New nonlocal exchange-energy functional from a kinetic-energy-density Padé-approximant model

Andrés Cedillo, Juvencio Robles, and José L. Gázquez

Departamento de Química, División de Ciencias Básicas e Ingeniería, Universidad Autónoma Metropolitana–Iztapalapa,
Apartado Postal 55-534, Iztapalapa, 09340 Distrito Federal, Mexico
(Received 1 March 1988)

A completely new nonlocal exchange-energy functional in terms of a $P_{4,3}(x)$ Padé approximant is derived from its kinetic-energy-functional counterpart. The new formula exhibits correct asymptotic behavior for large and small density gradients. It can be written in the form of an exchange functional recently proposed by Becke. Furthermore, our exchange functional yields very good exchange energies when evaluated with Hartree-Fock–quality densities. Its functional derivative does not diverge for atomic systems, allowing one to obtain fairly good variational densities and exchange energies.

I. INTRODUCTION

The exact, nonrelativistic energy functional for an atomic system in terms of its ground-state electron density $\rho(\mathbf{r})$ can be written as[1]

$$E[\rho] = T[\rho] + V_{ne}[\rho] + J[\rho] + K[\rho] , \tag{1}$$

where

$$V_{ne}[\rho] = -Z \int \frac{\rho(\mathbf{r})}{|\mathbf{r}|} d\mathbf{r} , \tag{2}$$

$$J[\rho] = \tfrac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} \, d\mathbf{r}' , \tag{3}$$

$T[\rho]$ is the exact kinetic-energy functional, and $K[\rho]$ is the exact exchange-energy functional. Both contain correlation effects and unfortunately are unknown. They can be formally written in terms of kinetic-energy density $t(\rho)$ and exchange-energy density $k(\rho)$ as

$$T[\rho] = \int t(\rho) d\mathbf{r} , \tag{4}$$

$$K[\rho] = \int k(\rho) d\mathbf{r} . \tag{5}$$

Traditionally, people have approximated both $T[\rho]$ and $K[\rho]$ by gradient expansions[2-7] and many other different ways,[8-16] but until recently[17-19] the common denominator has been that $T[\rho]$ is treated independently from $K[\rho]$. In this article, developing a suggestion by Ghosh, Parr, and Lee[17,18] (GPL), we propose that $K[\rho]$ is a functional of $t(\rho)$,

$$K[\rho] = K[\rho, t(\rho)] . \tag{6}$$

From here on our treatment will be explicitly spin polarized. GPL have shown that a Gaussian *Ansatz* for the spherical average of the first-order density matrix allows one to write, at the Hartree-Fock (HF) level,

$$K[\rho] = -\pi \sum_{\sigma} \int \rho_{\sigma}^2 \beta_{\sigma}(\rho_{\sigma}) d\mathbf{r} , \tag{7}$$

where

$$\rho = \sum_{\sigma=\alpha,\beta} \rho_{\sigma}$$

and

$$\beta_{\sigma}(\rho_{\sigma}) = \frac{3\rho_{\sigma}(\mathbf{r})}{2t_{\sigma}(\rho_{\sigma})} . \tag{8}$$

Thus

$$K[\rho_{\sigma}, t_{\sigma}(\rho_{\sigma})] = -\frac{3\pi}{2} \sum_{\sigma} \int \frac{\rho_{\sigma}(\mathbf{r})^3}{t_{\sigma}(\rho_{\sigma})} d\mathbf{r} . \tag{9}$$

Therefore, given Eq. (9), one would hope that a good model for $t(\rho)$ could be mapped into a good model of $K[\rho]$. The different models for $K[\rho]$ that one obtains should show the correct asymptotic behaviors. These are discussed in Sec. II.

We will show that a Padé-approximant model for the kinetic-energy density[12] with correct asymptotic limits is mapped through this procedure into a new Padé-approximant model for the exchange-energy density. The latter shows correct asymptotic behavior for large and small density gradients. The functional yields excellent exchange energies when evaluated with HF-quality densities[20] and its functional derivative does not diverge, allowing one to obtain very good variational densities and exchange energies.

II. SMALL- AND LARGE-GRADIENT BEHAVIOR OF THE KINETIC- AND EXCHANGE-ENERGY DENSITY FUNCTIONALS

A. Kinetic-energy functional

The treatment will be spin polarized, but for the sake of simplicity, from here on we will omit the σ subindices and ρ will symbolize either ρ_{α} or ρ_{β}. The traditional approach to $T[\rho]$ is through the gradient expansion[2,5]

$$T[\rho] = \sum_{n=0}^{\infty} T_{2n} = \int d\mathbf{r} \sum_{n=0}^{\infty} t_{2n}(\rho) , \tag{10}$$

where

$$t_0(\rho) = \tfrac{3}{10}(6\pi^2)^{2/3}\rho^{5/3} \tag{11}$$

is the Thomas-Fermi (homogeneous-gas) term and

$$t_2(\rho) = \frac{1}{9}t_W(\rho) = \frac{1}{72}\frac{|\nabla\rho|^2}{\rho} \tag{12}$$

is the first gradient correction, etc.

Approximate resummations and truncations of this infinite series have been proposed.[9,12] A lot of work has been done along these lines. The correct asymptotic behavior of $t(\rho)$ is known.[9,12] In the region where $\nabla\rho$ is small (far from the nucleus),

$$t(\rho) = t_0(\rho) = t_2(\rho) \quad \text{(small gradients)}, \tag{13}$$

and where $\nabla\rho$ is large (close to the nucleus),

$$t(\rho) = 9t_2(\rho) = t_W(\rho) = \frac{1}{8}\frac{|\nabla\rho|^2}{\rho}$$

$$\text{(large gradients)}. \tag{14}$$

Recently, DePristo and Kress[12] (DK) have given some arguments to propose a very interesting model for the resummation of $t(\rho)$ as a closed expression. This is a Padé approximant which exhibits the correct asymptotic limits given by Eqs. (13) and (14). This is

$$t(\rho) = t_0(\rho)P_{4,3}(x), \tag{15}$$

where the variable x is defined as

$$x = \frac{t_2(\rho)}{t_0(\rho)} = \frac{5}{108}\frac{1}{(6\pi^2)^{2/3}}\frac{|\nabla\rho|^2}{\rho^{8/3}}, \tag{16}$$

and

$$P_{4,3}(x) = \frac{1 + 0.95x + a_2x^2 + a_3x^3 + 9b_3x^4}{1 - 0.05x + b_2x^2 + b_3x^3}. \tag{17}$$

The parameters a_2, a_3, b_2, and b_3 are determined by fitting them to reproduce HF kinetic energies of He, Ne, Ar, and Kr. Results for atoms in the range $1 \le Z \le 36$ are quite good, especially for the first-row transition metals, when compared to truncated gradient expansions or to HF kinetic energies.

B. Exchange-energy functional

The gradient expansion for exchange energy is[6,7]

$$K[\rho] = \sum_{n=0}^{\infty} K_{2n} = \int d\mathbf{r}\sum_{n=0}^{\infty} k_{2n}(\rho), \tag{18}$$

where

$$k_0(\rho) = -\frac{3}{2}\left[\frac{3}{4\pi}\right]^{1/3}\rho^{4/3} \tag{19}$$

is the local-density approximation (LDA), or Dirac term, and

$$k_2(\rho) = -\frac{7}{432\pi(6\pi^2)^{1/3}}\frac{|\nabla\rho|^2}{\rho^{4/3}} \tag{20}$$

is the first gradient correction.[14]

Unfortunately, the functional derivative of K_2 diverges due to its incorrect large-gradient behavior.[7,14,16] This problem has prevented the so-called $X_{\alpha,\beta}$ method[7] from becoming more popular. In an attempt to mend the problem, Becke has recently proposed, first on empirical grounds[15] and later with some theoretical argumentation,[16] to model $k(\rho)$ as

$$k_B(\rho) = k_0(\rho) - \beta\frac{\dfrac{|\nabla\rho|^2}{\rho^{4/3}}}{\left[1 + \delta\dfrac{|\nabla\rho|^2}{\rho^{8/3}}\right]^\alpha}, \tag{21}$$

where β and δ are parameters determined by fitting k_B to reproduce HF exchange energies of He, Ne, Ar, Kr, and Xe. The exponent α can be either 1.0 or $\tfrac{4}{5}$, and any of these values gives very good results. The model does not possess the divergence problem of the gradient expansion, since the correct large-gradient behavior was imposed through its derivation. For small $\nabla\rho$,

$$k(\rho) \to k_0(\rho) + k_2(\rho) \quad \text{(small gradients)}. \tag{22}$$

Becke has suggested that an adequate large-gradient limit can be obtained by multiplying the short-range behavior of the exchange-hole density by an arbitrary damping function.[16] This leads, for large $\nabla\rho$, to

$$k(\rho) \to c\rho^{4/5}|\nabla\rho|^{2/5} \quad \text{(large gradients)}, \tag{23}$$

where the constant c depends on the particular choice for the arbitrary damping function. Actually, Becke's functional [Eq. (21)] is directly obtained from interpolation between the two extremes given by Eqs. (22) and (23).

In what follows, we provide a treatment that unifies the results of GPL, DK, and Becke. This is a new theoretical justification of Eq. (21), from a very different viewpoint.

III. DERIVATION OF A PADÉ-APPROXIMANT MODEL FOR THE EXCHANGE-ENERGY DENSITY FUNCTIONAL

If one directly substitutes Eq. (15) into Eq. (9), one obtains a new exchange-energy density functional in terms of a $P_{4,3}$ Padé approximant. It is

$$k(\rho) = \frac{10}{9}\frac{k_0(\rho)}{P_{4,3}(x)}, \tag{24}$$

$$k(\rho) = \frac{10}{9}k_0\left[\frac{1 - 0.05x + b_2x^2 + b_3x^3}{1 + 0.95x + a_2x^2 + a_3x^3 + 9b_3x^4}\right]. \tag{25}$$

Note that for the special case of $x = 0$, one obtains $k(\rho) = \tfrac{10}{9}k_0(\rho)$; this is the functional previously obtained by Ghosh and Parr.[17] These authors use it to explain why the α parameter in the $X\alpha$ method is so close to $(\tfrac{10}{9})(\tfrac{2}{3}) = 0.74$. Our Eq. (25) is a more general case.

Let us now examine the asymptotic behavior of the new functional. If one takes $x \to 0$,

$$k(\rho) \to \tfrac{10}{9}(k_0 - \tfrac{15}{7}k_2) \quad \text{(small gradients)}, \tag{26}$$

TABLE I. Exchange energies $(-K)$ from different models for noble-gas atoms, in atomic units. Values in parentheses are the relative errors as compared to HF values.

Model	He	Ne	Ar	Kr	Xe
HF[a]	1.026	12.11	30.19	93.89	179.2
BE[b] Eq. (21), $\alpha=\frac{4}{5}$	1.002(−0.02)	12.09(−0.00)	30.13(−0.00)	93.78(−0.00)	178.93(−0.00)
LDA[b] Eq. (19)	0.864(−0.16)	10.97(−0.09)	27.82(−0.08)	88.55(−0.06)	170.53(−0.05)
$(\frac{10}{9})$LDA[b] Eq. (19)$\times\frac{10}{9}$	0.960(−0.06)	12.19(+0.01)	30.91(+0.03)	98.39(+0.05)	189.48(+0.06)
K_0+K_2[b] Eqs. (18), (19), and (20)	0.948(−0.08)	11.49(−0.05)	28.81(−0.05)	90.66(−0.03)	173.83(−0.03)
CRG[b] Eq. (25)	0.879(−0.14)	11.51(−0.05)	29.49(−0.02)	95.25(+0.01)	184.53(+0.03)
CRGV[c] Eq. (25)	0.876(−0.15)	11.55(−0.05)	29.57(−0.02)	95.49(+0.02)	184.88(+0.03)

[a]Hartree-Fock values taken from Ref. 16.
[b]Evaluated with HF-quality densities (see Ref. 20).
[c]Evaluated with variational densities. These are obtained from solution of a Kohn-Sham–type calculation using the effective exchange potential given by Eq. (28) of the text.

which is of the form of Eq. (22), i.e., of a truncated gradient expansion, which we know is correct. On the other hand, if one takes $x \to \infty$,

$$k(\rho) \to -12\pi \frac{\rho^4}{|\nabla\rho|^2} \quad \text{(large gradients)} , \tag{27}$$

which is physically correct (it does not diverge). Thus our functional shows the correct asymptotic behavior for both small- and large-density gradients. Results for Eqs. (24) and (5) when evaluated with HF-quality densities[20] for noble gases are displayed in Table I, in the row labeled CRG, and compared against other current exchange-energy formulas. These values show that our model compares fairly well. While values for small-Z atoms are not very good, one can see that for those atoms in the range $10 \le Z \le 54$, our exchange energies are very competitive.

IV. SOLUTION OF THE EULER-LAGRANGE EQUATION

We have computed the functional derivative of Eq. (24) and solved numerically the resulting Euler-Lagrange equation. The result is

$$\frac{\delta K}{\delta\rho} = \frac{10}{9}\left[\frac{4}{3}\frac{C_0\rho^{1/3}}{P_{4,3}} - \frac{30}{7}C_2\frac{P'_{4,3}}{(P_{4,3})^2}\frac{\nabla^2\rho}{\rho^{4/3}} \right.$$
$$+ \frac{30}{7}C_1C_2\left[\frac{P''_{4,3}}{(P_{4,3})^2} - 2\frac{(P'_{4,3})^2}{(P_{4,3})^3} \right]$$
$$\left. \times \left[\frac{\nabla\rho\cdot\nabla(|\nabla\rho|^2)}{\rho^4} - \frac{8}{3}\frac{|\nabla\rho|^4}{\rho^5} \right] \right] , \tag{28}$$

where

$$C_0 = -\frac{3}{2}\left[\frac{3}{4\pi}\right]^{1/3} , \quad C_1 = \frac{5}{108}\frac{1}{(6\pi^2)^{2/3}} ,$$
$$C_2 = \frac{7}{432\pi(6\pi^2)^{1/3}} , \quad P'_{4,3} = \frac{\partial P_{4,3}}{\partial x} , \quad P''_{4,3} = \frac{\partial^2 P_{4,3}}{\partial x^2} .$$

Since as $r \to \infty$, $\rho(\mathbf{r}) \to e^{-\alpha r}$ (α being a given constant), one can show that for this asymptotic limit,

$$\frac{\delta K}{\delta\rho} \sim e^{-\alpha r} \quad \text{as } r \to \infty . \tag{29}$$

Thus our Euler-Lagrange equation does not diverge, as many other ones from different models of exchange do.

Variational densities obtained from the numerical solution of Eq. (28) in a Kohn-Sham–type calculation are tested by comparing some density momenta with their HF counterparts in Table II. They are also fed back into our functional, Eqs. (25) and (5), and the variational exchange energies obtained are compiled in Table I, in the row labeled CRGV. All these numbers are again quite good.

Furthermore, if one rearranges Eq. (25), one can rewrite the new functional as

$$k(\rho) = \frac{10}{9}\left[k_0(\rho) + \frac{\frac{15}{7}C_2\frac{|\nabla\rho|^2}{\rho^{4/3}} + \cdots}{1 + \frac{19}{7}\pi C_2\frac{|\nabla\rho|^2}{\rho^{8/3}} + \cdots} \right] . \tag{30}$$

This equation is of the same form as the functional pro-

TABLE II. Density momenta and total energy for noble-gas atoms in atomic units. Values in parentheses are the relative errors as compared to HF values.

	He	Ne	Ar	Kr	Xe
$\langle r^{-1} \rangle$					
HF[a]	3.37	31.11	69.72	182.80	317.90
Ours[b]	3.30(−0.02)	31.07(−0.00)	69.75(+0.00)	183.00(+0.00)	318.15(+0.00)
$\langle r \rangle$					
HF[a]	1.86	7.89	16.07	26.24	39.06
Ours[b]	1.92(+0.03)	7.95(+0.01)	16.00(−0.00)	26.07(−0.01)	38.74(−0.01)
$\langle r^2 \rangle$					
HF[a]	2.37	9.37	26.03	39.53	62.65
Ours[b]	2.58(+0.09)	9.67(+0.03)	25.92(−0.00)	38.99(−0.01)	61.32(−0.02)
$-E_{\text{tot}}$					
HF[c]	2.86	128.55	526.82	2752.05	7232.13
Ours[b]	2.75(−0.04)	128.08(−0.00)	526.31(−0.00)	2753.76(+0.00)	7238.0(+0.00)

[a]Hartree-Fock values taken from Ref. 21.
[b]Our numbers were obtained with variational densities (see footnote c, Table I).
[c]Hartree-Fock total energies from Ref. 22.

posed by Becke, Eq. (21). Therefore we have provided a different theoretical argumentation for that model.

Finally, the last two rows in Table II contain a comparison between the total energies obtained with a Kohn-Sham–type calculation using our $\delta K / \delta \rho$ as the effective exchange potential and variational densities versus HF total energies. The comparison is again very favorable.

V. CONCLUSIONS

Our work has provided a unified vision of the previously unrelated work of GPL,[17,18] Eqs. (7)–(9), the work of DK,[12] Eqs. (15)–(17), and that of Becke,[15,16] Eq. (21). Actually, we have given a new theoretical justification for Becke's model, through our Eq. (30).

One might be tempted to apply Eq. (9) to a number of different models of kinetic-energy density $t(\rho)$ to obtain the corresponding exchange models. However, some preliminary studies that we have done lead us to believe that this way of proceeding may not be universally valid. We have considered the following models.

(i) The truncated gradient expansion,[2−5] given by

$$t = t_0 + \tfrac{1}{9} t_W .$$ (31)

(ii) The truncated gradient expansion, including a Laplacian term, as recommended by Yang, Parr, and Lee,[11]

$$t = t_{\text{MP}} \eta(t_{\text{MP}}) + t_W [1 - \eta(t_{\text{MP}})] ,$$ (32)

with

$$t_{\text{MP}} = t_0 + \tfrac{1}{9} t_W + \frac{1}{12} \nabla^2 \rho ,$$ (33)

and $\eta(x)$ is the Heaviside function, which is inserted to impose positive kinetic-energy densities in all regions of

space, since the Laplacian term of Eq. (33) makes t_{MP} negative close to the nucleus. While Eqs. (32) and (4) provide excellent results for both local $t(\rho)$ and global $T[\rho]$, this cutoff unfortunately does not necessarily provide a continuous local $t(\rho)$.

(iii) The Gázquez and Robles functional,[10] given by

$$t = t_W + C(N) t_0 ,$$ (34)

where

$$C(N) = C_{\text{TF}} \left[1 - \frac{2}{N} \right] \left[1 - \frac{\delta}{N^{1/3}} \right] ,$$ (35)

with $C_{\text{TF}} = \tfrac{3}{10} (6\pi^2)^{2/3}$ and $\delta = 1.313$, a parameter adjusted to minimize the error relative to HF energies.

While all these models give fairly good results for atomic kinetic global energies, our preliminary studies show that their exchange counterparts are not good. However, in the present work the very attractive formulas of GPL have been successfully used to map a Padé-approximant model for the kinetic-energy density into its exchange-energy counterpart, giving a completely new formula for exchange.

We believe that the unsuccessful result with models (i) and (iii) is due to the fact that while they provide pretty good global kinetic energies, they are not good locally [they do not provide shell structure to $t(\rho)$], as discussed in Ref. 11. Furthermore, the GPL transcription must be regarded as a local rather than a global mapping. The function $\beta(\rho)$, as given by Eq. (8), is very sensitive from point to point, so that a bad local description of the kinetic energy will be carried over through Eq. (9) to give both bad local and global exchange energies.

For model (ii), we have a good local description of kinetic energy. It contains the Laplacian term which pro-

vides shell structure to $t(\rho)$.[11] However, this model does not provide good global exchange energies either. This may be due to the discontinuity of $t(\rho)$ that arises from the particular way of imposing positivity to the local kinetic energy via a Heaviside function.

On the other hand, as discussed previously, the Padé model for $t(\rho)$ behaves well locally. It is continuous and smooth in both the large- and small-density-gradient regions.[14] This flexibility of the Padé representation of $t(\rho)$ may be responsible for its successful mapping, as can be seen from the fact that it can be written in the same form of Becke's functional, thus providing support for both. Furthermore, our exchange functional yields very good exchange energies when evaluated with HF-quality densities[20] and its functional derivative does not diverge for atomic systems, allowing one to obtain fairly good variational densities and exchange energies.

ACKNOWLEDGMENTS

[1]See, for example, *Theory of the Inhomogeneous Electron Gas*, edited by S. Lundqvist and N. H. March (Plenum, New York, 1983); *Density Functional Theory*, Vol. 187 of *Lecture Notes in Physics*, edited by J. Keller and J. L. Gázquez, (Springer-Verlag, Berlin, 1983).

[2]C. H. Hodges, Can. J. Phys. **51**, 1428 (1973).

[3]W. P. Wang, R. G. Parr, D. R. Murphy, and G. Henderson, Chem. Phys. Lett. **43**, 409 (1976).

[4]D. R. Murphy and W. P. Wang, J. Chem. Phys. **72**, 429 (1980).

[5]D. R. Murphy, Phys. Rev. A **24**, 1682 (1981).

[6]W. Kohn and L. J. Sham, Phys. Rev. A **140**, 1133 (1965).

[7]F. Herman, J. P. Van Dyke, and I. B. Ortenburger, Phys. Rev. Lett. **22**, 807 (1969).

[8]J. L. Gázquez and J. Robles, J. Chem. Phys. **74**, 5927 (1981); M. Galván and J. L. Gázquez, *ibid.* **85**, 4203 (1986).

[9]P. K. Acharya, L. J. Bartolotti, S. B. Sears, and R. G. Parr, Proc. Natl. Acad. Sci. U.S.A. **77**, 6978 (1980).

[10]J. L. Gázquez and J. Robles, J. Chem. Phys. **76**, 1467 (1982).

[11]W. Yang, R. G. Parr, and C. Lee, Phys. Rev. A **34**, 4586 (1986).

[12]A. E. DePristo and J. D. Kress, Phys. Rev. A **35**, 438 (1987).

[13]A. Cedillo, E. Ortíz, J. L. Gázquez, and J. Robles, J. Chem. Phys. **85**, 7188 (1986).

[14]A. E. DePristo and J. D. Kress, J. Chem. Phys. **86**, 1425 (1987).

[15]A. D. Becke, J. Chem. Phys. **84**, 4524 (1986).

[16]A. D. Becke, J. Chem. Phys. **85**, 7184 (1986).

[17]S. K. Ghosh and R. G. Parr, Phys. Rev. A **34**, 785 (1986).

[18]C. Lee and R. G. Parr, Phys. Rev. A **35**, 2377 (1987).

[19]A. D. Becke, Int. J. Quantum Chem. **23**, 1915 (1983).

[20]Hartree-Fock–quality densities were obtained from a Kohn-Sham–type calculation, using the Gunnarsson-Lundqvist exchange potential [O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976)]. These densities are numerically quite similar to HF densities and may be used as an alternative to them, for testing purposes. [See A. Vela, A. Cedillo, and J. L. Gázquez, Int. J. Quant. Chem. **29**, 937 (1986).]

[21]C. F. Froese Fischer, *The Hartree-Fock Method for Atoms* (Wiley, New York, 1977).

[22]E. Clementi and C. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974).