

**Alternative separation of exchange and correlation in density-functional theory**

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It has recently been shown that local values of the conventional exchange energy per particle cannot be described by an analytic expansion in the density variation. Yet, it is known that the total exchange-correlation (XC) energy per particle does not show any corresponding nonanalyticity. Indeed, the nonanalyticity is here shown to be an effect of the separation into conventional exchange and correlation. We construct an alternative separation in which the exchange part is made well behaved by screening its long-ranged contributions, and the correlation part is adjusted accordingly. This alternative separation is as valid as the conventional one, and introduces no new approximations to the total XC energy. We demonstrate functional development based on this approach by creating and deploying a local-density-approximation-type XC functional. Hence, this work includes both the theory and the practical calculations needed to provide a starting point for an alternative approach towards improved approximations of the total XC energy.

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Kohn-Sham (KS) density-functional theory<sup>1</sup> (DFT) is a successful scheme for electron energy calculations. The long term goal is chemical accuracy for chemical and material properties without the need of a careful problem analysis prior to the calculation. This would enable computerized optimization of chemicals, materials, and compounds to an extent that is not possible today. The accuracy of the KS-DFT scheme is limited by the approximation for the exchange-correlation (XC) energy functional. Development towards improved generic XC functionals has been slow compared to the progress of algorithms and computer hardware. Almost 40 years of research have passed since the local-density approximation (LDA) was suggested. Even if LDA is not generally accurate enough for applications in molecular systems, it is still in use in calculations of properties of certain metallic and semiconductor systems. This is not for being “faster” than other functionals, but because it still often delivers the most accurate results in such applications. Progress made in functional developments have either (i) sacrificed generality, defining functionals working good only for certain systems but decreasing accuracy for others, or (ii) improved the separate exchange and correlation parts of the XC energy without much improvement of the combined quantity. It is fair to conclude that current approaches have not yet taken us a significant step forward towards generic XC functionals. The present work identifies an inherent problem with the current approach and supplies the starting point of an alternative path for approximations of the total XC energy.

KS-DFT is based on a total electron energy functional  $E_e[n(\mathbf{r})]$  that is minimized by the true ground-state electron density  $n(\mathbf{r})$  of a system. The minimization is done by self-consistently refining an effective potential  $v_{\text{eff}}(\mathbf{r})$  of a system of noninteracting electrons, to make that system’s electron orbitals  $\psi_\nu(\mathbf{r})$  give  $n(\mathbf{r})$  as their (noninteracting) electron density. The XC energy functional  $E_{xc}[n(\mathbf{r})]$  is the part of  $E_e$  that remains when all more easily treated parts have been accounted for (i.e., the potential energy, the kinetic energy of

a system of noninteracting electrons, and the internal potential energy of a classical repulsive gas).  $E_{xc}$  is decomposed into a local quantity by defining the XC energy per particle  $\epsilon_{xc}$  from the requirement:

$$E_{xc}[n(\mathbf{r})] = \int n(\mathbf{r}) \epsilon_{xc}(\mathbf{r}; [n]) d\mathbf{r}. \quad (1)$$

An approximation for  $\epsilon_{xc}(\mathbf{r}; [n])$  is referred to as a “DFT functional.” It is common to further separate this quantity as  $\epsilon_{xc} = \epsilon_x + \epsilon_c$  where the separation is defined from the requirement that  $\epsilon_x$  should give the exchange energy  $E_x$  when integrated in Eq. (1). The quantity  $E_x$  can be implicitly defined through the conventional choice<sup>2</sup> of the exchange energy per particle  $\epsilon_x^{\text{irxh}}$ . In rydberg atomic units (a.u.), for a spin-unpolarized system

$$\epsilon_x^{\text{irxh}} = -2 \int \frac{1}{n(\mathbf{r}) |\mathbf{r} - \mathbf{r}'|} \left| \sum_\nu \psi_\nu(\mathbf{r}) \psi_\nu^*(\mathbf{r}') \right|^2 d\mathbf{r}'. \quad (2)$$

Recent work<sup>3</sup> shows that local values of  $\epsilon_x^{\text{irxh}}$  cannot be described by an analytic expansion in the density variation. Yet, it is known that the total XC energy density does not show any corresponding nonanalyticity. Hence, this is not a problem inherent to the underlying physics, but artificially created. In the following we present a solution to this problem by separating the XC energy in an alternative way and show this solution to hold for systems of generic effective potentials. Finally the ideas are placed in the context of functional development through the construction of a LDA-type functional. We perform benchmark calculations using an implementation of this functional. Taken together, these parts provide a complete starting point for an alternative approach towards XC functionals that avoids the deficiency of the traditional separation in exchange and correlation.

If the long-range Coulomb potential is responsible for the nonanalytical behavior of  $\epsilon_x^{\text{irxh}}$ , then the insertion of a traditional screening factor of Yukawa type,  $e^{-k_Y|r-\mathbf{r}'|}$ , into the integration of Eq. (2), should give a well-behaved quantity  $\epsilon_{(x+Y)}^{\text{irxh}}$ . This introduces  $k_Y$  as the Yukawa wave vector, which effectively is an inverse screening length for the Coulomb potential that may be dependent on  $\mathbf{r}$ . A corresponding correlationlike term  $\epsilon_{(c-Y)}^{\text{irxh}}$  is defined by the relation  $\epsilon_{(x+Y)}^{\text{irxh}} + \epsilon_{(c-Y)}^{\text{irxh}} = \epsilon_{xc}^{\text{irxh}}$ . This can be seen as moving a term from correlation to exchange,

$$\epsilon_Y^{\text{irxh}} = 2 \int \frac{1 - e^{-k_Y|r-\mathbf{r}'|}}{n(\mathbf{r})|\mathbf{r}-\mathbf{r}'|} \left| \sum_{\nu} \psi_{\nu}(\mathbf{r}) \psi_{\nu}^*(\mathbf{r}') \right|^2 d\mathbf{r}', \quad (3)$$

$$\epsilon_{(x+Y)}^{\text{irxh}} = \epsilon_x^{\text{irxh}} + \epsilon_Y^{\text{irxh}}, \quad \epsilon_{(c-Y)}^{\text{irxh}} = \epsilon_c^{\text{irxh}} - \epsilon_Y^{\text{irxh}} \quad (4)$$

and is an alternative way of partitioning  $\epsilon_{xc}$  without introducing any new approximations. Screened exchange has been used previously. In the Hartree-Fock scheme, exchange is known to have singularities originating from the separation in exchange and correlation. Screening the Hartree-Fock exchange has been shown to remove these singularities.<sup>4</sup> In DFT, several recent functionals and schemes have been constructed based on screened exchange expressions.<sup>5</sup> However, in these works the long-range part has either been thrown away or handled with another approximative scheme. The present approach is fundamentally different in that the screening of the exchange is compensated for by redefining correlation to keep the total  $\epsilon_{xc}^{\text{irxh}}$  constant. This alternative separation provides as good a starting point for functional development as the commonly used separation into unscreened exchange,  $\epsilon_x^{\text{irxh}}$ , and conventional correlation,  $\epsilon_c^{\text{irxh}}$ .

In Eq. (3) the limit  $k_Y \rightarrow 0$  approaches the conventional partitioning between exchange and correlation (i.e.,  $\epsilon_Y \rightarrow 0$ ). In the following we use a scaled  $k_Y$ ,  $\bar{k}_Y = k_Y/p_F$  with  $p_F = \sqrt{\mu - v_{\text{eff}}(\mathbf{r})}$ , where  $\mu$  is the chemical potential. Our aim is now to show that this alternative separation removes the found problem for exchange, while not introducing any change in the combined XC energy.

The term of lowest order in density variation of  $\epsilon_{(x+Y)}^{\text{irxh}}$ , i.e., LDA for the exchangelike term, is obtained from inserting the KS orbitals for the uniform electron gas into  $\epsilon_{(x+Y)}^{\text{irxh}}$  [Eq. (4)]. Substituting  $p_F \rightarrow [3\pi^2 n(\mathbf{r})]^{1/3}$  gives

$$\epsilon_{(x+Y)}^{\text{LDA}}(n(\mathbf{r})) = -[3/(2\pi)][3\pi^2 n(\mathbf{r})]^{1/3} I_0(\bar{k}_Y), \quad (5)$$

$$I_0(\bar{k}_Y) = [24 - 4\bar{k}_Y^2 - 32\bar{k}_Y \arctan(2/\bar{k}_Y) + \bar{k}_Y^2(12 + \bar{k}_Y^2) \ln(4/\bar{k}_Y^2 + 1)]/24. \quad (6)$$

For each  $\mathbf{r}$  point with density  $n(\mathbf{r})$ , the value of  $\epsilon_{(x+Y)}^{\text{irxh}}$  for a uniform electron gas with the same density is used. In the limit  $\bar{k}_Y \rightarrow 0$ , this approaches regular LDA exchange.

We numerically study  $\epsilon_{(x+Y)}^{\text{irxh}}$  using the Mathieu gas (MG) family of electron densities. These densities are parametrized by two dimensionless quantities  $\bar{\lambda}$  and  $\bar{p}$ , and are obtained from a noninteracting system of electrons moving in  $v_{\text{eff}}(\mathbf{r})$

$= \mu \bar{\lambda} [1 - \cos(2\sqrt{\mu \bar{p} z})]$ . The limit of slowly varying densities is found as  $\bar{\lambda}, \bar{p} \rightarrow 0$ . To simplify the analysis of numerical data in this two-dimensional limit, the parameters are combined in a nontrivial way into a new parameter<sup>6</sup>  $\alpha$ , with the slowly varying limit  $1/\alpha \rightarrow 0$ . The MG family of densities was also used when demonstrating the nonanalytical behavior of  $\epsilon_x^{\text{irxh}}$  in Ref. 3. We use the computer program in that reference, modified for Yukawa screening, to calculate  $\epsilon_{(x+Y)}^{\text{irxh}}$  for  $1/\alpha \rightarrow 0$  in specific  $\mathbf{r}$  points, for several specific  $\bar{k}_Y$ . The results are investigated based on the expansion of  $\epsilon_{(x+Y)}^{\text{irxh}}$  in density variation,

$$\epsilon_{(x+Y)}^{\text{irxh}} = \epsilon_{(x+Y)}^{\text{LDA}} [1 + a_{(x+Y)}^{\text{irxh}} s^2 + b_{(x+Y)}^{\text{irxh}} q + \dots], \quad (7)$$

$$s = \frac{|\nabla n(\mathbf{r})|}{2(3\pi^2)^{1/3} n^{4/3}(\mathbf{r})}, \quad q = \frac{\nabla^2 n(\mathbf{r})}{4(3\pi^2)^{2/3} n^{5/3}(\mathbf{r})}, \quad (8)$$

Figure 1 confirms this expansion for  $\bar{k}_Y > 0$  with the dimensionless scalars  $a_{(x+Y)}^{\text{irxh}}$  and  $b_{(x+Y)}^{\text{irxh}}$  being functions of the value of  $\bar{k}_Y$ . The behavior is consistent for all investigated values of  $\bar{\lambda}/\bar{p}^2$ , i.e., convergence is independent of the path through the two-dimensional MG parameter space. However, for  $\bar{k}_Y = 0$  the expansion of Eq. (7) is not confirmed (this was a major point of Ref. 3).

A derivation of the convergence points for curves with  $\bar{k}_Y > 0$  in Fig. 1 for systems of generic  $v_{\text{eff}}(\mathbf{r})$  follows. We start from an expansion of the exchange energy per particle in  $p_F$  from Refs. 7 and 8 with all spatial integrations done,

$$\epsilon_{(x+Y)}^{\text{irxh}} = -\frac{1}{n} \left( \frac{p_F^4}{2\pi^3} I_0 + \frac{\nabla^2 p_F^2}{18\pi^3} I_B + \frac{(\nabla p_F^2)^2}{24\pi^3 p_F^2} I_C + \dots \right), \quad (9)$$

$$I_B = [40 + 12\bar{k}_Y^2 - 6\bar{k}_Y(4 + \bar{k}_Y^2) \arctan(2/\bar{k}_Y) - (4 + \bar{k}_Y^2) \ln(4/\bar{k}_Y^2 + 1)] / (16 + 4\bar{k}_Y^2), \quad (10)$$

$$I_C = [\bar{k}_Y(4 + \bar{k}_Y^2) \arctan(2/\bar{k}_Y) - 4 - 2\bar{k}_Y^2 - 2(\bar{k}_Y^2 - 4)/(\bar{k}_Y^2 + 4)] / (8 + 2\bar{k}_Y^2). \quad (11)$$

Using the expansion of the density in  $p_F$  from Ref. 8, Eq. (9) can be recast into the form of Eq. (7), with general coefficients as functions of  $\bar{k}_Y$ ,

$$a_{(x+Y)}^{\text{irxh}}(\bar{k}_Y) = \frac{8}{27} \left( \frac{3}{4} - \frac{1}{3} \frac{I_B}{I_0} + \frac{1}{2} \frac{I_C}{I_0} \right), \quad (12)$$

$$b_{(x+Y)}^{\text{irxh}}(\bar{k}_Y) = \frac{8}{27} \frac{I_B}{I_0} - \frac{4}{9}. \quad (13)$$

The values extracted from the numerical data from the MG family of densities (see Fig. 1) are in excellent agreement with these derived coefficients. This shows that our numerical data illustrate the behavior of a general system. When the generalized expansion approximation (GEA) gradient coefficient was established,<sup>8-10</sup> there was an order of limits prob-

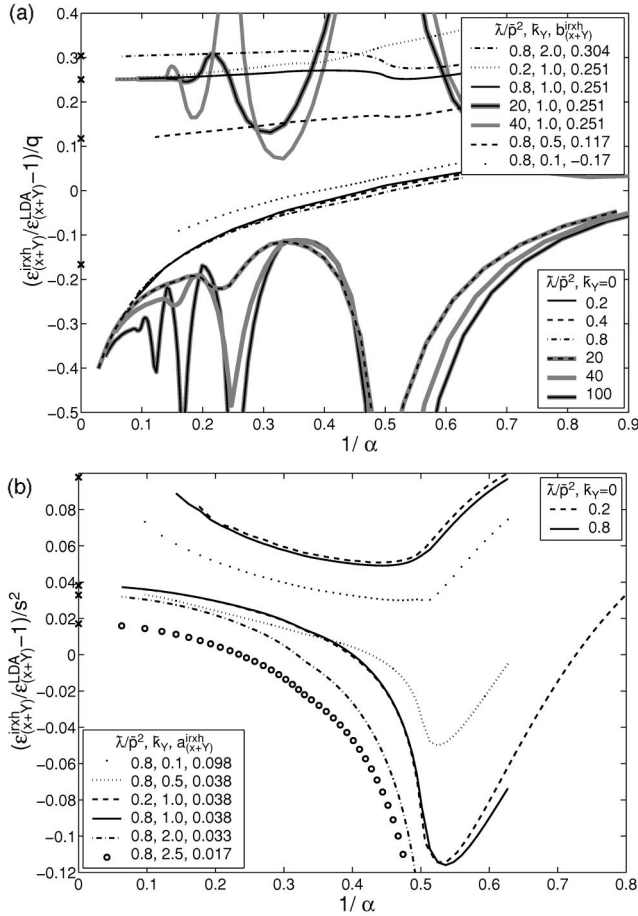


FIG. 1. Effective (a) Laplacian coefficient  $(\epsilon_{(x+Y)}^{\text{irxh}}/\epsilon_{(x+Y)}^{\text{LDA}} - 1)/q$ , (b) gradient coefficient  $(\epsilon_{(x+Y)}^{\text{irxh}}/\epsilon_{(x+Y)}^{\text{LDA}} - 1)/s^2$ , for space points  $\mathbf{r}$  where (a)  $s=0$  (density maxima; effective potential minima), (b)  $q$  is close to zero, for different values of  $\bar{\lambda}/\bar{p}^2$  and  $\bar{k}_Y$ . The quantities are expected to approach (a)  $b_{(x+Y)}^{\text{irxh}}$ , (b)  $a_{(x+Y)}^{\text{irxh}}$ , in Eq. (7) in the limit of slowly varying densities  $1/\alpha \rightarrow 0$ . All curves where  $\bar{k}_Y > 0$  show convergent trends towards values predicted by Eqs. (12) and (13) (shown in legend and marked on the y axes). The oscillating behavior was explained in Ref. 3, and is not important in this context. Due to involved numerics, explicit divergence for  $\bar{k}_Y = 0$  can only be demonstrated in (a), but the values in (b) are consistent with an expected divergence towards  $+\infty$ . The similarity of convergence values for  $\bar{k}_Y = 0.5$  and  $1.0$  in (b) is coincidental.

lem between the limit  $\bar{k}_Y \rightarrow 0$  and the limit of slowly varying electron densities. In contrast, our calculations show that an expansion involving both the gradient and the Laplacian, Eq. (7), cannot describe the conventional exchange energy per particle regardless of the order of the limits. The solution is instead to use the alternative separation given by Eq. (4), keeping  $k_Y > 0$ .

The alternative separation needs to be substantiated to be useful. In the following we show how to create a LDA-type functional by approximating both the exchange-like and correlation-like terms. The reasons this derivation is important are that (i) it shows how functional development using the alternative separation use very similar methods to conventional functional development; (ii) when deployed, its nu-

merical accuracy shows that the alternative separation indeed provides an alternative approach to conventional functional development; (iii) it provides a starting point for further refined approximations of the  $\epsilon_{(x+Y)}^{\text{irxh}}$  and  $\epsilon_{(c-Y)}^{\text{irxh}}$  parts.

The expression for  $\epsilon_{(x+Y)}^{\text{LDA}}$  [Eq. (5)] has one free parameter  $\bar{k}_Y$  for which a natural choice is a scaled Thomas-Fermi wave vector  $\bar{k}^{\text{TF}} = k^{\text{TF}}/p_F = \sqrt{4r_s}/(\pi\gamma)$ , where  $\gamma = (9\pi/4)^{1/3}$  and  $r_s = \gamma/[3\pi^2 n(\mathbf{r})]^{1/3}$  (a.u.) is a  $\mathbf{r}$  dependent density parameter. A generalized choice is

$$\bar{k}_Y^a = \sqrt{a r_s}. \quad (14)$$

The Yukawa exchange-like term, Eq. (5), is expanded around  $r_s = 0$  and  $\infty$ , giving

$$\epsilon_{(x+Y)}^{\text{LDA}} \xrightarrow{r_s \rightarrow 0} -\frac{3\gamma}{2\pi} \left( \frac{1}{r_s} - \frac{2\pi\sqrt{a}}{3} \frac{1}{\sqrt{r_s}} + a \left[ \ln 2 - \frac{1}{2} \ln a - \frac{1}{2} \ln r_s + \frac{1}{2} \right] \right), \quad (15)$$

$$\epsilon_{(x+Y)}^{\text{LDA}} \xrightarrow{r_s \rightarrow \infty} -\frac{3\gamma}{2\pi} \left( \frac{4}{9a} \frac{1}{r_s^2} - \frac{8}{15a^2} \frac{1}{r_s^3} \right). \quad (16)$$

The expansions for the total XC energy of a uniform electron gas are known:<sup>11-13</sup>

$$\epsilon_{xc}^{\text{unif}} \xrightarrow{r_s \rightarrow 0} -(3\gamma)/(2\pi r_s) + c_0 \ln r_s - c_1 + c_2 r_s \ln r_s, \quad (17)$$

$$\epsilon_{xc}^{\text{unif}} \xrightarrow{r_s \rightarrow \infty} -(3\gamma)/(2\pi r_s) - d_0/r_s + d_1/r_s^{3/2}, \quad (18)$$

where  $c_0 - c_4$ ,  $d_0$ , and  $d_1$  are scalars.<sup>14</sup> Setting  $a = c_0 4\pi/(3\gamma)$  makes the leading logarithmic term compatible with Eq. (15). It is now easy to produce a suitable expression to model  $\epsilon_{(c-Y)}^{\text{LDA}}$ ,

$$\epsilon_{(c-Y)}^{\text{LDA,1}} = \frac{b_1 \sqrt{r_s} + b_2}{r_s^{3/2} + b_3 r_s + b_4 \sqrt{r_s}}. \quad (19)$$

Of the four free parameters,  $b_1 - b_4$ , two are fixed by eliminating the  $1/\sqrt{r_s}$  in the low  $r_s$  limit (Eq. 15), and by rendering the total constant term equal to  $c_1$ . The remaining two parameters are determined by a least-squares fit, minimizing

$$\sum_{r_s} [ [\epsilon_{(x+Y)}^{\text{LDA}}(r_s) + \epsilon_{(c-Y)}^{\text{LDA}}(r_s) - \kappa(r_s)] / \Delta \kappa(r_s) ]^2, \quad (20)$$

where  $\kappa(r_s)$  and  $\Delta \kappa(r_s)$  are the Ceperley-Alder<sup>15</sup> (CA) data and errors, respectively. This gives Yukawa LDA1 (YLDA1), composed by Eqs. (5), (14), and (19) with parameters:  $a = 0.135718$ ,  $b_1 = -1.71478$ ,  $b_2 = -7.57697$ ,  $b_3 = 5.13452$ ,  $b_4 = 10.7168$ . In Table I it is compared with the CA data and other XC parametrizations currently in use.<sup>11</sup> In the fitting, YLDA1 uses one fitting parameter less than the other parametrizations but still performs at least as well as Perdew-Zunger correlation (PZ) and approximately as well as Vosko-Wilk-Nusair correlation (VWN).

TABLE I. (a) Correlation from original CA data (in mRy) and from different parametrizations of this data, compared to  $\epsilon_{xc} - \epsilon_x^{\text{irxh}}$  for the YLDA's. (b) Differences between the values in (a), and the CA data, scaled with the errors in the CA data. An absolute value  $\leq 1$  means that the parametrization is within the error bars of the CA data and can be considered exact.

(a)	$r_s$	CA	PZ	VWN	PW	YLDA1	YLDA2
	1	120	119.3	120.0	119.5	120.5	120.3
	2	90.2	90.18	89.57	89.52	89.70	90.05
	5	56.3	56.68	56.27	56.43	56.21	56.43
	10	37.22	37.137	37.089	37.145	37.044	37.104
	20	23.00	22.995	23.095	23.060	23.094	23.091
	50	11.40	11.332	11.407	11.385	11.421	11.377
	100	6.379	6.3429	6.3693	6.3820	6.3695	6.3829
(b)	$r_s$	PZ	VWN	PW	YLDA1	YLDA2	
	1	-0.31	0.47	-0.02	0.94	0.76	
	2	-0.07	-1.61	-1.73	-1.27	-0.40	
	5	3.48	-0.62	1.03	-1.18	1.01	
	10	-1.58	-2.54	-1.43	-3.44	-2.23	
	20	-0.11	3.24	2.06	3.20	3.08	
	50	-6.55	0.96	-1.21	2.36	-2.01	
	100	-7.15	-1.88	0.66	-1.83	0.84	

An improved YLDA is given by the additional requirements of an independent  $r_s \ln r_s$  term and a zero coefficient for  $\sqrt{r_s}$  in the small  $r_s$  limit. This is achieved through extending  $\bar{k}_Y$  in Eq. (14) to

$$\bar{k}_Y^{ab} = \sqrt{ar_s} + br_s^{3/2} \quad (21)$$

and adding two parameters to the  $\epsilon_{(c-Y)}^{\text{LDA}}$  part,

$$\epsilon_{(c-Y)}^{\text{LDA,2}} = \frac{e_1 r_s + e_2 \sqrt{r_s} + e_3}{r_s^2 + e_4 r_s^{3/2} + e_5 r_s + e_6 \sqrt{r_s}}. \quad (22)$$

Hence four parameters are fitted to the CA data. This gives YLDA2 (Ref. 16) with  $a=0.135718$ ,  $b=0.0426055$ ,  $e_1 = -1.81942$ ,  $e_2 = 2.74122$ ,  $e_3 = -14.4288$ ,  $e_4 = 0.537230$ ,  $e_5 = 1.28184$ ,  $e_6 = 20.4080$ . The performance of YLDA2 is comparable with the Perdew-Wang correlation (PW) (Table I).

To make sure that there is no major difference between the YLDA's and the other LDA XC functionals we have calculated the surface energy of jellium surfaces using self-consistent densities obtained by the PW correlation. Ranging over surface systems with constant bulk  $r_s = 2, 2.07, 2.30, 2.66, 3, 3.28, 4, 5$ , and  $6$ , we find no systematic differences. They all differ from each other in the order of  $0.1\%$ , with a total error in the order of a few percent.<sup>17</sup> Furthermore, self-consistent calculations for bulk silicon<sup>18</sup> give a lattice constant of  $5.38 \text{ \AA}$ , and a bulk modulus between  $95.2$  and  $95.6 \text{ GPa}$ , regardless of parameterization; i.e., PZ, VWN, PW, YLDA1, YLDA2 give essentially equal values.

In this paper we have (i) established that the lack of analytical behavior in the slowly varying limit of  $\epsilon_x^{\text{irxh}}$  in the MG model is caused by the long rangedness of the Coulomb potential; (ii) shown that this is a general artifact of the conventional definition of  $\epsilon_x^{\text{irxh}}$ , and is not restricted to limits taken through MG densities; (iii) shown that an analytical behavior can be obtained by using a nonconventional separation of exchange and correlation within  $\epsilon_{xc}$ ; (iv) derived and implemented a LDA-type functional based on this alternative separation. This LDA-type functional provides a starting point for further approximate functionals.

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<sup>6</sup>The definition is  $\alpha = (\mu - \epsilon_{\eta_1}) / (\epsilon_{\eta_2} - \epsilon_{\eta_1}) + |\eta_1|$ , where, if  $\mu$  is inside a  $z$ -dimension energy band,  $\epsilon_{\eta_1}$  is the lowest energy in this band. If  $\mu$  is not inside an energy band,  $\epsilon_{\eta_1}$  is the lowest energy in the band which contains the  $z$ -dimension energy state with highest energy  $\leq \mu$ . Furthermore,  $\epsilon_{\eta_2}$  is the lowest possible

energy of all  $z$ -dimension energy states within bands that only contain energies  $> \mu$ . By construction  $\eta_1$  and  $\eta_2$  are integer. Details on this parameter are found in Ref. 3.

<sup>7</sup>The exchange energy per particle expanded in  $p_F$  is derived in Ref. 8. The derivation uses an implicit Yukawa screening, but takes the limit  $\bar{k}_Y \rightarrow 0$  in the end result. Clarifications are found in Ref. 10.

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<sup>14</sup>Since none of the correlation functionals in use today (Ref. 11) use the proper value of  $c_1$  [found as late as 1992 (Ref. 13)], we here give:  $c_0 = 2(1 - \ln 2)/\pi^2$ ,  $c_1 = [22 + 32 \ln 2 - 24 \ln^2 2 + 9\zeta(3)]/6\pi^2 - 1/2 - (\ln 2)/3 - c_0[\ln(4/(\pi\gamma)) - 1/2 + \langle R \rangle]$ , where  $\zeta(x)$  is the Riemann Zeta function,  $\langle R \rangle = \int_{-\infty}^{\infty} R^2(u) \ln R(u) du / \int_{-\infty}^{\infty} R^2(u) du$  and  $R(u) = 1 - u \arctan(1/u)$ . Numerical values to six relevant digits are  $c_0 = 0.0621814$ , and  $c_1 = 0.0938406$  (a.u.).

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<sup>16</sup>The  $c_2$  coefficient of YLDA2 is 0.00151 (a.u.), which is closer to the exact value than PW (Ref. 11).

<sup>17</sup>S. Kurth, J.P. Perdew, and P. Blaha, Int. J. Quantum Chem. **75**, 889 (1999).

<sup>18</sup>For the Si calculations we used the software SOCORRO, developed at Sandia National Laboratories. Norm-conserving Don Hamann LDA pseudopotential was used; D.R. Hamann, Phys. Rev. B **40**, 2980 (1989).