

Alternative separation of exchange and correlation in density-functional theory

R. Armiento*

*Department of Physics, Royal Institute of Technology,
AlbaNova University Center, SE-106 91 Stockholm, Sweden*

A. E. Mattsson†

*Surface and Interface Science Department MS 1415,
Sandia National Laboratories Albuquerque, NM 87185-1415*

(Dated: February 28, 2003)

Slow progress towards increasingly accurate exchange-correlation functionals in density functional theory is holding back calculational methods based more on automatization and less on user 'intuition'. Work aiming for improved functional accuracy, in particular the subsystem functional approach, is hindered by a recent discovery [R. Armiento, A. E. Mattsson, Phys. Rev. B, **66** 165117 (2002)]: local values of the conventional exchange energy per particle cannot be described by an analytic expansion in the density variation in the limit of slowly varying electron densities. In this paper, we show the non-analyticity to be caused by the long-rangedness of the Coulomb potential. The exchange energy per particle is made well-behaved by screening its long-ranged part, and the correlation part is adjusted to get an alternative separation of the exchange-correlation energy. We demonstrate functional development using this approach by constructing an LDA-type functional.

PACS numbers: 71.15.Mb, 31.15.Ew

Kohn-Sham (KS) density-functional theory (DFT) [1] is a successful scheme for electron energy calculations. A long term goal is chemical accuracy for chemical and material properties without the need of an intelligent choice of exchange-correlation (XC) functional. Fulfillment of this goal will have impact on much of physics and chemistry. However, progress towards generic functionals of higher accuracy have been slow compared to the progress of algorithms and computer hardware. The present work lifts an obstacle holding back such development, in particular the subsystem functional approach [2].

KS-DFT is based on a total 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 non-interacting electrons, to make that system's electron orbitals $\psi_\nu(\mathbf{r})$ give $n(\mathbf{r})$ as their (non-interacting) electron density. A crucial part of this scheme is the XC energy functional $E_{xc}[n(\mathbf{r})]$ which is the usually small but difficult 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 non-interacting electrons, and the internal potential energy of a classical repulsive gas).

It is common to reduce E_{xc} by subtracting the well-defined Kohn-Sham Hartree-Fock (KSHF) exchange energy E_x (definition given below), leaving the correlation energy E_c . This separation is only weakly related to the underlying physics, and one of the main points of this paper is that it introduces an artificial non-analyticity.

E_{xc} is decomposed into a local quantity by defining the XC energy per particle ϵ_{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 commonly referred to as a 'DFT functional'. The XC energy can be separated on this local level, $\epsilon_{xc} = \epsilon_x + \epsilon_c$, where ϵ_x must give the correct total E_x in the exchange part of Eq. (1). E_x is implicitly defined via one choice [3] of ϵ_x , ϵ_x^{irxh} (based on the inverse radius of the exchange hole [4] (irxh), created from results of Refs. [5]). In rydberg atomic units (a.u.), for a spin unpolarized system

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

In recent work [2] we discussed partitioning the integration in Eq. (1) into a sum of integrals over different regional parts of a system, applying different functionals in each subsystem, i.e., 'subsystem functionals'. The aim of this approach is a better approximation of the total XC energy, as each subsystem functional can be tailored for a specific class of systems. However, calculations for the Mathieu Gas (MG) model system have shown that ϵ_x^{irxh} in the limit of slowly varying densities cannot be described by an analytic power expansion. This is an obstacle for attempts to approximate Eq. (2) in the limit of slowly varying densities without using the freedom of transformations given by the implicit definition of Eq. (1) (e.g., subsystem functionals).

In this paper we present and motivate an alternative separation of the XC energy. We demonstrate how this eliminates the non-analyticity in the MG model system. The results are shown to hold for systems of generic effective potentials. Finally the ideas are placed into the context of functional development through the construction of an LDA-type functional. We perform benchmark calculations using an implementation of this functional.

If the long-range Coulomb potential is responsible for the non-analytical behavior of ϵ_x^{irxh} , then the insertion of a traditional screening factor of Yukawa-type, $e^{-k_Y|\mathbf{r}-\mathbf{r}'|}$, 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 correlation-like term $\epsilon_{(c-Y)}^{\text{irxh}}$ is defined by the relation $\epsilon_{(x+Y)}^{\text{irxh}} + \epsilon_{(c-Y)}^{\text{irxh}} = \epsilon_{xc}^{\text{irxh}}$. A way of viewing this is that a term is moved from correlation to exchange,

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

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

This describes an alternative way of partitioning ϵ_{xc} without introducing any new approximations. Since the conventional correlation term screens the long range behavior of the exchange, this redistribution is well-founded. In the limit $k_Y \rightarrow 0$ it 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 μ is the chemical potential.

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

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

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

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 parameterized by two dimensionless quantities, $\bar{\lambda}$ and \bar{p} , and are obtained from a non-interacting system of electrons moving in $v_{\text{eff}}(\mathbf{r}) = \mu\bar{\lambda}[1 - \cos(2\sqrt{\bar{\mu}\bar{p}}z)]$. 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 non-trivial way into a new parameter α [6], with the slowly varying limit, $1/\alpha \rightarrow 0$. The MG family of densities was also used when demonstrating the non-analytical behavior of ϵ_x^{irxh} in Ref. 2. 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,

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

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

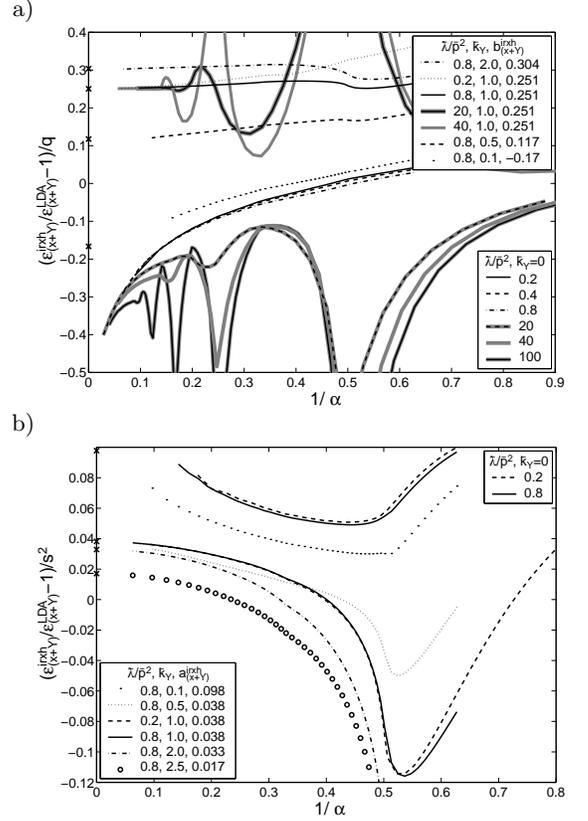


FIG. 1: Effective (a) Laplacian coefficient $(\epsilon_{(x+Y)}^{\text{irxh}}/\epsilon_{(x+Y)}^{\text{LDA}} - 1)/q$, (b) gradient coefficient $(\epsilon_{(x+Y)}^{\text{irxh}}/\epsilon_{(x+Y)}^{\text{LDA}} - 1)/s^2$, for space points \mathbf{r} where (a) $s = 0$ (density maxima; effective potential minima) (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 Eq. (12) and (13) (shown in legend and marked on the y axes). The oscillating behavior was explained in Ref. 2, 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 $k_Y = 0.5$ and 1.0 in (b) is coincidental.

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. 2).

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 [7, 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 [8], Eq. (9) can be recasted into the form of Eq. (7). This gives the general coefficients as functions of \bar{k}_Y ,

$$a_{(x+Y)}^{\text{irxh}}(\bar{k}_Y) = 16 \left(\frac{1}{72} - \frac{1}{162} \frac{I_B}{I_0} + \frac{1}{108} \frac{I_C}{I_0} \right), \quad (12)$$

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

There is an excellent agreement between these derived coefficients and the values extracted from the numerical data from the MG family of densities. This indicates that our numerical data illustrate the behavior of a general system. When the GEA gradient coefficient was established [8–10], there was an order of limits problem 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 $k_Y > 0$.

To further substantiate these ideas, an LDA-type functional is derived in the following. 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 an \mathbf{r} dependent density parameter. A generalized choice is

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

The Yukawa exchange-like term, Eq. (5), is expanded around $r_s = 0$ and ∞ , 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 [11–13]:

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

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

where c_0 – c_4 , d_0 , and d_1 are scalars [15]. 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 to 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

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

where $\kappa(r_s)$ and $\Delta\kappa(r_s)$ are the Ceperley-Alder (CA) [14] data and errors respectively. This gives 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 to the CA data and other XC parameterizations currently in use. In the fitting, YLDA1 uses one fitting parameter less than the other parameterizations but still performs at least as well as PZ and approximately as well as VWN.

The expansion of YLDA1 for small r_s is now

$$\epsilon_{xc}^{\text{YLDA1}} \xrightarrow{r_s \rightarrow 0} -\frac{3\gamma}{2\pi} \frac{1}{r_s} + c_0 \ln r_s - c_1 - 0.0098291 \sqrt{r_s} + r_s (-0.00540532 + 0.000351631 \ln r_s). \quad (21)$$

Since the $r_s \ln r_s$ coefficient is set by the value of a (as $\epsilon_{(c-Y)}^{\text{irxh}}$ does not contain any logarithmic terms), this term is not used in a fitting procedure. Instead the $\sqrt{r_s}$ term is used to mimic the additional influence of this term in the low r_s limit. An improved YLDA is given by the additional requirements of an independent $r_s \ln r_s$ term, and a zero coefficient for $\sqrt{r_s}$. This is achieved through extending \bar{k}_Y in Eq. (14) to

$$\bar{k}_Y^{ab} = \sqrt{ar_s} + br_s^{3/2} \quad (22)$$

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

$$\epsilon_{(c-Y)}^{\text{LDA},2} = \frac{e_1 r_s + e_2 \sqrt{r_s} + e_3}{r_s^2 + e_4 r_s^{3/2} + e_5 r_s + e_6 \sqrt{r_s}}. \quad (23)$$

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

To make sure that there is no major difference between the YLDAs and the other parameterizations of the CA data 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

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

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

in the order of 0.1%, with a total error in the order of a few percent [17]. Furthermore, self-consistent calculations for bulk silicon [18] give a lattice constant of 5.38 Å, and a bulk modulus between 95.2 and 95.6 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 ϵ_x^{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 ϵ_x^{irxh} , and is not restricted to limits taken through MG densities; iii) shown that an analytical behavior can be obtained by using a non-conventional separation of exchange and correlation within ϵ_{xc} ; iv) derived and implemented an LDA-type functional based on this alternative separation. This LDA-type functional provides a starting point for further approximate functionals within schemes where the lack of analytical behavior in the slowly varying limit provides an obstacle, such as the subsystem functional approach.

We thank Walter Kohn for inspiring discussions. This work was partly funded by the Göran Gustafsson Foundation and the project ATOMICS at the Swedish research council SSF. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract No. DE-AC04-94AL85000.

* Electronic address: rar@theophys.kth.se

† Electronic address: aematts@sandia.gov

- [1] P. Hohenberg and W. Kohn, *Physical Review* **136**, B864 (1964); W. Kohn and L. J. Sham, *Physical Review* **140**, A1133 (1964).
[2] R. Armiento and A. E. Mattsson, *Physical Review B* **66**, 165117 (2002).
[3] Implications of Eq. (1) allowing more than one definition of ϵ_x was thoroughly discussed in Ref. 2
[4] W. Kohn and A. E. Mattsson, *Physical Review Letters* **81**, 3487 (1998).
[5] J. Harris and R. O. Jones, *J. Phys. F* **4**, 1170 (1974); D. C. Langreth and J. P. Perdew, *Solid State Communications* **17**, 1425 (1975); O. Gunnarsson and B. I. Lundqvist, *Physical Review B* **13**, 4274 (1976).

- [6] The definition is $\alpha = (\mu - \epsilon_{\eta_1}) / (\epsilon_{\eta_2} - \epsilon_{\eta_1}) + |\eta_1|$, where, if μ is inside a z -dimension energy band, ϵ_{η_1} is the lowest energy in this band. If μ is not inside an energy band, ϵ_{η_1} is the lowest energy in the band which contains the z -dimension energy state with highest energy $\leq \mu$. Furthermore, ϵ_{η_2} is the lowest possible energy of all z -dimension energy states within bands that only contain energies $> \mu$. By construction η_1 and η_2 are integer. Details on this parameter are found in Ref. 2
[7] 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 $k_Y \rightarrow 0$ in the end result. Clarifications are found in Ref. [10].
[8] E. K. U. Gross and R. M. Dreizler, *Z. Phys. A* **302**, 103 (1981).
[9] L. J. Sham, *Computational Methods in Band Structure* (Plenum Press, New York, 1971), p. 458; P. R. Antoniewicz and L. Kleinman, *Physical Review B* **31**, 6779 (1985); L. Kleinman and S. Lee, *Physical Review B* **37**, 4634 (1988).
[10] J. P. Perdew and Y. Wang, *Mathematics Applied to Science* (Academic Press, Boston, 1988), pp. 187–209.
[11] J. P. Perdew and Y. Wang, *Physical Review B* **45**, 13244 (1992); J. P. Perdew and A. Zunger, *Physical Review B* **23**, 5048 (1981); S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* **58**, 1200 (1980).
[12] M. Gell-Mann and K. A. Brueckner, *Physical Review* **106**, 364 (1957).
[13] G. G. Hoffman, *Physical Review B* **45**, 8730 (1992).
[14] D. M. Ceperley and B. J. Alder, *Physical Review Letters* **45**, 566 (1980).
[15] Since none of the correlation functionals in use today [11] use the proper value of c_1 (found as late as 1992 [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.).
[16] The c_2 coefficient of YLDA2 is 0.00151 (a.u.), which is closer to the exact value than PW [11].
[17] S. Kurth, J. P. Perdew, and P. Blaha, *International Journal of Quantum Chemistry* **75**, 889 (1999).
[18] For the Si calculations we used the software SOCORRO, developed at Sandia National Laboratories. For pseudopotentials, Don Hamann's norm-conserving pseudopotential code was used; D. R. Hamann, *Phys. Rev. B* **40**, 2980 (1989).