$$\int d\mathbf{r}_2\, \rho(\mathbf{r}_2) h(\mathbf{r}_1,\mathbf{r}_2) = -1. \quad (6)$$

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The total interaction energy in Eq. (1) can be split into the classical Coulomb (Hartree) term associated with $\rho(\mathbf{r})$ and the nonclassical (indirect) part associated with the xc energy,

$$E_{ee} = E_H + E_{\rm xc} = \frac{1}{2}\int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{1}{2}\int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)h(\mathbf{r}_1,\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (7)$$

It should be noted that, compared with the conventional DFT formalism, $E_{\rm xc}$ as defined here neglects the kinetic-energy contribution to the correlation energy. The Hartree term can be computed in a straightforward fashion, but the integration in the xc part is nontrivial due to the pair correlation function $h(\mathbf{r}_1,\mathbf{r}_2)$. The key point in the present work is to obtain an approximation for $h(\mathbf{r}_1,\mathbf{r}_2)$ satisfying the sum rule in Eq. (6). Before proceeding with that, we will briefly introduce the CS approach which is relevant for the derivation.

The CS scheme starts with the following ansatz for the many-body wave function [5,6]:

$$\Psi(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_N\sigma_N) = \Psi_{\rm HF}(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_N\sigma_N)\prod_{i>j}[1-\varphi(\mathbf{r}_i,\mathbf{r}_j)], \quad (8)$$

where HF refers to the single-determinant Hartree-Fock wave function, and

$$\varphi(\mathbf{r}_1,\mathbf{r}_2) = [1-\Phi(\mathbf{R})(1+\zeta r)]\exp[-\beta^2(\mathbf{R})r^2] \quad (9)$$

describes the correlated part of the wave function written in center-of-mass, $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$, and relative, $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, coordinates. The parameter ζ comes from the cusp conditions, and the quantities Φ and β act as correlation factors. In Refs. [19] and [8] dealing with 3D and 2D systems, respectively, β was introduced as a *local* factor for the correlation length, $\beta(\mathbf{R}) = q\rho^{1/D}(\mathbf{R})$, where D is the dimension, q is a fitting parameter, and $\rho(\mathbf{R})$ is the electron density. The CS approach assumes that the first- and second-order density matrices can be written as $\rho_1(\mathbf{r}_1,\mathbf{r}_2) = \rho_1^{\rm HF}(\mathbf{r}_1,\mathbf{r}_2)$ and $\rho_2^{\rm CS}(\mathbf{r}_1,\mathbf{r}_2) = \rho_2^{\rm HF}(\mathbf{r}_1,\mathbf{r}_2)[1-\varphi(\mathbf{r}_1,\mathbf{r}_2)]^2$, respectively [22].

To approximate $h(\mathbf{r}_1,\mathbf{r}_2)$, we extend the strategy of Salvetti and Montagnani [21] to 2D by introducing the correlation factors in the following way:

$$\beta(\mathbf{r}_1,\mathbf{r}_2) = \gamma\rho^{1/2}(\mathbf{r}_1)\rho^{1/2}(\mathbf{r}_2), \quad (10)$$

$$\Phi = \frac{\beta^\alpha}{\sqrt{\pi}+\beta^\alpha}, \quad (11)$$

$$\varphi(\beta) = [1-\Phi(1+r)]\Phi\, e^{-\beta r^2} \quad (12)$$

with $r = |\mathbf{r}_1 - \mathbf{r}_2|$. Above, γ and α are optimizable parameters (γ with dimension of ρ^{-1}), and Φ is a monotonic function varying between zero and one. The differences from the original CS scheme are obvious; most importantly, β is now a nonlocal functional of the density.

We may now search for the pair correlation function

$$h(\mathbf{r}_1,\mathbf{r}_2) = \frac{\varphi^2 - 2\varphi}{f}, \quad (13)$$

where f is assumed to be a simple polynomial of the form

$$f(\Phi) = a_0\Phi^n + a_1\Phi^{n-1} + \cdots. \quad (14)$$

The nominator in the expression for $h(\mathbf{r}_1,\mathbf{r}_2)$ is similar to the CS functional [5,6], whereas the denominator is chosen such that the sum rule in Eq. (6) is satisfied. Substitution of Eq. (13) into Eq. (6) yields

$$\begin{aligned}\int d\mathbf{r}_2\rho(\mathbf{r}_2)h(\mathbf{r}_1,\mathbf{r}_2) &= \int d\mathbf{r}\rho(\mathbf{r}_1+\mathbf{r})h(\mathbf{r}_1,\mathbf{r}_1+\mathbf{r})\\ &= \int d\mathbf{r}\frac{\rho(\mathbf{r}_1+\mathbf{r})}{f}\big\{\Phi^4 e^{-2\beta r^2}(1+r)^2\\ &\quad - 2\Phi^3 e^{-2\beta r^2}(1+r) + \Phi^2 e^{-\beta r^2}\\ &\quad \times\big[e^{-\beta r^2} + 2(1+r)\big] - 2\Phi e^{-\beta r^2}\big\}\\ &= -1. \end{aligned} \quad (15)$$

This expression involves integrals that can be computed by using the mean-value theorem and the regularity of the functions. By following the procedure of Ref. [21], we obtain

$$\int d\mathbf{r}\, g(\mathbf{r}_1,\mathbf{r}_1+\mathbf{r})e^{-b(\mathbf{r}_1,\mathbf{r}_1+\mathbf{r})r^2}r^n \simeq 2\pi g(\mathbf{r}_1)\int dr\, e^{-br^2}r^{n+1}. \quad (16)$$

Utilizing this approximate integration, which becomes more accurate as b becomes large, leads to

$$\begin{aligned}&\int d\mathbf{r}_2\rho(\mathbf{r}_2)h(\mathbf{r}_1,\mathbf{r}_2)\\ &\quad\simeq \frac{2\pi\rho(\mathbf{r}_1)}{f\beta}[\Phi^4(i_0+2i_1+i_2) - \Phi^3(2i_0+2i_1)\\ &\qquad + \Phi^2(i_0+2j_0+2j_1) - 2\Phi j_0] = -1, \end{aligned} \quad (17)$$

where we define i_n and j_n as

$$i_n = \sqrt{2^{-n-2}\beta^{-n}}\int dx\, e^{-x^2}x^{n+1} \quad (18)$$

and

$$j_n = \sqrt{\beta^{-n}}\int dx\, e^{-x^2}x^{n+1}. \quad (19)$$

Using the definition of β and calculating the integrals, we obtain the final result for the polynomial function,

$$f = -2\left(\frac{\pi}{\gamma}\right)\Phi(a_0\Phi^3 + a_1\Phi^2 + a_2\Phi - 1), \quad (20)$$

where the coefficients are given by

$$\begin{aligned} a_0 &= \frac{1}{4} + \frac{1}{8\beta} + \frac{1}{4}\left(\frac{\pi}{2\beta}\right)^{1/2},\\ a_1 &= -\frac{1}{2} - \frac{1}{4}\left(\frac{\pi}{2\beta}\right)^{1/2},\\ a_2 &= \frac{5}{4} + \frac{1}{2}\left(\frac{\pi}{\beta}\right)^{1/2}. \end{aligned} \quad (21)$$

Computation of the integral in Eq. (7) is performed by a similar procedure,

$$\begin{aligned} E_{\rm xc} &= \frac{1}{2}\int d\mathbf{r}_1 d\mathbf{r}_2\frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)h(\mathbf{r}_1,\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\\ &= \frac{1}{2}\int d\mathbf{r}_1\rho(\mathbf{r}_1)\int d\mathbf{r}\rho(\mathbf{r}_1+\mathbf{r})\frac{\varphi^2-2\varphi}{fr}\\ &= \pi\int d\mathbf{r}_1\rho^2(\mathbf{r}_1)\frac{\Phi}{f}\sqrt{\frac{\pi}{\beta}}[b_0\Phi^3 + b_1\Phi^2 + b_2\Phi - 1], \end{aligned} \quad (22)$$

where the coefficients are given by

$$\begin{aligned} b_0 &= \frac{1}{2\sqrt{\pi\beta}} + \frac{1}{2\sqrt{2}} + \frac{1}{8\beta\sqrt{2}}, \\ b_1 &= -\frac{1}{2\sqrt{\pi\beta}} - \frac{1}{\sqrt{2}}, \\ b_2 &= \frac{1}{\sqrt{\pi\beta}} + \frac{1}{2\sqrt{2}} + 1. \end{aligned} \tag{23}$$

Using Eq. (20) and the definition of β, we obtain the final result for the xc energy in 2D,

$$E_{\mathrm{xc}} = \int d\mathbf{r}\rho^{3/2}(\mathbf{r})q(\rho) \tag{24}$$

with

$$q(\rho) = -\sqrt{\frac{\pi\gamma}{4}}\left(\frac{b_0\Phi^3 + b_1\Phi^2 + b_2\Phi - 1}{a_0\Phi^3 + a_1\Phi^2 + a_2\Phi - 1}\right). \tag{25}$$

The remaining task is to find a reasonable pair of values for γ and α which determine $q(\rho)$ through Eqs. (10), (11), (21), and (23). Here we choose to fit these parameters to reproduce the xc energies of parabolic QDs with $N = 6$, which is the smallest closed-shell system beyond the simplest $N = 2$ case. In the external potential $v_{\mathrm{ext}}(r) = \omega^2 r^2/2$, we use the confinement strengths $\omega = 1/4$ and $1/16$ for which numerically exact configuration-interaction (CI) data are available [24]. These confinements have a rather wide range with respect to the relative weight of the xc effects, and, moreover, the chosen values are realistic regarding the modeling of real QD devices [1,2]. The reference xc energy is obtained from

$$E_{\mathrm{xc}}^{\mathrm{ref}} = E_x^{\mathrm{ref}} + E_c^{\mathrm{ref}} = E_x^{\mathrm{EXX}} + E_{\mathrm{tot}}^{\mathrm{exact}} - E_{\mathrm{tot}}^{\mathrm{EXX}}, \tag{26}$$

where $E_{\mathrm{tot}}^{\mathrm{exact}}$ is the reference total energy, $E_{\mathrm{tot}}^{\mathrm{EXX}}$ is the total energy from the exact-exchange (EXX) calculation performed here within the Krieger-Li-Iafrate approximation [25] and using the OCTOPUS code [26], and E_x^{EXX} is the exchange energy. The best fit with $E_{\mathrm{xc}}^{\mathrm{ref}}$ is obtained with parameter values $\gamma = 1.12$ and $\alpha = 0.45$.

III. TESTING THE FUNCTIONAL

Next we test whether the chosen parameter values yield reasonable and consistent results for different 2D systems. This is naturally a desired property in any density functional in order to be a *predictive* approximation. First we consider parabolic QDs with $N = 2,\ldots,12$ and $\omega = 1/16,\ldots,1$. The results are summarized in Table I. The reference xc energies have been calculated from Eq. (26) using the total-energy data from analytic [27], CI [24], and quantum Monte Carlo (QMC) [28] calculations as indicated in the table. Overall, we find a very good performance of our functional, the mean error being 1.86%, which is smaller than that of the 2D LDA (2.19%). Although the LDA is also this accurate for the xc energy, it should be noted that both the exchange and correlation parts have significant errors (see, e.g., Refs. [10] and [14]), and the good overall performance follows from the well-known error cancellation. It is also noteworthy that the 12-electron case is very accurate, and it can be expected that the accuracy is preserved for larger systems when N is increased further.

TABLE I. Exchange-correlation energies for parabolic quantum dots. The optimal parameters $\gamma = 1.12$ and $\alpha = 0.45$ have been used for the calculation of $E_{\mathrm{xc}}^{\mathrm{model}}$. The last row contains the mean percentage error.

N	ω	$-E_{\mathrm{xc}}^{\mathrm{ref}}$	$-E_{\mathrm{xc}}^{\mathrm{model}}$	$-E_{\mathrm{xc}}^{\mathrm{LDA}}$
2	1	1.246[a]	1.195	1.174
2	1/4	0.5987[b]	0.5794	0.5821
2	1/6	0.4936[a]	0.4678	0.4721
2	1/16	0.2774[b]	0.2789	0.2820
6	$1/1.89^2$	2.156[b]	2.138	2.137
6	1/4	2.014[b]	2.008	2.011
6	1/16	0.9265[b]	0.9309	0.9429
12	$1/1.89^2$	4.708[c]	4.716	4.701
Δ			1.86%	2.19%

[a] Total energy from the analytic solution in Ref. [27].

[b] Total energy from the CI data in Ref. [24].

[c] Total energy from the QMC data in Ref. [28].

Table I raises a natural question of whether the good performance simply follows from the fact that γ and α were fitted to a similar system with $N = 6$. Therefore, in Figs. 1(a)

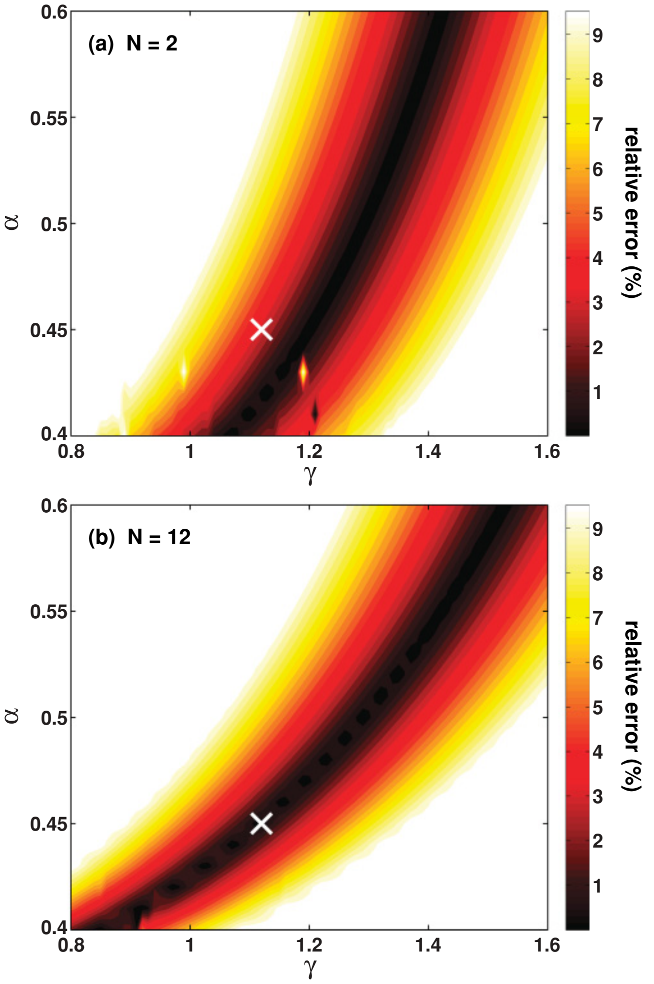

FIG. 1. (Color online) Absolute relative error for parabolic quantum dots, (a) $N = 2$, $\omega = 1$ and (b) $N = 12$, $\omega = 1/1.89^2$, with respect to parameters γ and α. The crosses mark the values chosen from the fit to the $N = 6$ case.

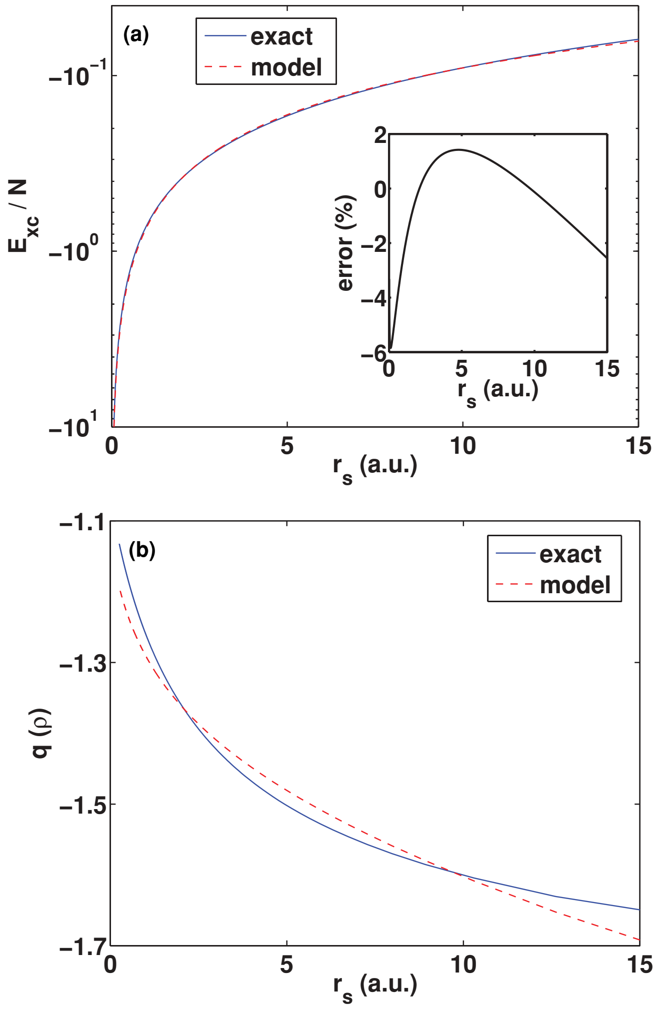

FIG. 2. (Color online) (a) Exchange-correlation energy per particle for the two-dimensional homogeneous electron gas obtained using our functional with the chosen parameters $\gamma = 1.12$ and $\alpha = 0.45$ (dashed line) in comparison with the exact result (solid line). The inset shows the relative error. (b) Result for the function $q(\rho)$ obtained using our functional (dashed line) in comparison with the optimal values required to reproduce the exact exchange-correlation energy of the two-dimensional homogeneous electron gas.

and 1(b) we examine the "extreme" cases of Table I with $N = 2$ ($\omega = 1$) and $N = 12$ ($\omega = 1.89^2$), respectively. The figures show the absolute relative errors as functions of both γ and α, so that here the parameter values have been left undetermined for both cases. The white crosses show the *chosen* values $\gamma = 1.12$ and $\alpha = 0.45$ based on the $N = 6$ data. In both cases, the crosses match very well with the optimal regime where the relative error is smallest for $N = 2$ and $N = 12$. Hence, Fig. 1 confirms that, at least for parabolic QDs, the functional is consistent. The figure also demonstrates the strong correlation between the two parameters as well as the uniqueness of their relationship—for each γ (α) there is only one compatible α (γ).

Finally we consider the important limit case of the homogeneous 2DEG. Figure 2(a) shows the comparison of the xc energy per particle with respect to the exact 2DEG result. Here we have used the same parameter values $\gamma = 1.12$ and $\alpha = 0.45$ as before. We find an excellent agreement through a wide range of the density parameter $r_s = (\pi\rho)^{-1/2}$. In the realistic density range the relative error is within a few percent (see the inset). In Fig. 2(b) we show the function $q(\rho)$ of our functional (dashed line) in comparison with the optimal values to reproduce the exact xc energy of the 2DEG. Overall, we find good consistency in the results at varying r_s. More importantly, regarding the values for γ and α the present functional is also consistent in the comparison between the 2DEG and the QDs above.

IV. SUMMARY

To summarize, we have used the Colle-Salvetti scheme, and in particular its recent generalizations, to derive an approximate local density functional for the exchange-correlation energy of electrons in two dimensions. The functional has a simple polynomial form and it fulfills the sum-rule constraint of the exchange-correlation hole. We have fitted the remaining free parameters against exact results for six-electron quantum dots and found an excellent consistency in the results for a set of quantum dots with varying electron numbers and varying relative proportion of the exchange-correlation energy. The functional is precise also for the two-dimensional homogeneous electron gas with the same fixed parameters. Therefore, we may expect the functional to have predictive power in density-functional calculations for various two-dimensional electron systems. In this respect, generalization to spin-polarized systems would be the most important future extension of the method.

This work was funded by the Academy of Finland.

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