Inhomogeneity Induced and Appropriately Parameterized Semilocal Exchange and Correlation Energy Functionals in Two-Dimensions

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The construction of meta generalized gradient approximations based on the density matrix expansion (DME) is considered as one of the most accurate technique to design semilocal exchange energy functionals in two-dimensional density functional formalism. The exchange holes modeled using DME possess unique features that make it a superior entity. Parameterized semilocal exchange energy functionals based on the DME are proposed. The use of different forms of the momentum and flexible parameters is to subsume the non-uniform effects of the density in the newly constructed semilocal functionals. In addition to the exchange functionals, a suitable correlation functional is also constructed by working upon the local correlation functional developed for 2D homogeneous electron gas (2D-HEG). The non-local effects are induced into the correlation functional by a parametric form of one of the newly constructed exchange energy functionals. The proposed functionals are applied to the parabolic quantum dots with a varying number of confined electrons and the confinement strength. The results obtained with the aforementioned functionals are quite satisfactory which indicates why these are suitable for two-dimensional quantum systems.

I. INTRODUCTION

The Density functional theory (DFT) is a most favored formalism in condensed matter physics and quantum chemistry for electronic structure calculations. The Kohn-Sham (KS) formalism is the mainstay of DFT which solves an auxiliary one particle Schrödinger like equations and provides ground state energy and other properties as a functional of density and density derived quantities. In density functional formalism the only unknown part is the exchange-correlation (xc) functional, which is a small fraction but most important part of the total energy. So, several techniques and approximations are introduced which play crucial role in designing the non-trivial entity of DFT with different formal properties. Therefore, precise approximations to XC energy functional ($E_{xc}$) are always been an exciting and enthralling research field. The first ever XC functional construction is the spin-polarized approximation from uniform electron gas limit called the local spin-density approximation (LSDA) i.e. the $E_{xc}$ is a function of only electron density. Then inhomogeneity is added to this functional through the gradient of density and kinetic energy density, which gave rise to the generalized gradient approximations (GGAs) and meta-GGAs. All these functionals are developed for three-dimensional (3D) systems. Previous studies show that the semilocal density functional proposed for 3D systems cannot be applied directly to the (pure) two-dimensional (2D) systems due to the dimensional crossover problem.

Over the last few decades, increasing attention has been paid to the density functional study of the low dimensional quantum systems, which includes semiconductor quantum dots, quantum point contacts, and quantum Hall systems. For this, meticulous developments of $E_{xc}$ in 2D is very essential. The 2D-LDA seems to be a valuable option instead of the 3D-LDA for accurately studying pure 2D systems in a pure 2D grid. So, within DFT formalism, quantum dots (QDs) are commonly studied using 2D-LSDA exchange along with locally approximated correlation. But, to take care of the inhomogeneity present in the system, further improvements over 2D-LSDA, such as 2D-GGAs and 2D-meta-GGAs are also proposed in recent years.

In this present work, our focus is on the development of semilocal exchange energy functionals using the advanced DME techniques as an intellectual basis. Then, we will propose an appropriate correlation energy functional using one of the semilocal exchange energy functionals designed for the 2D systems. Thus, as a first step, three exchange energy functionals are constructed with four adjustable parameters each. The newly constructed semilocal exchange energy functionals depend on the gradient of density and kinetic energy density. The inhomogeneity associated with the system is imposed on the functional construction through the modification of the Fermi momentum. Thus, the Fermi momentum is modified by adding appropriate functional forms involving the reduced density gradient and kinetic energy density with suitable remodeling. These transformed momenta are used in the newly developed exchange energy functionals. Since, the popularly used 2D-LDA correlation energy was constructed for 2D electron gas, by fitting with Monte-Carlo simulation data and including low- and high-density limits. So, to construct the correlation functional compatible with the above exchange functionals, we have modified the 2D-LDA correlation functional by imposing the non-local effects through an exchange energy functional using appropriate parameters. The numerical investigations of these newly con-
structured semilocal functionals are done by applying these to parabolic QD systems. The calculations are done by varying the number of confined electrons and confinement strength of the parabolic quantum dots. We have compared our results with the 2D exact exchange (2D-EXX) within the Krieger-Li-Iafrete (KLI) approximation, 2D-LSDA exchange, and some of extensively used 2D-GGA exchange functionals. All the calculations are performed self-consistently.

II. DENSITY MATRIX EXPANSION BASED EXCHANGE HOLE MODEL

The recently proposed semilocal exchange energy functionals based on the DME of the Hartree-Fock exchange gained more attention for studying the low dimensional quantum systems. Not only, it is one of the best strategies to construct an analytic expression for the exchange energy functional in 3D but also in 2D as well. In 2D, the Hartree-Fock exchange energy in terms of density and exchange hole is given by,

$$E_x = \frac{1}{2} \int d^2r \int d^2r' \frac{\rho(r)r_x(r', r')}{|r - r'|},$$

where $\rho_x(r, r')$ be the cylindrically averaged exchange hole density. It can be expressed in terms of the 1st order reduced density matrix $\gamma_1(r, r')$ as

$$\rho_x(r, r') = -\frac{\langle |\gamma_1(r, r')|^2 \rangle}{2\rho(r)}, \tag{2}$$

with

$$\gamma_1(r, r') = 2 \sum_{i=1}^{\text{occu}} \phi^*_i(r)\phi_i(r'), \tag{3}$$

where $\phi_i$ are the occupied KS orbitals. On using the general coordinate transformation $(r, r') \rightarrow (r_\lambda, u)$ with $r_\lambda = \lambda r + (1-\lambda)r'$ and $u = r' - r$. Here, $\lambda$ is a real number between 1/2 and 1 (i.e. exchange hole varies between maximally localized and conventional one). Now, due to the above coordinate transformation, the exchange energy expression i.e. Eq. (1) reduces to

$$E_x = \frac{1}{2} \int d^2u \rho(r_\lambda) \rho_x(r_\lambda, u), \tag{4}$$

and Eq. (2) can be rewritten as

$$\rho_x(r_\lambda, u) = -\frac{\langle |\gamma'_1(r_\lambda - (1-\lambda)u, r_\lambda + u)|^2 \rangle}{2\rho(r_\lambda)}, \tag{5}$$

where $\gamma'_1(r_\lambda - (1-\lambda)u, r_\lambda + u)$ be the transformed single-particle density matrix. Now, expanding the density matrix about $u = 0$ and replacing the exponential term arising in it with the Bessel and Hypergeometric functions $21, 22$, the transformed density matrix reduces to

$$\Gamma_1 = 2\rho \frac{J_1(ku)}{ku} \left( \frac{6J_4(ku)}{k^4u^2} \right) \left[ 4 \cos^2 \phi \left( \lambda^2 - \lambda + \frac{1}{2} k^2 \right) \right] + \left( \frac{6J_4(ku)}{k^4u^2} \right) \left[ 4 \cos^2 \phi \left( \lambda^2 - \lambda + \frac{1}{2} k^2 \right) \right]. \tag{6}$$

The choice of the expansion is comprehensible since the first term recovers the exact LDA for the homogeneous systems in 2D. The additional terms present besides the zeroth order LDA term takes care of the inhomogeneity involved in the system. Now following similar procedure as $23$ for 2D, the cylindrically averaged exchange hole from the DME expression Eq. (6) is given by,

$$\rho_x(r, u) = -\frac{2J_1(ku)\rho}{k^2u^2} - \frac{12J_4(ku)J_6(ku)}{k^4u^2}A + \frac{18J_6(ku)}{k^6u^2}A^2, \tag{7}$$

where, $A = (\lambda^2 - \lambda + \frac{1}{2})\lambda \rho - 4\tau + k^2 \rho$. Now, in order to further achieve the reliable accuracy of the newly constructed semilocal exchange functional, the expansion up to 4th order in ‘’u’’ is taken into consideration. It is noteworthy to mention that the first term in the Eq. (7) corresponds to the exchange hole for systems with uniform electronic density. So, the coordinate transformation involved here is responsible for including the inhomogeneity effects but keeps the homogeneous term unaffected. It’s because the homogeneity of the system is translationally-invariant. Therefore, we have $\lambda$ dependency appearing only in the higher order terms (i.e. the 2nd and 3rd terms).

III. EXCHANGE ENERGY FUNCTIONALS

Now, for constructing the desired semilocal exchange functionals, the density matrix expansion and exchange hole model given by Eq. (6) and Eq. (7) are used. Here, we have replaced the laplacian term involved with help of the integration by parts. Thus, using these ideas and plugging Eq. (7) back in Eq. (1), the exchange energy functional becomes,

$$E_x = -\int d^2r \left[ \frac{8\rho^2}{3k} + \frac{16\rho^3}{15k^3}B + \frac{32\rho^4}{35k^5}B^2 \right], \tag{8}$$

where

$$B = \left( \lambda^2 - \lambda + \frac{1}{2} \right) x^2 - \left( \frac{4\tau - k^2 \rho}{\rho^2} \right), \tag{9}$$

and $x = \frac{\nabla\rho}{\rho}$, be the dimensionless quantity called the reduced density gradient in 2D. Now, the newly constructed exchange energy functional given above depends on $\rho$, $\tau$, $\lambda$ and momentum ‘$k’$. The first and obvious choice of ‘$k’’ is the Fermi momentum. Upon replacing
Using spin scaling relation of the exchange energy, i.e.,

\[ E_x[p_\uparrow, p_\downarrow] = \frac{1}{2} E_x[2p_\uparrow] + \frac{1}{2} E_x[2p_\downarrow], \]

the spin-polarized exchange energy functional corresponding to Eq. 8 becomes,

\[ E_x = - \sum_{\sigma=\uparrow,\downarrow} \int d^2r \left[ \frac{32\rho_\sigma^2}{3k_\sigma^3} + \frac{128\rho_\sigma^3}{15k_\sigma^3} \mathcal{G}_\sigma(x_\sigma, z_\sigma) \right. \]

\[ + \left. \frac{512\rho_\sigma^4}{35k_\sigma^3} \mathcal{G}_\sigma^2(x_\sigma, z_\sigma) \right], \tag{11} \]

where

\[ \mathcal{G}_\sigma(x_\sigma, z_\sigma) = (\lambda^2 - \lambda + \frac{1}{2}) \frac{z_\sigma^2}{2} - z_\sigma \tag{12} \]

\( z_\sigma = \frac{x_\sigma}{r_\sigma} - \frac{2\pi}{r_\sigma} \) is a dimensionless quantity. The functional form of the momentum present in the denominator of all these terms is not unique. Only one constraint should be taken care for the momentum i.e. it should have the dimension of length inverse. In 3D, some forms of momentum are proposed\textsuperscript{12-14}. The prime and transparent choice for \( k' \) is \( k_F \) and the exchange functional using this becomes,

\[ E_x = - \sum_{\sigma=\uparrow,\downarrow} \int d^2r \left[ \frac{32\rho_\sigma^2}{3k_F^3} \left( 1 + \frac{4\rho_\sigma \mathcal{G}_\sigma(x_\sigma, z_\sigma)}{5k_F^2} \right) \right. \]

\[ + \left. \frac{48\rho_\sigma^2 \mathcal{G}_\sigma^2(x_\sigma, z_\sigma)}{35k_F^3} \right]. \tag{13} \]

However, here we are interested in adding non-uniformity of the electronic density by making various choices for momentum. We have used different choices of \( k' \) other than \( k_F \) and based on the physically relevant choices of \( k' \), different exchange energy functionals are developed. So, in order to add the inhomogeneity of the system to the functional through momentum, one needs to add suitable terms intuitively having density dependency, which upon imposing the homogeneity limit should correctly recover the LDA exchange functional. In principle, this happens because the new exchange energy functional i.e., Eq. (13) depends on dimensionless quantities \( x_\sigma \) and \( z_\sigma \) as for homogeneous systems, \( x_\sigma \) becomes zero as it depends on \( \nabla \rho \). Similarly, \( z_\sigma \) goes to zero when \( \tau = \tau_{unif}/(\text{HEG}) \). Using these ingredients, functionals are developed in the next subsections.

### A. Density gradient dependent momentum

We have added the dimensionless reduced density gradient based terms to the Fermi momentum. The addition of \( x_\sigma^2 \) to \( k_F \), obeys all the conditions i.e. new momentum \( k_{F,g} \) has the dimension of length inverse and becomes \( k_F \) in the uniform density limit. We have proposed the first modification to the Fermi momentum through

\[ k_{F,g} = k_F \left( 1 + \alpha x_\sigma^2 \right), \tag{14} \]

where \( \alpha \) is an adjustable parameter which takes care of the gradient effect. Using \( k_{F,g} \) from Eq. (13), in Eq. (13) the new semi-local exchange energy functional \( E_x^{GDM} \) (exchange energy with gradient dependent momentum) becomes,

\[ E_x^{GDM}[x_\sigma, z_\sigma] = - \sum_{\sigma=\uparrow,\downarrow} \int d^2r \left[ \frac{32\rho_\sigma^2}{3k_{F,g}} + \frac{128\rho_\sigma^3}{15k_{F,g}^3} \mathcal{G}_\sigma(x_\sigma, z_\sigma) \right. \]

\[ + \left. \frac{512\rho_\sigma^4}{35k_{F,g}^3} \mathcal{G}_\sigma^2(x_\sigma, z_\sigma) \right]. \tag{15} \]

Since, in the present study, the density matrix expansion is terminated at the 2\textsuperscript{nd} order. As a matter of which, the exchange hole is not exact. To take care the above fact, we have introduced two adjustable parameters \('A' and '\('B' which will be fixed later. Also, the first term within square bracket is different from the LSDA exchange energy because of the presence of \( k_{F,g} \) in the denominator. For this parameterization of higher order terms are necessary.

### B. Kinetic energy dependent momentum

Our next attempt is to construct the semi-local exchange functional through K.E. dependent momentum. Since, the term \( z_\sigma \) present in the exchange functional expression i.e., Eq. (13), contains the kinetic energy density as one of its main ingredients. Hence, the inclusion of such terms in \( k_F \), makes the momentum kinetic energy density dependent. In this way, we have included the non-uniformity through momentum by means of \( r \). It is conspicuous that addition of some fraction of \( z_\sigma \) to \( k_F \) obeys the dimension and uniform density limit restrictions. Thus, a new form of the transformed momentum is proposed to be,

\[ k_{F,t} = k_F \left( 1 + \alpha z_\sigma \right), \tag{16} \]

where \( \alpha \) be an adjustable parameter introduced to add a small fraction of the inhomogeneity through \( z_\sigma \). Now, upon substituting the changed momentum from Eq. (16) in the exchange expression of Eq. (13), readily leads to the following exchange energy functional \( E_x^{TD,M} \) (\( \tau \) dependent momentum) similar to Eq. (13) having the form,

\[ E_x^{TD,M}[x_\sigma, z_\sigma] = - \sum_{\sigma=\uparrow,\downarrow} \int d^2r \left[ \frac{32\rho_\sigma^2}{3k_{F,t}} + \frac{128\rho_\sigma^3}{15k_{F,t}^3} \mathcal{G}_\sigma(x_\sigma, z_\sigma) \right. \]

\[ + \left. \frac{512\rho_\sigma^4}{35k_{F,t}^3} \mathcal{G}_\sigma^2(x_\sigma, z_\sigma) \right]. \tag{17} \]
TABLE I. Tabulated are the adjusted values of all the constants present in the exchange energy functionals $E_x^{GTDM}$, $E_x^{TD}$, and $E_x^{GTM}$.

| Functional | $\alpha$ | $A$ | $B$ |
|------------|----------|-----|-----|
| $E_x^{GTM}$ | 0.001    | 0.1 | 0.3951 |
| $E_x^{TD}$  | 0.001    | 0.1 | 0.0946 |
| $E_x^{GTDM}$| 0.001    | 0.1 | 0.442 |

FIG. 1. Shown are the mean error of exchange energies for few electron parabolic quantum dots plotted against the electron number.

So far we have used $x_\sigma$ and $z_\sigma$ individually, to enhance the inhomogeneity effects in the semilocal functionals through the momentum. It is indicative that, use of both $x_\sigma$ and $z_\sigma$ together is a noticeable option because the addition of both terms in appropriate order satisfies the inverse length dimension of momentum and the modified momentum recovers the Fermi momentum for uniform densities. The simplest form of both kinetic energy density and reduced density gradient dependent momentum is,

$$\tau_{F,\sigma} = k_F \{1 + \alpha (x_\sigma^2 + z_\sigma)\},$$  

where $\alpha$ is an adjustable parameter defined in the same manner as Eq. (14) and Eq. (15). The exchange energy functional $E_x^{GTDM}$ (gradient and $\tau$ dependent momentum) with $k_{F,\sigma}$ is,

$$E_x^{GTDM}[x_\sigma, z_\sigma] = - \sum_{\sigma = \uparrow, \downarrow} \int d^2r \left[ \frac{32\rho_s^2}{3k_{F,\sigma}} + A \frac{128\rho_s \sigma(x_\sigma, z_\sigma)}{15k_{F,\sigma}} + B \frac{512\rho_s^2 G_s^2(x_\sigma, z_\sigma)}{35k_{F,\sigma}} \right],$$  

where ‘$A$’ and ‘$B$’ are again tunable constants. The effects of higher-order terms in the density matrix expansion can be included through these parameters.

IV. THE CORRELATION ENERGY FUNCTIONAL

Now, we will try to construct the correlation energy functional compatible with the three semilocal exchange energy functionals constructed above. The 2D-LDA correlation energy functional is commonly used in the calculations of 2D quantum systems. This functional was constructed by the interpolation of the low-density limit from Diffusion Monte Carlo (DMC) data and high-density limit from 2D-LDA exchange-correlation energy functional having a parameterized form,

$$\epsilon_c^{LDA}(r_s, \zeta) = \epsilon_c^{(6)}(r_s, \zeta) + \alpha_0(r_s) + \alpha_1(r_s)\zeta^2 + \alpha_2(r_s)\zeta^4, \quad (20)$$

where $r_s = 1/\sqrt{\pi \rho_s}$, $\zeta$ be the usual spin-polarization and $\epsilon_c^{(6)}(r_s, \zeta) = \epsilon_c(r_s, \zeta) - (1 + \frac{3}{8}\zeta^2 + \frac{3}{128}\zeta^4)\epsilon_c(r_s, 0)$ be the Taylor expansion of $\epsilon_c$ beyond fourth order in $\zeta$. Here, the 2D-LSDA exchange energy term, $\epsilon_x = -2\sqrt{2}[(1 + \zeta)^{3/2} + (1 - \zeta)^{3/2}]3\pi r_s$. The functional form of $\alpha_i(r_s)$ is taken as a 2D generalization form from electron-gas correlation of Perdew-Wang and is given by,

$$\alpha_i(r_s) = A_i + \left( B_i + C_i r_s^2 + D_i r_s^3 \right) \times \ln \left( 1 + \frac{1}{E_i r_s + F_i r_s^{3/2} + G_i r_s^2 + H_i r_s^3} \right). \quad (21)$$

The values of all the constants present in the above Eq. (21) are given in the Table II of reference. This correlation functional depends on spin-polarization $\zeta$ and electron density $\rho$ via $r_s$, which make this functional local. However, the application of this LDA functional to the parabolic QDs overestimates the correlation energy up to a large extent which can be observed from the Table III. So, in order to apply this correlation functional to non-uniform systems, modifications to the correlation functional is desirable. Thus, we have proposed that the non-local effects of the real system can be engineered into the LDA correlation energy via a parametric form of our exchange energy functional constructed above. In fact,
TABLE II. Shown in the table are the exchange energies (in atomic units) for parabolic QDs calculated using the new 2D exchange energy functionals $-E_{x}^{2D-LDA}$, $-E_{x}^{2D-GDM}$, and $-E_{x}^{2D-GTBDM}$. The 1st column is for the number of electrons 'N', 2nd is for confinement strength $\omega$. The self-consistent calculations for 2D-EXX (KLI), 2D-LDA, 2D modified B86, 2D-B88 are shown in succeeding columns. The last three columns are the results for our constructed functionals. The last row contains the MAPE ($\Delta$).

| N  |  $\omega$ | $-E_{x}^{2D-LDA}$ | $-E_{x}^{2D-GDM}$ | $-E_{x}^{2D-GTBDM}$ |
|----|-----------|-------------------|-------------------|-------------------|
| 2  | 1/6       | 0.380             | 0.337             | 0.368             |
| 2  | 0.25      | 0.485             | 0.431             | 0.470             |
| 2  | 0.50      | 0.729             | 0.649             | 0.707             |
| 2  | 1.00      | 1.083             | 0.967             | 1.051             |
| 2  | 1.50      | 1.358             | 1.214             | 1.319             |
| 2  | 2.50      | 1.797             | 1.610             | 1.748             |
| 2  | 3.50      | 2.157             | 1.934             | 2.097             |
| 6  | 0.25      | 1.618             | 1.531             | 1.603             |
| 6  | 0.50      | 2.470             | 2.339             | 2.444             |
| 6  | 1.00      | 3.732             | 3.537             | 3.690             |
| 6  | 1.50      | 4.726             | 4.482             | 4.672             |
| 6  | 2.50      | 6.331             | 6.008             | 6.258             |
| 6  | 3.50      | 7.651             | 7.264             | 7.562             |
| 12 | 0.50      | 5.431             | 5.257             | 5.406             |
| 12 | 1.00      | 8.275             | 8.013             | 8.230             |
| 12 | 1.50      | 10.535            | 10.206            | 10.476            |
| 12 | 2.50      | 14.204            | 13.765            | 14.122            |
| 12 | 3.50      | 17.237            | 16.709            | 17.136            |
| 20 | 0.50      | 9.765             | 9.553             | 9.746             |
| 20 | 1.00      | 14.957            | 14.638            | 14.919             |
| 20 | 1.50      | 19.108            | 18.704            | 19.053             |
| 20 | 2.50      | 25.875            | 25.334            | 25.796             |
| 20 | 3.50      | 31.491            | 30.837            | 31.392             |
| 30 | 1.00      | 23.979            | 23.610            | 23.953             |
| 30 | 1.50      | 30.707            | 30.237            | 30.665             |
| 30 | 3.50      | 50.882            | 50.115            | 50.794             |
| 42 | 1.00      | 35.513            | 35.099            | 35.503             |
| 42 | 1.50      | 45.560            | 45.032            | 45.538             |
| 42 | 2.50      | 62.051            | 61.339            | 62.007             |
| 42 | 3.50      | 75.814            | 74.946            | 75.748             |
| 56 | 1.00      | 49.710            | 49.256            | 49.722             |
| 56 | 1.50      | 63.869            | 63.289            | 63.871             |
| 56 | 2.50      | 87.164            | 86.378            | 87.148             |
| 56 | 3.50      | 106.639           | 105.684           | 106.609            |
| 72 | 1.00      | 66.708            | 66.219            | 66.746             |
| 72 | 1.50      | 85.814            | 85.186            | 85.844             |
| 72 | 2.50      | 117.312           | 116.456           | 117.327           |
| 72 | 3.50      | 143.696           | 142.650           | 143.697           |
| 90 | 1.00      | 86.631            | 86.111            | 86.698             |
| 90 | 1.50      | 115.558           | 110.889           | 111.622           |
| 90 | 2.50      | 152.723           | 151.808           | 152.770           |
| 90 | 3.50      | 187.262           | 186.139           | 187.306           |
| 110| 1.00      | 109.595           | 109.048           | 109.695           |
| 110| 1.50      | 141.255           | 140.548           | 141.357           |
| 110| 2.50      | 193.617           | 192.647           | 193.715           |
| 110| 3.50      | 237.612           | 236.420           | 237.706           |

$\Delta$ 4.2 0.71 1.04 0.44 0.40 0.40

The use of exchange energy enhancement factor in the correlation energy is encountered in previous studies of 3D correlation functionals. Analogous to 3D, here, we have used a modified form of $E_{x}^{GTBM}$ with some convenient parameters. The modified form of momentum from Eq. (18) with a different constant can be written as,

$$k_{F,\sigma,t} = k_{F}\{1 + \delta(x_{\sigma}^2 + z_{\sigma})\} = k_{F}\Gamma_{\sigma}(x_{\sigma}, z_{\sigma}). \quad (22)$$

Now, using the above form of momentum from Eq. (22) in place of $k_{\sigma}$ present in the Eq. (11), one can easily rewrite.
energy functionals like 2D-LDA functionals. To compare the results of exchange energies of EXX are used as input for the newly constructed polarized density and spin-polarized kinetic energy den-
self-consistent calculations and the outputs such as spin-

where L, M, and N are parameters introduced to account the effects of neglected higher order terms. The above Eq. (23) is written in a similar way as \( E^{GTDM}_x \) but with a small modification in the enhancement factor. This modification is necessary to give proper multiplicative factor to the correlation functional. In this section, we are not interested in calculating exchange energy functional Eq. (23). But to incorporate the non-local effects in the correlation functional, multiplication by enhancement factor like term present within square bracket in the above Eq. (23) is desirable. We denote this term as ‘\( f_\sigma \)’. The term ‘\( f_\sigma \) ’ is a dimensionless quantity and will not change the dimension of any quantity when it will be multiplied by the same. Hence, taking the local contribution from Eq. (24) and inducing non-uniformity via ‘\( f_\sigma \)’, we have proposed a new spin-polarized correlation energy functional to be,

\[
E^{NIL}_{c,\sigma} = \sum_{\sigma=\uparrow,\downarrow} \int d^2r \ L^{DA}_{c,\sigma}(r,\zeta) f_\sigma(x_\sigma, z_\sigma) . \tag{24}
\]

The above non-local effect induced LDA correlation functional \( E^{NIL}_{c,\sigma} \) will be completed when appropriate values for all the parameters will be defined successfully. This task will be completed in the next section by comparing the result with the exact values for the parabolic quantum dots.

V. RESULTS AND DISCUSSION

For numerical calculations, we have applied the newly proposed functionals to parabolically confined quantum dots (QD) which are also known as artificial atoms. The external potential for the QD is \( \phi \omega^2r^2/2 \) with confinement strength \( \omega \). The exact exchange (EXX) results for the QDs are calculated using optimized potential method (OPM) with Krieger-Li-Iafrate (KLI)\textsuperscript{16} approximation. The OCTOPUS\textsuperscript{22} code is used for all the self-consistent calculations and the outputs as spin-polarized density and spin-polarized kinetic energy densities of EXX are used as input for the newly constructed functionals. To compare the results of exchange energy functionals, some of the previously constructed exchange functionals like 2D-LDA\textsuperscript{19}, 2D-B88\textsuperscript{22}, and 2D-modified GGA\textsuperscript{21} are also calculated self-consistently using OCTOPUS. All the exchange energy functionals are analyzed, by varying the number of electrons from 2 to 110 and the confinement strength from 0.25 to 3.5 in the parabolic quantum dot.

Here, our first task is to give appropriate values to all the constants present in the exchange and correlation energy functionals. All the three exchange energy functionals \( E^{GDM}_x \), \( E^{TDM}_x \), and \( E^{GTDM}_x \) contain four adjustable parameters such as \( A, B, \lambda, \) and \( \alpha \). The constant \( \lambda \) was defined for the localization of the exchange hole and for the present calculations, we have chosen maximally localized exchange hole, which implies \( \lambda = 0.5 \). The first term in all these exchange functionals is LSDA like term. Hence, all the succeeding terms should be corrections to the LSDA and the effects should decrease gradually. So, keeping this in mind and comparing results for two electrons parabolic QD with EXX-KLI, we have fixed the value of ‘\( A \)’. Now, we are left with two more parameters \( \alpha \) and \( B \). The parameter ‘\( \alpha \)’ is the constant introduced to take care the addition of inhomogeneity to \( k_F \) and ‘\( B \)’ is multiplied to the coefficient of 3rd term present within all the square brackets of exchange energy functionals. Thus, the choice of \( \alpha \) and \( B \) are interdependent. We select \( \alpha \) as a very small real number. This will add a little non-uniformity to \( k_F \). Because for a higher value of \( \alpha \) the result will exceed from exact values. We have calculated exchange energies for two electron parabolic quantum dot varying ‘\( \omega \)’ from 0.25 to 3.5, and for each system, we have determined ‘\( B \)’ which gave zero error. Finally, the mean value of all ‘\( B \)’s is taken as concluding value of it. All these procedures are followed to fix the parameters of exchange energy functionals and values for these parameters are given in Table II. The settled values for all the adjustable parameters depend on QD systems.

The Table II comprises of the number of electrons (\( N \)), confinement strength (\( \omega \)), and four known functionals, in the first six columns. The last three columns are results obtained from the newly constructed exchange energy functionals. The mean absolute percentage of error (MAPE) for all the functionals are given for comparison. The competitive and better performance of the new functionals to calculate the exchange energies are clear from the Table II Exchange energy functional \( E^{GDM}_x \), \( E^{TDM}_x \), and \( E^{GTDM}_x \) make MAPE as 0.44, 0.40, and 0.40 respectively for all 46 calculations. Figure II is the mean error (ME) plot for all the discussed functionals. The heights of different color bars represent the ME corresponding to the exchange energy functionals considered in the present study.

The correlation functional \( E^{NIL}_{c,\sigma} \) from Eq. (24) contains four parameters \( L, M, N, \) and \( \delta \), to be fixed by comparing the correlation energy with the exact results. In DFT correlation energy can be written as \( E^{ref}_{corr} = E^{ref}_{tot} - E^{EXX}_{tot} \), where \( E^{ref}_{tot} \) is the exact total energy of the system and \( E^{EXX}_{tot} \) is the total energy of the system taking EXX without any correlation. By analyzing the correlation energy of the parabolic QD with 2 electrons and \( \omega = 1 \), we have fixed the constants \( \delta = 0.01 \), \( L = 0.8825 \), and \( M = 0.1 \). The value of \( N \) is taken as the mean of all \( N \)'s that gives zero difference between the exact and calculated values for a set of parabolic quantum dots. We have considered the first two closed shell
TABLE III. The first two columns represent the number of electrons (N) and the confinement strength (ω). All the references for exact values of total energies of different quantum dots are given below the table. The last row contains the MAPE (Δ).

| N  | ω | $E_{xc}^{ref}$ | $E_{tot}^{2D-EXX}$ | $E_{xc}^{mod}$ | $E_{tot}^{2D-LDA}$ | $E_{xc}^*$ | $E_{tot}^{c,σ}$ | $E_{tot}^{NIL}$ | $E_{xc}^{mod}$ | $E_{tot}^{ref}$ | $E_{xc}^{mod}$ |
|----|---|---------------|-----------------|--------------|-----------------|--------|----------------|---------------|--------------|---------------|--------------|
| 2  | 1/6 | 0.7686       | 0.1029          | 0.1221       | 0.1055          | 0.4936 | 0.4721         | 0.4935        |
| 2  | 0.25 | 0.9324b     | 1.0462          | 0.1138       | 0.1193          | 0.5897 | 0.5819         | 0.6133        |
| 2  | 1.00 | 3a         | 3.1619          | 0.1619       | 0.1987          | 0.1641 | 1.246          | 1.1737        |
| 6  | 0.25 | 6.995b     | 7.3910          | 0.3960       | 0.4574          | 0.3924 | 2.014          | 2.0112        |
| 6  | 1/1.89  | 7.6001c   | 8.0211          | 0.4210       | 0.4732          | 0.4054 | 2.156          | 2.1372        |
| 6  | 0.42168 | 10.37d    | 10.8204         | 0.4504       | 0.5305          | 0.4524 | 2.6784         | 2.6604        |

| Δ  | -  | -            | -               | -             | -               | -        | -               | -             |
|----|----|---------------|-----------------|---------------|-----------------|---------|-----------------|---------------|
| 2.46 | - | 2.46          | -               | -             | -               | -        | -               | -             |
| 2.44 | 0.84 | 2.44          | 0.84            | -             | -               | -        | -               | -             |

* All the reference results are discussed in Refs. 38,39.
† $E_{xc}^{ref} = E_x^{2D-EXX} + E_{xc}^{I}$

a-Analytic solution by Taut from Ref. 40.
b-Cl data from Ref. 41.
c-Diffusion QMC data from Ref. 42.
d-Variational QMC data from Ref. 43.

VI. CONCLUSIONS

We have developed three semi-local exchange energy functionals based on the density matrix expansion and a correlation energy functional based on the modification of LDA correlation functional by one of the newly constructed exchange energy functional. The non-local effects are added to the functionals by modifying the Fermi momentum. The Fermi momentum is modified by using reduced density gradient and kinetic energy density. The parameters introduced in the exchange and correlation energy functionals are set by some restrictions and comparing the result with the exact values. In principle, a new set of parameters can be proposed, taking different 2D systems which will give the better result for that system. All the functionals are tested and analyzed for quantum dot systems with a different number of confined electrons. The newly proposed exchange energy functionals are believed to achieve encouraging performance in two-dimensional many-electron calculations. The proposed correlation energy functional excellently improves over the LDA correlation energy functional when applied to quantum dots.

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