Exchange and correlation energy functionals for two-dimensional open-shell systems

E. Räsänen\textsuperscript{a}, S. Pittalis\textsuperscript{b,c}
\textsuperscript{a}Nanoscience Center, Department of Physics, University of Jyväskylä, FI-40014 Jyväskylä, Finland
\textsuperscript{b}Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany
\textsuperscript{c}European Theoretical Spectroscopy Facility (ETSF)

Abstract

We consider density functionals for exchange and correlation energies in two-dimensional systems. The functionals are constructed by making use of exact constraints for the angular averages of the corresponding exchange and correlation holes, respectively, and assuming proportionality between their characteristic sizes. The electron current and spin are explicitly taken into account, so that numerical results show that in finite systems the proposed functionals outperform the standard two-dimensional local spin-density approximation, still performing well also in the important limit of the homogeneous two-dimensional electron gas.

Key words: density-functional theory, electron gas, quantum dot
PACS: 73.21.La, 71.15.Mb

1. Introduction

Practical success of density-functional theory (DFT) depends on finding good approximations for exchange and correlation energy functionals. So far, most density functionals have been developed in three dimensions (3D) with a view to studying the properties of atoms, molecules, and solids. Apart from very recent progress \cite{2, 3, 4, 5, 6, 7, 8}, such efforts for two-dimensional (2D) systems have been relatively scarce beyond the commonly-used 2D local spin-density approximation (LSDA). However, the rapidly increasing theoretical, experimental, and technological interest in 2D structures such as semiconductor layers and surfaces, quantum Hall systems, graphene, and various types of quantum dots, calls for further developments.

Here we consider expressions of density functionals for exchange and correlation energies of 2D systems. These approximations are derived \cite{2, 3} by modeling the angular average of the exchange and correlation holes and using first-principle arguments along the lines of Refs. \cite{2, 10}. The resulting spin- and current-dependent density functionals are then combined to obtain a new approximation for the exchange plus correlation energy beyond the LSDA. Numerical tests, performed on systems for which accurate reference data is available, show that our functionals are superior to the LSDA. Moreover, we find a good agreement with the exact result for the homogeneous 2D electron gas (2DEG).

2. Basic formalism

Within the Kohn-Sham (KS) method of spin-DFT, \cite{11} the ground state energy and spin densities \( \rho_{\uparrow}(r) \) and \( \rho_{\downarrow}(r) \) of a system of \( N = N_{\uparrow} + N_{\downarrow} \) interacting electrons are determined. The formalism is general in terms of dimensionality and the form of interaction. However, here we focus on Coulomb-interacting particles in 2D. The total energy, which is minimized to obtain the ground-state energy, is written as a functional of the spin densities (in Hartree atomic units)

\[
E_{\text{KS}}[\rho_{\uparrow}, \rho_{\downarrow}] = E_{\text{H}}[\rho_{\uparrow}, \rho_{\downarrow}] + E_{\text{xc}}[\rho_{\uparrow}, \rho_{\downarrow}] + \sum_{\sigma=\uparrow,\downarrow} \int d\mathbf{r} \, v_{\sigma}(\mathbf{r}) \rho_{\sigma}(\mathbf{r}),
\]

where \( E_{\text{H}}[\rho_{\uparrow}, \rho_{\downarrow}] \) is the KS kinetic energy functional, \( v_{\sigma}(\mathbf{r}) \) is the external (local) scalar potential acting upon the interacting system, \( E_{\text{H}}[\rho] \) is the classical electrostatic or Hartree energy of the total charge density \( \rho(\mathbf{r}) = \rho_{\uparrow}(\mathbf{r}) + \rho_{\downarrow}(\mathbf{r}) \), and \( E_{\text{xc}}[\rho_{\uparrow}, \rho_{\downarrow}] \) is the exchange-correlation energy functional. The latter can be further decomposed into the exchange and correlation parts as

\[
E_{\text{xc}}[\rho_{\uparrow}, \rho_{\downarrow}] = E_{\text{x}}[\rho_{\uparrow}, \rho_{\downarrow}] + E_{\text{c}}[\rho_{\uparrow}, \rho_{\downarrow}],
\]

This is the central quantity which is formally well defined and exact, but needs to be approximated in practical applications of DFT.

3. Modeling the exchange

The exchange-energy functional can be expressed as

\[
E_{\text{x}}[\rho_{\uparrow}, \rho_{\downarrow}] = \frac{1}{2} \sum_{\sigma} \int d\mathbf{r} \rho_{\sigma}(\mathbf{r}) U_{\sigma}^{\uparrow}(\mathbf{r}),
\]

where

\[
U_{\sigma}^{\uparrow}(\mathbf{r}) = 2\pi \int_{0}^{\infty} ds \, \bar{h}_{\sigma}^{\uparrow}(\mathbf{r}, s)
\]

Email address: erasanen@jyu.fi (E. Räsänen)
is the exchange-hole potential, and
\[
\bar{h}^{\sigma}_{x}(r, s) = \frac{1}{2\pi} \int_0^{2\pi} d\phi h^{\sigma}_{x}(r, r + s)
\] (5)
is the 2D cylindrical average of the exchange-hole function

\[
h^{\sigma}_{x}(r_1, r_2) = \frac{|\sum_{k, \sigma} \psi_{k, \sigma}(r_1)\psi_{k, \sigma}(r_2)|^2}{\rho_{\sigma}(r_1)}
\] (6)
where the sum in the numerator is the one-body spin-density matrix of the ground state \{Slater determinant constructed from the KS orbitals, \(\psi_{k, \sigma}\). As the basis of our exchange model [2], we consider

\[
\bar{h}^{\sigma}_{x}(a, b; s) = \frac{1}{a} \exp \left[-a \left( b + s^2 \right) \right] I_0(2a \sqrt{bs})
\] (7)
where \(I_0(x)\) is the zeroth order modified Bessel function of the first kind (note that \(I_0(0) = 1\)). This function provides a non-positive exchange hole and satisfies the normalization

\[
\int ds \bar{h}^{\sigma}_{x}(r, s) = -1.
\] (8)
In Eq. (7), \(a\) and \(b\) are position-dependent functions, which are chosen to locally reproduce the short-range behavior of the exact exchange hole. Furthermore, application of the above model to the Taylor expansion leads to relations \(a = \pi \rho_{\sigma, e0}\) and \(b = y/a\), where \(y := ab\) is the solution of

\[
(y - 1) \exp(y) = \frac{C^\sigma}{\pi \rho^\sigma},
\] (9)
where

\[
C^\sigma = \frac{1}{2} \left[ \nabla^2 \rho_{\sigma} - 2 \tau_{\sigma} + \frac{1}{2} \frac{(\nabla \rho_{\sigma})^2}{\rho_{\sigma}} + 2 \frac{\partial \rho_{\sigma}}{\rho_{\sigma}} \right]
\] (10)
is the so-called curvature of the exchange hole, \(\tau_{\sigma}\) is (twice) the spin-dependent kinetic-energy density, and \(\nabla \rho_{\sigma}\) is the spin-dependent paramagnetic current density. Both \(\tau_{\sigma}\) and \(\nabla \rho_{\sigma}\) depend explicitly on the KS orbitals. Thus the expression in Eq. (10) has an implicit dependence on the spin-densities \(\rho_{\sigma}\).

Note that the model introduced in Eq. (7) is exact in the case of the ground-state single-electron wave function of a 2D harmonic oscillator. Furthermore, application of the above model to the 2DEG yields the exchange energy per particle as

\[
\epsilon_{x}[r_{\sigma}, \rho_{\sigma}] = -\frac{\sqrt{\pi}}{4 \sqrt{2} r_{\sigma}} \left[ (1 + \xi)^{3/2} - (1 - \xi)^{3/2} \right],
\] (11)
where \(r_{\sigma} = 1/\sqrt{\rho_{\sigma}}\) and \(\xi = (\rho_1 - \rho_1)/\rho\) is the spin polarization. This energy is about 4.4% smaller than the exact one [13].

Interestingly, Eq. (11) may be seen as a correction of the LSDA exchange functional suitable for dealing with finite few-electron systems.

### 4. Modeling the correlation

The correlation-energy functional can be expressed as follows

\[
E_{c}[ho_{\sigma}, \rho_{\sigma}] = E_{c}^{\uparrow\uparrow}[ho_{\sigma}, \rho_{\sigma}] + E_{c}^{\downarrow\downarrow}[ho_{\sigma}, \rho_{\sigma}] + 2E_{c}^{\uparrow\downarrow}[ho_{\sigma}, \rho_{\sigma}]
\] (12)
where we have used \(E_{c}^{\uparrow\uparrow}[ho_{\sigma}, \rho_{\sigma}] = E_{c}^{\uparrow\uparrow}[ho_{\sigma}, \rho_{\sigma}]\)

and

\[
E_{c}^{\sigma\sigma'}[ho_{\sigma}, \rho_{\sigma}] = \pi \int dr \rho_{\sigma}(r) \int ds \bar{h}^{\sigma\sigma'}_{x}(r, s)
\] (13)

with \(\bar{h}^{\sigma\sigma'}_{x}(r, s)\) being the cylindrical average of the correlation-hole function, \(\bar{h}^{\sigma\sigma'}_{x}(r_1, r_2)\), computed in the same way as \(\bar{h}^{\sigma}_{x}(r, s)\). We remind that the correlation-hole functions can be obtained by the coupling constant integration

\[
h^{\sigma\sigma'}_{x}(r_1, r_2) = \int_0^1 d\lambda h^{\sigma\sigma'}_{x\lambda}(r_1, r_2),
\] (14)
where \(h^{\sigma\sigma'}_{x\lambda}(r_1, r_2) = h^{\sigma\sigma'}_{x\lambda}(r_1, r_2) - h^{\sigma\sigma'}_{x\lambda}(r_1, r_2)\delta_{\sigma\sigma'}\). \{\(\sigma\sigma'\) = \{\(\uparrow\uparrow\), \(\uparrow\downarrow\), \(\downarrow\uparrow\), \(\downarrow\downarrow\)\}\}. and the parameter \(\lambda\) is \([0, 1]\) is the electronic coupling strength [1]. Now, we model [3] the cylindrical averages of the \(\lambda\)-dependent correlation-hole functions as

\[
h^{\sigma\sigma'}_{x\lambda}(r_1, r_2) = \frac{2}{3} |D_{\sigma}(r)| \left[ \frac{\rho_{\sigma}}{1 + 2 \lambda r^{\sigma\sigma'}_{\lambda}(r)} \right] F(\gamma_{\sigma\sigma'}(r)),
\] (15)
and

\[
h^{\sigma\sigma'}_{x\lambda}(r, s) = 2 |D_{\sigma}(r)| \left[ \frac{\rho_{\sigma}}{1 + 2 \lambda r^{\sigma\sigma'}_{\lambda}(r)} \right] F(\gamma_{\sigma\sigma'}(r)).
\] (16)
for the same spin and opposite spin case, respectively (note that, \(\delta\) indicates an opposite value w.r.t. \(\sigma\)). In Eq. (15),

\[
|D_{\sigma}(r)| := 1/|\nabla\rho_{\sigma} - 4\rho_{\sigma}|
\] (17)
is satisfied by setting \(\gamma_{\sigma\sigma'} = 3 \sqrt{\rho_{\sigma}/(4 \rho_{\sigma})}\) and \(\gamma_{\sigma\sigma'} = \sqrt{\rho_{\sigma}/(2 \rho_{\sigma})}\). Functions \(\rho_{\sigma}\) and \(\rho_{\sigma}\) are defined as the characteristic sizes of the correlation holes, for which \(h^{\sigma\sigma'}_{x\lambda}(r, \rho_{\sigma}) = 0\), \(h^{\sigma\sigma'}_{x\lambda}(r, \rho_{\sigma}) = 0\). As for the 3D case, [10] we set \(\rho_{\sigma} := 2\epsilon_{\sigma\sigma} U_{\sigma}^0 |U_{\sigma}^0|^{-1}\) and \(\rho_{\sigma} := 2\epsilon_{\sigma\sigma} U_{\sigma}^0 |U_{\sigma}^0|^{-1}\) where \(U_{\sigma}^0\) is the exchange-hole potential calculated in the previous section, and \(\epsilon_{\sigma\sigma}\) and \(\epsilon_{\sigma\sigma}\) are constants to be determined (see below). In this way, the characteristic size of the correlation hole is proportional to the characteristic size of the corresponding exchange hole. This is suggested by a picture in which electrons are correlated as long as their interaction is not screened by their respective exchange holes. A more elaborate model may require to consider \(\epsilon_{\sigma\sigma}\) as a density functional, which is, however, beyond the scope of this work.

The approximations given above are \textit{implicit} density functionals due to the \textit{explicit} dependence on the KS orbitals appearing in the expressions for \(\tau\) and \(J_{\sigma\sigma}\). Therefore, these functionals can be classified as current-dependent meta-generalized-gradient approximations, and we expect them to be ideally suited to deal with a large class of spin-polarized and/or current-carrying ground-states of two-dimensional systems.
5. Applications

We test the present 2D functionals for a set of N-electron parabolic quantum dots described by a Hamiltonian,

\[ H = \sum_{i=1}^{N} \left( -\frac{1}{2} \nabla_i^2 + \frac{1}{2} \omega^2 r_i^2 \right) + \sum_{\langle i<j \rangle} \left| \frac{1}{r_i - r_j} \right|, \]

where \( \omega = 1/4 \) is the confinement strength. The exchange energies obtained using the approximation given in Sec. 3 are compared with the exact-exchange (EXX) results within the Krieger-Li-Iafrate approximation [12]. Then, the correlation energies obtained according to Sec. 4 are compared to the reference results \( E_{\text{tot}}^\text{ref} - E_{\text{tot}}^{\text{EXX}} \), where \( E_{\text{tot}}^\text{ref} \) is the numerically accurate total energy of a configuration-interaction calculation reported in Ref. [14]. The KS orbitals from self-consistent EXX calculations – performed using the octopus DFT code [13] – are used as the input for the functionals.

In Table 1 we show the results for fully spin-polarized quantum dots with different \( N = 2 \ldots 6 \), spin \( S = N/2 \), and total angular momentum (z component) \( L \). Note that different values of \( L \) correspond to different paramagnetic current densities. Overall, we find excellent performance in both the exchange and correlation functionals. A significant improvement over the LSDA as seen in the mean errors \( \Delta \) on the last row of Table 1. It should be noted that the error of the LSDA correlation is huge. This error is typically partially compensated by an error of an opposite sign in the LSDA exchange. However, our functionals are able to reproduce both the exchange and correlation energies with a good accuracy.

In the correlation functional we have used a fixed value \( c_{\text{corr}} = 1.25 \) as the prefactor in the characteristic size of the correlation hole (see the end of Sec. 4). We point out that although this value is fundamentally a post-hoc choice, the variations in optimal \( c_{\text{corr}} \) (and \( c_{\text{exch}} \)) for different systems are typically rather small [3]. This becomes obvious also within the 2DEG below, where results for various densities, corresponding to amounts of correlation, are shown with the same fixed \( c_{\text{corr}} \).

Finally we turn our attention from finite systems to the 2DEG. Figure 1 shows the exchange (left) and correlation energies (right) per particle in the 2DEG as a function of the density parameter \( r_s = 1/\sqrt{\pi n} \) against exact results available from analytic [15] and quantum Monte Carlo calculations [18], respectively. As pointed out in Sec. 3 in this limit our exchange functional deviates consistently 4% from the exact (LSDA) result. Also for the correlation the agreement is very good up to strong correlations – it should be noted that in quantum dots, for example, typical densities correspond roughly to \( 1 \lesssim r_s \lesssim 5 \). In the correlation functional we have consistently used fixed values \( c_{\text{corr}} = 1.25 \), i.e., the same value as with the quantum dots above, and \( c_{\text{exch}} = 0.75 \).

6. Conclusions

We have presented two-dimensional density functionals for exchange and correlation energies. The functionals have been derived by modeling the angular averages of the corresponding exchange and correlation holes along first-principle arguments and by enforcing known exact constraints. Tests of our functionals for few-electron open-shell quantum dots and the homogeneous two-dimensional electron gas show very good performance. Hence, we may propose an accurate alternative to the commonly used local spin-density approximation for electronic-structure calculations in two dimensions.

This work was supported by the Academy of Finland, Magnus Ehrnrooth Foundation, Deutsche Forschungsgemeinschaft, and the EU’s Sixth Framework Programme through the ETSF e-13.

References

[1] See, e.g., R. M. Dreizler and E. K. U. Gross, Density functional theory (Springer, Berlin, 1990).
[2] S. Pittalis, E. Räisänen, N. Helbig, and E. K. U. Gross, Phys. Rev. B 76 (2007) 235314.
[3] S. Pittalis, E. Räisänen, C. R. Proetto, and E. K. U. Gross, Phys. Rev. B 79 (2009) 085316.
[4] E. Räisänen, S. Pittalis, C. R. Proetto, and E. K. U. Gross, Phys. Rev. B 79 (2009) 121305(R).
[5] S. Pittalis, E. Räisänen, and M. A. L. Marques, Phys. Rev. B 78 (2008) 195322.
[6] S. Pittalis, E. Räisänen, J. G. Vilhena, and M. A. L. Marques, Phys. Rev. A 79 (2009) 012503.
[7] S. Pittalis and E. Räisänen, Phys. Rev. B 80 (2009) 165112.
[8] S. Pittalis, E. Räisänen, and E. K. U. Gross, Phys. Rev. A 80 (2009) 032515.
[9] A. D. Becke and M. R. Roussel, Phys. Rev. A 39, 3761 (1989).
[10] A. D. Becke, J. Chem. Phys. 88 (1988) 1053; A. D. Becke, Can. J. Chem. 74 (1996) 995.
[11] U. von Barth and L. Hedin, J. Phys. C 5 (1972) 1629.
[12] J. B. Krieger, Y. Li, and G. J. Iafrate, Phys. Rev. A 46 (1992) 5453.
[13] M. A. L. Marques, A. Castro, G. F. Bertsch and A. Rubio, Comp. Phys. Comm. 151 (2003) 60; A. Castro, H. Appel, M. Oliveira, C. A. Rozzi, X. Andrade, F. Lorenzen, M. A. L. Marques, E. K. U. Gross, and A. Rubio, Phys. Stat. Sol. (b) 243 (2006) 2465.
Table 1: Exchange and correlation energies for fully spin-polarized quantum dots. The last row shows the mean percentage error $\Delta$ of our functional and the LSDA for both exchange and correlation, respectively.

| $N$ | $L$ | $-E_{\text{model}}^{\text{ex}}$ | $-E_{\text{ref}}^{\text{ex}}$ | $-E_{\text{model}}^{\text{cx}}$ | $-E_{\text{ref}}^{\text{cx}}$ | $\Delta$ |
|-----|-----|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-----|
| 2   | 1   | 0.626                         | 0.631                         | 0.583                         | 0.010                         | 0.0108 | 0.0346 | 2.3% |
| 3   | 0   | 1.021                         | 1.038                         | 0.963                         | 0.023                         | 0.0212 | 0.0540 | 4.7% |
| 4   | 2   | 1.374                         | 1.428                         | 1.332                         | 0.034                         | 0.0375 | 0.0731 | 6.9% |
| 5   | 0   | 1.816                         | 1.864                         | 1.745                         | 0.048                         | 0.0517 | 0.0931 | 133% |
| 6   | 0   | 2.213                         | 2.267                         | 2.126                         | 0.064                         | 0.0636 | 0.1125 | 133% |

$\Delta$ = $\frac{\text{abs}(\text{model} - \text{ref})}{\text{ref}} \times 100$

[14] M. Rontani, C. Cavazzoni, D. Bellucci, and G. Goldoni, J. Chem. Phys. 124 (2006) 124102.
[15] A. K. Rajagopal and J. C. Kimball, Phys. Rev. B 15 (1977) 2819.
[16] C. Attaccalite, S. Moroni, P. Gori-Giorgi, and G. B. Bachelet, Phys. Rev. Lett. 88 (2002) 256601.