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We derive a local approximation for the correlation energy in two-dimensional electronic systems. In the derivation we follow the scheme originally developed by Colle and Salvetti for three dimensions and consider a Gaussian approximation for the pair density. Then, we introduce an *ad hoc* modification which better accounts for both the long-range correlation and the kinetic-energy contribution to the correlation energy. The resulting functional is *local* and depends parametrically on the number of electrons in the system. We apply this functional to the homogeneous electron gas and to a set of two-dimensional quantum dots covering a wide range of electron densities and thus various amounts of correlation. In all test cases we find an excellent agreement between our results and the exact correlation energies. Our correlation functional has a form that is simple and straightforward to implement but broadly outperforms the commonly used local-density approximation.

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I. INTRODUCTION

In the last couple of decades, the growing world of nanotechnology put at our disposal several classes of low-dimensional materials. Particularly interesting examples are two-dimensional (2D) quantum dots (QDs) (Refs. 1 and 2) formed at the interface between two semiconductors. These systems are not only important from a technological point of view but are also remarkable from a purely theoretical perspective. In fact, as they can be built with different shapes and sizes and with a varying number of electrons, they are the ideal system to study electronic correlation.

The problem of electronic correlation is perhaps the most challenging in the field of condensed-matter physics. Numerous approaches to handle this problem, with varying degrees of sophistication and complexity, have been put forward since the very birth of quantum mechanics. Few-electron QDs can be studied accurately by, e.g., configuration interaction (CI) (Ref. 3) or by quantum Monte Carlo (QMC) techniques.^{4–6} To describe the electronic properties of larger dots one has to resort to alternative approaches such as Hartree-Fock (HF) methods (Ref. 7) or density-functional theory (DFT) (Refs. 2, 8, and 9).

In DFT, the complexity of the many-body problem is embodied in the so-called exchange and correlation functional. Several approximations exist for this quantity, allowing for very accurate calculations of electronic properties in atoms, molecules, and solids. Clearly, most exchange-correlation functionals are derived for three-dimensional electronic systems. However, these approximations are known to break down when applied in the 2D limit.¹⁰ This calls for new formulas specialized for the 2D case. Particularly challenging in these applications is the fact that compared with atomic systems, correlation effects in 2D typically have a more prominent role due to the large size of the systems (from 10^{-8} to 10^{-6} m), and to their low electronic densities.

Within DFT, 2D systems such as QDs are commonly studied using the 2D version of the local-density approximation (LDA). It is a combination of the exchange functional derived for the uniform 2D electron gas by Rajagopal and Kimball¹¹ and the corresponding correlation functional fitted to accurate QMC calculations. The first of these LDA correlation functionals was put forward by Tanatar and Ceperley¹² in 1989. Later on, it was generalized for the complete range of collinear spin polarizations by Attaccalite *et al.*¹³ Applications of the 2D-LDA to QDs have been generally successful, even up to high magnetic fields.^{2,9} The LDA, however, suffers from several shortcomings, already well known from the three-dimensional world, especially for strongly inhomogeneous systems or in the low-density (strong correlation) regime.

Several alternative paths exist to go beyond the simple LDA. A particularly successful approach starts with the seminal work of Colle and Salvetti (CS) (Refs. 15 and 16) who, starting with a physically motivated ansatz for the many-body wave function, developed a closed formula for the correlation energy. This formula has received a large interest especially because it was used to derive the popular Lee-Yang-Parr (LYP) (Ref. 17) generalized gradient functional. Together with the exchange functional of Becke¹⁸ it forms the BLYP functional, and in hybrid schemes it is a part of B3LYP,¹⁹ X3LYP,²⁰ etc.

Interestingly, the same CS formula can also be interpreted as an orbital-dependent correlation functional especially suited for DFT calculations beyond the exact exchange.²¹ It should, however, be emphasized that the CS correlation-energy functional has several known limitations.^{22–24} In particular, while short-range correlations are well described,²³ important long-range correlations are missing. Even if these latter effects often cannot be ignored in large molecules and solids, they can be energetically negligible in small systems such as atoms. However, it has been shown recently that the long-range correlation problem may be cured to some

extent.^{25,26} Second, in the CS functional the kinetic-energy contribution to the correlation energy (named below as the kinetic-energy correlation) is taken into account only in an empirical fashion through the fitting parameter. In this context, an interesting modification of the original CS approach have been recently proposed.²⁷

In this work, we generalize the CS scheme^{15,16} to 2D. Then we use a Gaussian approximation for the pair probability function. Finally, we introduce an *ad hoc* modification which, *post factum*, seems to recover both the long-range and the kinetic-energy correlation to some good extent.

II. THEORY

Our starting point is the following ansatz^{15,16} for the many-body wave function Ψ ,

$$\Psi(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N) = \Psi_{\text{SD}}(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N) \prod_{i<j} [1 - \varphi(\mathbf{r}_i, \mathbf{r}_j)]. \quad (1)$$

Here, \mathbf{r} and σ denote, respectively, the space and spin coordinates of the electrons and Ψ_{SD} indicates the *single* Slater determinant (SD) of HF theory, which in the DFT context should be replaced by the Slater determinant generated from the occupied Kohn-Sham orbitals. The function φ describes the correlated part of the wave function. In the center of mass, $\mathbf{r} = (\mathbf{r}_1 + \mathbf{r}_2)/2$, and relative, $\mathbf{s} = \mathbf{r}_1 - \mathbf{r}_2$, coordinate system, it can be written as

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

where the quantities Φ , α , and β act as correlation factors. We point out that we introduce $\beta(\mathbf{r})$ as a *local* \mathbf{r} -dependent quantity for reasons which become obvious below. To find a reasonable value for β , which determines the local correlation length, we estimate the area where the electron is correlated as

$$A(\mathbf{r}) = \int d^2s e^{-\beta^2(\mathbf{r})s^2} = \frac{\pi}{\beta^2(\mathbf{r})}. \quad (3)$$

Then, we assume that this area is proportional to the area of the Wigner circle πr_s^2 , where the density parameter r_s is given through the total electron density as $r_s(\mathbf{r}) = 1/\sqrt{\pi\rho(\mathbf{r})}$. Thus, we find the relation

$$\beta(\mathbf{r}) = q\sqrt{\rho(\mathbf{r})}, \quad (4)$$

where q is a fitting parameter.

The SD wave function in Eq. (1) is recovered when all pairs of electrons are far apart from each other. In contrast, when two electrons are brought to the same point, the parameter α is chosen to satisfy the *cusp condition* (for the singlet case) of the wave function. It can be shown²⁸ that, for the 2D case, $\alpha = 1$. The function controlling the exponential decay is given by

$$\Phi(\mathbf{r}) = \frac{\beta(\mathbf{r})}{\beta(\mathbf{r}) + \sqrt{\pi}/2}, \quad (5)$$

which can be deduced by imposing the condition^{16,29}

$$\int d^2s \varphi(\mathbf{r}, \mathbf{s}) = 0. \quad (6)$$

By using wave function (1) and the definition of the correlation factor φ given by Eq. (2), we can obtain a formula for the correlation energy,^{15,16}

$$E_c = \int d^2r \int d^2s \rho_{2,\text{SD}}(\mathbf{r}, \mathbf{s}) \frac{\varphi^2(\mathbf{r}, \mathbf{s}) - 2\varphi(\mathbf{r}, \mathbf{s})}{s}, \quad (7)$$

where $\rho_{2,\text{SD}}(\mathbf{r}, \mathbf{s})$ refers to the SD pair density. To simplify this expression, we write a Gaussian approximation for this function,

$$\rho_{2,\text{SD}}(\mathbf{r}, \mathbf{s}) = \rho_{2,\text{SD}}(\mathbf{r}) e^{-s^2/\gamma^2(\mathbf{r})}. \quad (8)$$

The use of this Gaussian approximation was proposed in the context of the CS scheme by Moscardó and San-Fabian;²⁹ but it has been used in the field of DFT even further back.³⁰ To obtain the function $\gamma(\mathbf{r})$, which defines the width of the Gaussian, we apply the exact sum rule,

$$\rho_{\text{SD}}(\mathbf{r}) = \frac{2}{N-1} \int d^2s \rho_{2,\text{SD}}(\mathbf{r}, \mathbf{s}) = \frac{2\pi}{N-1} \rho_{2,\text{SD}}(\mathbf{r}) \gamma^2(\mathbf{r}), \quad (9)$$

from which follows

$$\gamma(\mathbf{r}) = \sqrt{\frac{(N-1)\rho_{\text{SD}}(\mathbf{r})}{2\pi\rho_{2,\text{SD}}(\mathbf{r})}}. \quad (10)$$

To simplify this expression, we apply the relation

$$\rho_{2,\text{SD}}(\mathbf{r}) = \frac{1}{4} \rho_{\text{SD}}^2(\mathbf{r}), \quad (11)$$

as well as Eq. (4) for the SD density $\rho_{\text{SD}}(\mathbf{r})$ and find

$$\frac{1}{\gamma^2(\mathbf{r})} = c\beta^2(\mathbf{r}), \quad (12)$$

where

$$c = \frac{\pi}{2(N-1)q^2}. \quad (13)$$

Using these results in Eq. (7) and performing the integration over s , leads to the final result

$$E_c^{\text{local}} = \int d^2r \rho_{\text{SD}}(\mathbf{r}) \epsilon_c^{\text{local}}(\mathbf{r}), \quad (14)$$

where we have defined $\epsilon_c(\mathbf{r})$ as the local correlation energy per electron having the lengthy expression,

$$\epsilon_c(\mathbf{r}) = \frac{\pi}{2q^2} \left\{ \frac{\sqrt{\pi}\beta(\mathbf{r})}{2\sqrt{2+c}} [\Phi(\mathbf{r}) - 1]^2 + \frac{\Phi(\mathbf{r})[\Phi(\mathbf{r}) - 1]}{2+c} + \frac{\sqrt{\pi}\Phi^2(\mathbf{r})}{4\beta(\mathbf{r})(2+c)^{3/2}} + \frac{\sqrt{\pi}\beta(\mathbf{r})}{\sqrt{1+c}} [\Phi(\mathbf{r}) - 1] + \frac{\Phi(\mathbf{r})}{1+c} \right\}. \quad (15)$$

Up to this point, the only inputs for the correlation energy are the fitting parameter q (we will come back to the choice of this parameter later on), the total number of electrons N ,

TABLE I. Comparison of the correlation energies (in atomic units) for parabolic quantum dots. The reference value E_c^{ref} is obtained by subtracting the exact-exchange energy from accurate data for the total energy. The last row contains the mean percentage error, Δ , for the parabolic dots (excluding the one used in the fitting procedure).

N	ω	$E_{\text{tot}}^{\text{ref}}$	$E_{\text{tot}}^{\text{EXX}}$	$-E_c^{\text{ref}}$	$-E_c^{\text{local}}$	$-E_{c,\text{mod}}^{\text{local}}$	$-E_c^{\text{LDA}}$
2	1	3 ^a	3.1619	0.1619	0.1619 ^b	0.1619 ^b	0.1988
2	1/4	0.9324 ^c	1.0463	0.1137	0.0957	0.1212	0.1391
2	1/16	0.3031 ^c	0.3732	0.0701	0.0477	0.0757	0.0852
2	1/36	0.1607 ^c	0.2094	0.0487	0.0299	0.0527	0.0607
6	0.42168	10.37 ^d	10.8204	0.4504	0.3805	0.4453	0.5305
6	1/1.89 ²	7.6001 ^e	8.0211	0.4210	0.3205	0.4060	0.4732
6	1/4	6.995 ^c	7.3911	0.3961	0.3047	0.3946	0.4574
12	1/1.89 ²	25.636 ^e	26.5528	0.9168	0.6837	0.8504	1.0000
Δ					26.1%	5.9%	18.4%

^aAnalytic solution by Taut from Ref. 31.

^bFitted result (see text).

^cCI data from Ref. 3.

^dVariational QMC data from Ref. 14.

^eDiffusion QMC data from Ref. 5.

and the electron density $\rho(\mathbf{r})$. We remind that the parameter c is defined through q and N in Eq. (13) and $\beta(\mathbf{r})$ is given in terms of $\rho(\mathbf{r})$ in Eq. (4). This particular dependency on N conflicts with the extent requirement of the correlation functional. For example, situations where two systems are very far apart from each other are expected to be problematic. However, semiconductor QDs with fixed N , which are main applications of the present functional, are free from this problem. We note also that there are no nuclei directly involved in the system: QDs are principally all-electron systems confined by a electrostatic potential and modeled in the effective-mass approximation, which accounts for the surrounding semiconductor material.^{1,2}

In conclusion, Eq. (14) is an *explicit density functional* for the correlation energy with a single fitting parameter q . This functional is self-interaction free, in the sense that it is identically zero for one-electron systems. Note that to recover this important property within the standard ladder of exchange-correlation functionals, one has to resort to highly sophisticated orbital functionals.

III. APPLICATION AND REFINEMENT OF THE APPROXIMATION

Here we complete and apply the approximation for the correlation energy in 2D. In particular, along the applications, we shall present an *ad hoc* modification which better accounts for both the long-range and the kinetic-energy correlation.

To choose a value for the fitting parameter q , we use Taut's analytic result³¹ for the singlet state of a two-electron parabolic QD with confining strength $\omega=1$. In terms of energy components, the correlation energy can be written as $E_c = E_{\text{tot}} - E_{\text{tot}}^{\text{EXX}}$, where EXX refers to the exact-exchange result. Applying this formula yields $E_c \approx -0.1619$ for the N

$=2$ singlet when $\omega=1$. To obtain the same value from Eq. (14), we need to set $q=2.258$. Of course the choice may be refined if needed. But aiming at providing ideally a *predictive* approximation, the fitting should not be carried out for each new system (to obtain every time the correct answer) but rather carried out once forever. This is a quite general and a well known way of defining or refining new approximations for the central quantities of DFT. In the following, we will show that our fitting procedure, outlined just above, guarantees a very good performance for a large class of systems.

Tables I and II show results for parabolically confined and for square ($\pi \times \pi$) quantum dots. The results obtained with our local formula for the correlation energy (denoted by E_c^{local}) are compared to reference results E_c^{ref} , as well as with LDA correlation energies E_c^{LDA} . We computed the EXX and LDA values using the real-space code OCTOPUS.³³ The EXX result was calculated in the Krieger-Li-Iafrate (KLI) approach,³⁴ which is an accurate approximation in the static case.³⁵ For E_c^{LDA} we applied the parametrization of Attacalite *et al.*¹³ Note that we used a perturbative approach to calculate E_c^{local} from Eq. (14). The self-consistent EXX density was the input for our local functional. We also found that using the LDA density as input did not make a considerable difference.

The QDs studied here span a wide range of density parameters r_s , determined in a parabolic QD as $r_s = N^{-1/6} \omega^{-2/3}$ and in our square QD as $r_s = \sqrt{\pi/N}$. This parameter corresponds to the average radius of an electron in a QD with an average number density $n_0 = 1/(\pi r_s^2)$. Thus, the cases shown in the tables are between $0.44 < r_s < 9.71$. In fact, the upper limit exceeds the threshold of $r_s \sim 7.5$ for Wigner crystallization in the impurity-containing 2D electron gas.³⁶ One should, however, bear in mind that in QDs the concept of Wigner localization is ambiguous and no general formula

TABLE II. Comparison of the correlation energies (in atomic units) for square ($\pi \times \pi$) quantum dots. The reference value E_c^{ref} is obtained by subtracting the exact-exchange energy from the quantum Monte Carlo result for the total energy (Ref. 32).

N	$E_{\text{tot}}^{\text{QMC}}$	$E_{\text{tot}}^{\text{EXX}}$	$-E_c^{\text{ref}}$	$-E_c^{\text{local}}$	$-E_{c,\text{mod}}^{\text{local}}$	$-E_c^{\text{LDA}}$
2	3.2731	3.4643	0.1908	0.1905	0.1763	0.2226
6	26.9679	27.5928	0.6249	0.6578	0.5763	0.7624
8	46.7940	47.5962	0.8022	0.9168	0.7836	1.0514
12	103.3378	104.5620	1.2242	1.4494	1.2026	1.6419
16	178.5034	179.9804	1.4770	2.0096	1.6282	2.2534
Δ				19.3%	6.8%	33.6%

exists for the density parameter at the onset of localization. It can be also seen that in our examples the ratio of the correlation to the total energy varies from less than 1% up to around 30%.

Results with our local formula are roughly of the same quality as the LDA, slightly worse for the parabolic dots but slightly better for the square dots. Furthermore, a calculation for the homogeneous electron gas (Fig. 1) reveals that this functional agrees with the LDA (which is exact for this system) in the limit of vanishing r_s but underestimates the correlation energy otherwise.

The derived functional not only gives already very reasonable results but is also a very good starting point for further developments. In fact, we found an alternative functional (that we will denote by $E_{c,\text{mod}}^{\text{local}}$) obtained by modifying the first term between the parentheses in Eq. (15) by

$$[\Phi(\mathbf{r}) - 1]^2 \rightarrow \Phi(\mathbf{r}) - 1. \quad (16)$$

To finish the derivation of this functional we need to refit the parameter q , which now reads $q^{\text{mod}}=3.9274$ (in such a way, we again obtain the exact value of the correlation energy for the two-electron quantum dot as described above).

Sensu stricto, Eq. (16) is an empirical approximation. Our results suggest, *post factum*, that the proposed modification better accounts for the long-range^{23,26} and kinetic-energy correlation.^{27,37} However, a deeper theoretical understanding

of these results would be appropriate. Along these lines, we plan to undertake additional analysis in a future work.

According to Tables I and II, our corrected functional agrees very well with the reference results. We find that, in all the cases studied, our approximation is vastly superior to the LDA correlation. Note that our results exhibit the correct scaling with respect to both confinement strength and number of electrons even if the adjustable parameter q has only been fitted to the case $N=1$ and $\omega=2$. Also for the homogeneous electron gas (Fig. 1), our modified functional yields results that are remarkably close to the reference LDA curve, departing significantly from the exact curve only for very small r_s (weak correlation limit).

Finally, we wish to make a few remarks on the usage of the present correlation functional. First, we point out that in practical purposes within, e.g., the Kohn-Sham scheme of DFT, the functional should be combined with an adequate recipe for the exchange energy, such as the exact exchange or the functionals suggested in Ref. 38. Second, for many systems—such as, e.g., QDs in magnetic fields—one requires a spin-polarized version of the exchange-correlation functional. This has already been taken into account in the LDA functional by Attaccalite *et al.*,¹³ but a spin-polarized extension of the present functional is still missing. Work to solve these two issues is already under way.

IV. CONCLUSIONS

We developed a correlation energy functional for the two-dimensional electron gas starting from the Colle and Savetti ansatz for the many-body wave function and a Gaussian approximation to the pair density. To better account for the long-range and kinetic-energy correlation, we have then introduced an additional *ad hoc* modification. The resulting functional has a very simple form depending parametrically on the total number of electrons N and locally on the electronic density $n(\mathbf{r})$. It only contains a single parameter, q , that was adjusted to the exact calculation of a two-electron quantum dot. Calculations performed for several systems, with a wide range of density parameters r_s , show that our functional gives results in very good agreement with reference values. This agreement is maintained even for very dilute electron gases where the correlation energy amounts to 30% of the total energy.

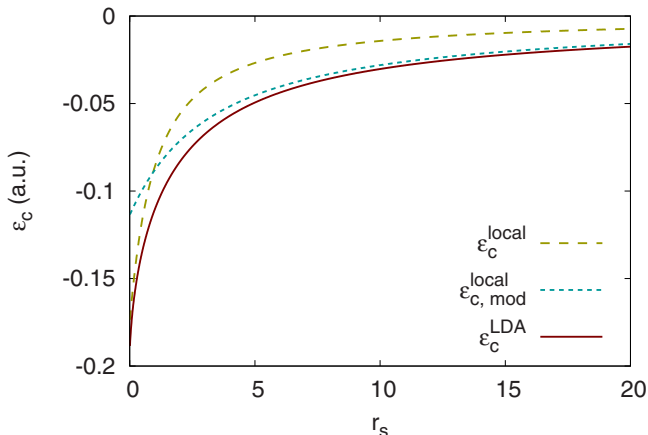


FIG. 1. (Color online) Correlation energy per unit particle for the uniform 2D electron gas in various approximations.

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