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Study of the density-gradient expansion for the exchange energy

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It is well known that the density-gradient expansion of the Hartree-Fock exchange energy for the bare-Coulomb interaction contains divergent terms of order e^4 where e is the electronic charge. We argue that the exchange energy evaluated with Kohn-Sham orbitals (i.e., those derived from a local effective potential) is purely of order e^2 and therefore its gradient expansion is well defined. This density-gradient expansion, with the *a priori* coefficient of Sham, is shown to converge by comparison with numerically refined values for the exact exchange energy of a metal surface in the linear-potential model. As the electron density profile becomes more slowly varying, the relative error of the zeroth-order (local-density) term tends to zero. We present here the first demonstration that, in addition, the absolute error is increasingly canceled by the second-order (gradient) term. Like the gradient expansion for the kinetic energy but unlike the one for correlation, the gradient expansion for exchange gives useful results even for "physical" surface profiles. One- and many-electron atoms are also discussed. It is observed that, as the atomic number increases, the relative errors of the local-density and gradient-expansion approximations decrease in magnitude, but the gradient term corrects only a small fraction of the error of the local-density approximation. This is a consequence of the fact that the convergence condition $|\nabla n|/2k_F n \lesssim 1$ is increasingly satisfied as the atomic number increases but the second convergence condition $|\nabla^2 n|/2k_F|\nabla n| \ll 1$ is not so well satisfied.

I. INTRODUCTION

The total energy of a many-electron system and the separate energy components are functionals of the electron density $n(\vec{r})$.[1] When $n(\vec{r})$ varies slowly over space, i.e., when

$$|\nabla n|/2k_F n \lesssim 1 \tag{1}$$

and

$$|\nabla^2 n|/2k_F|\nabla n| \ll 1 \tag{2}$$

[where $k_F=(3\pi^2 n)^{1/3}$ is the local Fermi momentum], the kinetic and exchange components can each be approximated by an asymptotic expansion in the density gradients.[1] These expansions are "useful" in themselves for some problems in the sense that the error of the zeroth-order term is not too large and is substantially corrected by the second- or higher-order terms. Gradient expansions may also guide the construction of more accurate approximations to the density functionals. The gradient expansion for the kinetic energy unequivocally converges as the density becomes more slowly varying[2]; we will demonstrate here that the same is true for the exchange energy.

The exchange energy is defined[3] in density-functional theory[1,4] as

$$E_x[n]=-\frac{e^2}{2}\sum_\sigma\int d^3r\int d^3r'\frac{\left|\sum_\alpha \psi^*_{\alpha\sigma}(\vec{r})\psi_{\alpha\sigma}(\vec{r}\,')\right|^2}{|\vec{r}-\vec{r}\,'|}, \tag{3}$$

where

$$n(\vec{r})=\sum_\sigma n_\sigma(\vec{r})=\sum_\sigma\sum_\alpha|\psi_{\alpha\sigma}(\vec{r})|^2 \tag{4}$$

and

$$[-\tfrac{1}{2}\nabla^2+v_{\text{eff}}(\vec{r})]\psi_{\alpha\sigma}(\vec{r})=\epsilon_{\alpha\sigma}\psi_{\alpha\sigma}(\vec{r})\,. \tag{5}$$

Here σ (= ↑ or ↓) labels the spin, and α stands for the other quantum numbers. The local potential $v_{\text{eff}}(\vec{r})$ is a functional of $n(\vec{r})$ since it must be chosen to satisfy Eq. (4). For a given density $n(\vec{r})$, the local effective potential $v_{\text{eff}}(\vec{r})$ in Eq. (5) may be varied until its orbitals $\psi_{\alpha\sigma}(\vec{r})$ yield $n(\vec{r})$ via Eq. (4). The exchange energy of Eq. (3) is then obtained from these orbitals.

In the Kohn-Sham density-functional theory,[4] the total energy $E[n]$ is defined as the sum of several terms: the kinetic energy $T_s[n]$ of a system of noninteracting electrons with density $n(\vec{r})$, the electrostatic energy, and the exchange-correlation energy $E_{\text{xc}}[n]$, which for exchange alone becomes $E_x[n]$. The Kohn-Sham orbitals and density minimize $E[n]$, i.e.,

$$v_{\text{eff}}(\vec{r})=\delta(E[n]-T_s[n])/\delta n(\vec{r}) \ .$$

(The exact Kohn-Sham formalism discussed here must not be confused with the local-density approximation for $E_{\text{xc}}[n]$ and $v_{\text{eff}}(\vec{r})$.)

We now discuss the relationship between exchange-only Kohn-Sham and Hartree-Fock theories. The difference is only that in the Hartree-Fock theory the effective potential is allowed to be nonlocal, i.e., $v_{\text{eff}}(\vec{r},\vec{r}\,')$ replaces $v_{\text{eff}}(\vec{r})\delta(\vec{r}-\vec{r}\,')$. In Hartree-Fock theory, the Hartree-Fock orbitals are used in Eq. (3) instead of the Kohn-Sham orbitals. The difference between the Hartree-Fock and Kohn-Sham definitions of the exchange energy should be numerically negligible. For example, in jellium metal the two sets of orbitals are identical. The orbitals are also identical for the atoms H and He, where the Hartree-Fock effective potential is local. For larger atoms, Aashamar, Luke, and Talman[5] have constructed the proper exchange-only Kohn-Sham orbitals, i.e., they have found the *local* effective potential which minimizes the total energy in the atom. The resulting Kohn-Sham energy exceeds the absolute Hartree-Fock energy minimum (with a *nonlocal* effective potential) by less than fifty parts per million. (By the virial theorem, the exchange-only Kohn-Sham and Hartree-Fock kinetic energies are also similarly close.)

Despite the numerical similarity of the Kohn-Sham and Hartree-Fock exchange energies, the difference is important in principle since the gradient expansion exists only for the Kohn-Sham exchange energy and not for the Hartree-Fock[6] or other definitions.[7] The Hartree-Fock exchange energy contains terms of order e^2, e^4, etc., where e is the electron charge, and the e^4 term of its gradient expansion diverges due to the long range of the Coulomb interaction.[6] Examination of Eq. (3) shows that the e^4 and higher-order terms arise from the e dependence of the Hartree-Fock orbitals. Since the Kohn-Sham orbitals depend only on the electron density and not otherwise on e, the gradient expansion of the density-functional exchange energy is purely of order e^2 and therefore well defined. The fact that the gradient series for the Kohn-Sham exchange energy terminates at order e^2 is already implicit in the work of Langreth and Perdew.[8] This important fact is not widely known.

The form of the gradient expansion was proposed on dimensional grounds by Herman, Van Dyke, and Ortenburger[9]:

$$E_x[n]=-A_x\int d^3r\,n^{4/3}-C_x\int d^3r\,|\nabla n|^2/n^{4/3}+\cdots \ . \tag{6}$$

The terms not shown are of order ∇^4 and diverge in regions where the density tends to zero.[9,10] The first term of Eq. (6) is the local-density approximation (LDA) for exchange, which has the Gaspar[11]-Kohn-Sham[4] coefficient

$$A_x=(3/4\pi)(3\pi^2)^{1/3}=0.738\,56 \text{ a.u.}$$

(In our atomic units, $\hbar=m=e^2=1$.)

The gradient-expansion approximation (GEA) retains the first two terms of Eq. (6). The first *a priori* calculation of the coefficient

$$C_x=7\pi/144(3\pi^2)^{4/3}=0.001\,667 \text{ a.u.}$$

was reported by Sham.[12] (This coefficient has recently been rederived by the method of wave-vector analysis.[8]) Sham's coefficient is only $\frac{1}{3}$ to $\frac{1}{5}$ of the empirical coefficient proposed for atoms by Herman *et al.*[9,10] This fact and recent evidence for poor convergence of the gradient expansion for exchange and correlation in the metal-surface problem[8,13] prompt a closer examination of the gradient expansion for exchange.

The conditions (1) and (2), taken together, ought to be sufficient to ensure convergence of the gradient expansions for the kinetic and exchange energies. From Eq. (6) we can see that satisfaction of condition (1) guarantees that the gradient term will be *small* compared to the local term. The further satisfaction of condition (2) should then guarantee that the gradient term will correct nearly all of the error of the local term.

The gradient expansion can only be tested for systems in which the exact exchange energy is known, e.g., atoms or models of the metal surface.

II. METAL-SURFACE ENERGIES

In the jellium model of a metal surface, the potential $v_{\mathrm{eff}}(\vec{r})$ in Eq. (5) depends only on x, the distance from the edge of the semi-infinite uniform positive background filling the half space $x<0$. The exchange energies determined from Eq. (3) are thus exact within the density-functional definition of this property. The gradient expansion for the exchange contribution to the surface energy takes the form

$$\sigma_x[n]=\int_{-\infty}^{\infty} dx \left[-A_x n(n^{1/3}-\bar{n}^{1/3}) - C_x \left| \frac{dn}{dx} \right|^2 \Big/ n^{4/3} + \cdots \right] \tag{7}$$

for a neutral surface, where $\bar{n}=n(-\infty)=\bar{k}_F^3/3\pi^2$ is the bulk density.

The exact exchange energy has been evaluated for certain model potentials $v_{\mathrm{eff}}(x)$: the infinite square barrier,[3] the finite square barrier,[14–16] and the linear-potential models.[16] Observations about the accuracy of the LDA and GEA for the square-barrier models[15,16] are not conclusive evidence for convergence[17] because the surface density profiles cannot be made to vary arbitrarily slowly—the barrier height can never fall below the Fermi level. In contrast, the linear-potential model[18] is well suited to test the convergence of gradient expansions, and has already been employed to demonstrate convergence of the fourth-order expansion for the kinetic energy[2] and the zeroth-order (LDA) expansion for exchange.[16]

In the linear-potential model

$$v_{\mathrm{eff}}(x)=F(x-a)\theta(x-a)\ , \tag{8}$$

where the cutoff position a is determined by charge neutrality and the slope is

$$F=\tfrac{1}{2}\bar{k}_F^3/y_F\ . \tag{9}$$

The parameter y_F may vary from 0 (infinite square-barrier limit) to ∞ (the limit of arbitrarily slow density variations). The "physical" range found variationally for jellium[19] and real-metal[20] surfaces is $0.6 \lesssim y_F \lesssim 4.6$. Within this model, the reduced density $n(x)/\bar{n}$ is a universal function of $\bar{k}_F x$ and y_F, and the reduced surface exchange energy $\sigma_x/\bar{k}_F^3$ is a universal function of y_F.

The exact exchange energy of Eq. (3) for the linear-potential model has been evaluated by Ma and Sahni.[16] The calculation is demanding, and involves the Monte Carlo evaluation of integrals over as many as five dimensions. In order to test the gradient term in Eq. (7), which is relatively small for large y_F, we have had to refine the numerical calculation of the exact exchange energy to an accuracy of $\pm 1\%$.

Our results are displayed in Table I and Fig. 1. As others have shown,[3,14,21] the LDA is not very good and the GEA is even worse in the infinite

TABLE I. Surface exchange energy in the linear-potential model as a function of slope parameter y_F. The local-density (LDA) and second-order gradient-expansion (GEA) values are compared with the exact exchange energy. Numbers in parentheses show the numerical uncertainty in the exact exchange energy, e.g., for $y_F=10$ we have $\sigma_x^{\mathrm{exact}}/\bar{k}_F^3=(5.382 \pm 0.037)\times 10^{-3}$ a.u.

Parameter y_F	Surface exchange energy $\sigma_x(\bar{k}_F^3 \times 10^{-3}$ a.u.) LDA	GEA	Exact
0.0000	0.8939	−0.3157	0.576(1)
0.0001	0.894	−0.026	0.577(2)
0.001	0.894	0.059	0.579(2)
0.01	0.898	0.172	0.585(3)
0.1	0.934	0.349	0.605(5)
0.5	1.078	0.620	0.736(8)
1	1.252	0.860	0.899(10)
2	1.609	1.293	1.268(13)
3	1.999	1.737	1.703(18)
4	2.439	2.219	2.177(20)
6	3.438	3.274	3.274(33)
8	4.469	4.336	4.309(36)
10	5.513	5.400	5.382(37)

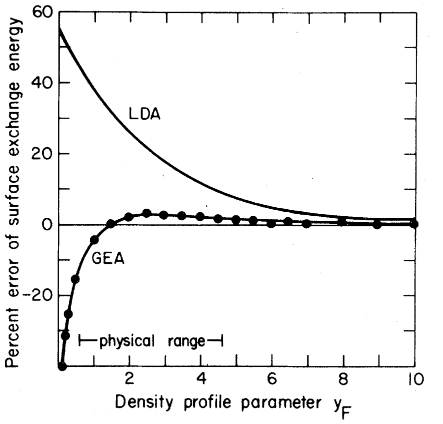

FIG. 1. Percent errors of the local-density (LDA) and gradient-expansion (GEA) approximations to the surface exchange energy as the density profile becomes more slowly varying (i.e., as y_F increases). For the LDA we have only shown a smooth curve, but for the GEA we have also plotted the actual calculated points which display a small scatter due to numerical uncertainties in the exact exchange energies.

barrier limit ($y_F = 0$). At $y_F = 1$, the LDA is still substantially in error, but this error is nicely corrected by the gradient term for all $y_F \gtrsim 1$. The relative error of the LDA gradually vanishes as $y_F \to \infty$.

We also display the "small parameters" of Eqs. (1) and (2), and the exchange energy density of Eq. (7), for the infinite barrier limit (Fig. 2), a physical surface density profile (Fig. 3), and a very slowly varying profile (Fig. 4). Conditions for convergence are clearly unfavorable for the infinite barrier model, especially near the position of the barrier, and favorable for the slowly varying profile.

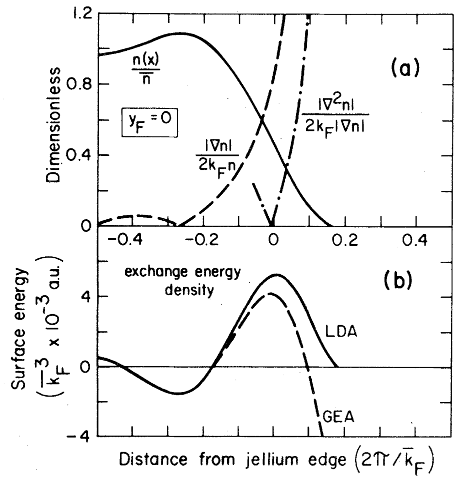

FIG. 2. Details for the infinite barrier model ($y_F = 0$) of the metal surface. (a) displays the "small" parameters of Eqs. (1) and (2) as well as the reduced density profile $n(x)/\bar{n}$. (b) shows the LDA and GEA exchange energy densities; the area under each curve gives the corresponding exchange contribution to the surface energy.

For this same slowly varying profile ($y_F = 8$), where the gradient term is correcting essentially all of the LDA error of the surface exchange energy, there are indications that the gradient term in the *exchange and correlation* energy may still be too large by a factor of 2 to successfully correct the LDA for exchange and correlation.[8] The difference is explained by an analysis of the gradient coefficient into contributions from dynamic density fluctuations of various wave vectors.[8] This analysis suggests[8] that sufficient conditions for convergence of the gradient expansion for correlation are usally much more severe than the conditions of Eqs. (1) and (2).

III. ATOMIC ENERGIES

We begin by discussing the one-electron atom for which the exchange energy of Eq. (3) is purely a self-interaction correction and the exact density functional is known:

$$E_x[n] = -\frac{1}{2}\int d^3r \int d^3r' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} . \tag{10}$$

Since the one-electron atom is fully spin polarized, we will need the spin-density gradient expansion

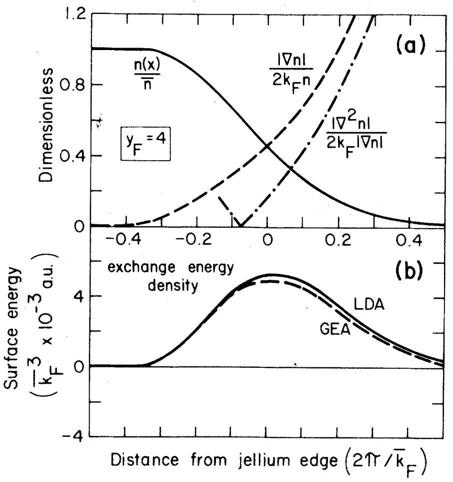

FIG. 3. Details for a physical ($y_F = 4$) density profile at the metal surface (see caption of Fig. 2).

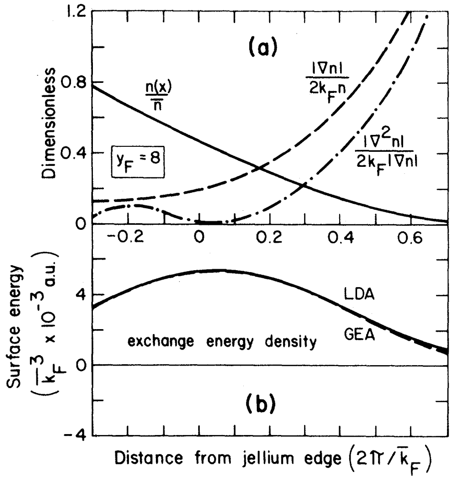

FIG. 4. Details for a very slowly varying ($y_F=8$) density profile at the metal surface (see caption of Fig. 2).

$$E_x[n_\uparrow,n_\downarrow]=\sum_\sigma\left[-2^{1/3}A_x\int d^3r\,n_\sigma^{4/3}-\frac{C_x}{2^{1/3}}\int d^3r\frac{|\nabla n_\sigma|^2}{n_\sigma^{4/3}}+\cdots\right], \tag{11}$$

which has been deduced from Eq. (6) by a simple argument.[22]

Figure 5 shows the small parameters of Eqs. (1) and (2), and the exact [from Eq. (10)], LDA and GEA [from Eq. (11)] exchange energy densities. In spite of the fact that the conditions (1) and (2) are not well satisfied, the LDA is surprisingly good and the GEA is slightly better. Note that the relative errors of LDA and GEA are unaffected by the nuclear charge Z in this one-electron atom.

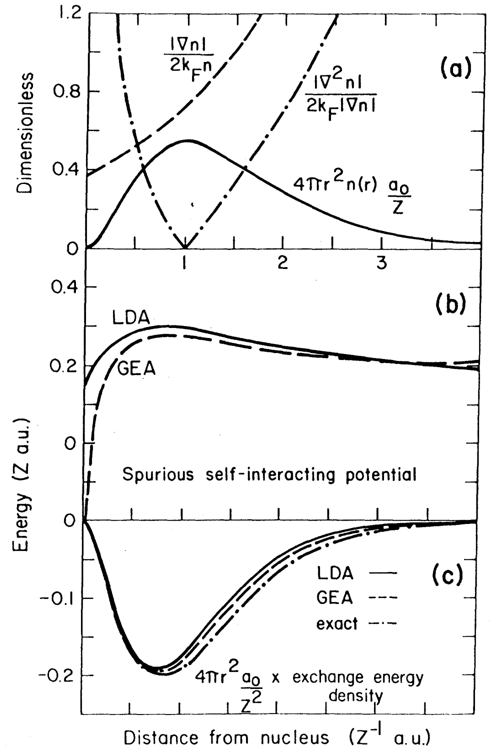

FIG. 5. Details for the one-electron atom with nuclear charge Z. (a) shows the small parameters of Eqs. (1) and (2) [note $k_F=(6\pi^2 n)^{1/3}$ for this fully spin-polarized system] and the radial probability density. (b) displays the "spurious self-interacting potentials" described after Eq. (12). (c) shows the LDA, GEA, and exact exchange energy densities; the area under each curve gives the corresponding exchange energy.

The self-consistent Kohn-Sham potential for electrons of spin σ (neglecting correlation) is[4,23]

$$v^\sigma_{\text{eff}}(\vec r)=v_{\text{ext}}(\vec r)+\int d^3r'\frac{n(\vec r\,')}{|\vec r-\vec r\,'|}+\frac{\delta E_x[n_\uparrow,n_\downarrow]}{\delta n_\sigma(\vec r)}, \tag{12}$$

where v_{ext} is the external (nuclear) potential. In the one-electron atom, the last two terms of Eq. (12) constitute a "spurious self-interacting potential" which is zero in the exact treatment of exchange [Eq. (10)]. In Fig. 5(b) we show this spurious self-interacting potential in the LDA and GEA. Over the region of greatest radial probability, these potentials are large but nearly constant, i.e., they seriously contaminate the eigenvalue of the Kohn-Sham equation (5), but still yield rather good electron densities and total energies.[24] The eigenvalue contamination leads, in particular, to incorrect long-range behavior of the density.[24] The functional derivative of the gradient term

$$\frac{\delta}{\delta n(\vec r)}\int d^3r'\frac{|\nabla n|^2}{n^{4/3}}=\frac{4}{3}\frac{|\nabla n|^2}{n^{7/3}}-2\frac{\nabla^2 n}{n^{4/3}} \tag{13}$$

diverges both at large and small r.[9,10]

Figure 6 shows a similiar analysis of the small parameters and the exchange energy density for a many-electron atom, krypton. The condition (1) is now well satisfied so the gradient correction to LDA is relatively small, but the condition (2) is still not satisfied very well—we cannot be sure that the gradient term will give the *right* correction to LDA.

In Table II we present results for the exact exchange[25] and kinetic[26] energies for a series of

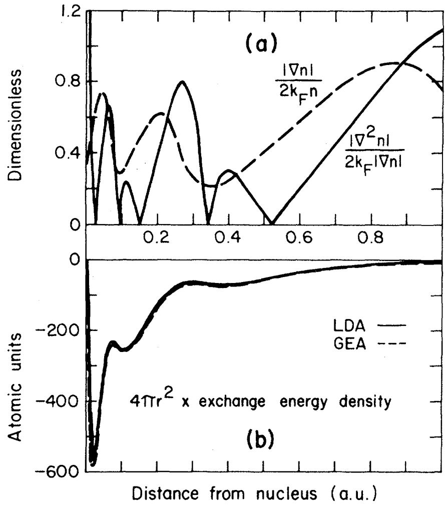

FIG. 6. Details for the krypton atom using Hartree-Fock densities from Ref. 28. (a) shows the small parameters of Eqs. (1) and (2). (b) shows the LDA and GEA exchange energy densities; the area under each curve gives the corresponding exchange energy.

atoms evaluated with Hartree-Fock[27] orbitals, and results obtained by Talman and co-workers[5,28] from the proper exchange-only Kohn-Sham orbitals. These two sets of results are essentially equivalent. Table II also summarizes the errors of the LDA and GEA calculations for the magnitude of the exchange energy[25] ($-E_x$) and the kinetic energy[26] (T_s) taken with respect to the Kohn-Sham results. Except for H, all the LDA and GEA results are from Refs. 25 and 26. However, the *a priori* coefficients,[12] appropriate for slow density variations, have been used instead of empirical coefficients.

The LDA errors are similar for $-E_x$ and T_s and decrease with increasing atomic number because the condition (1) is progressively better satisfied. The gradient term corrects essentially all of the LDA error for the kinetic energy, but only a fraction of the LDA error for exchange.

IV. CONCLUSIONS

We have demonstrated the convergence of the second-order gradient expansion for the exchange energy with the *a priori* coefficient of Sham,[12] as the density becomes more slowly varying. This expansion gives useful results for the metal surface even for physical density profiles, like the gradient expansion for the kinetic energy[2] and apparently unlike the one for correlation.[8] It has also recently been shown[29] that the second-order gradient expansion can usefully replace the exact exchange energy in *variational* calculations of surface energies and work functions for a Pauli-correlated jellium metal surface. On the other hand, the *a priori* gradient expansion for exchange is not particularly useful

TABLE II. Hartree-Fock and Kohn-Sham exchange E_x (and kinetic T_s) energies for a series of atoms and the % errors (relative to Kohn-Sham) of the local-density (LDA) and second-order gradient-expansion (GEA) approximations for $-E_x$ (and T_s).

Atom	Exact values (a.u.) $-E_x$ (T_s) Hartree-Fock	Kohn-Sham	% errors LDA	GEA
H	0.3125 (0.5000)	0.3125 (0.5000)	-14.2 (-8.2)	-5.9 ($+2.9$)
He	1.03 (2.86)	1.03 (2.86)	-13.6 (-10.5)	-5.3 ($+0.6$)
Ne	12.13 (128.55)	12.10 (128.55)	-8.8 (-8.4)	-4.6 (-0.6)
Ar	30.30 (526.82)	30.16 (526.81)	-7.5 (-7.0)	-4.2 (-0.5)
Kr	94.63 (2752.05)	93.78 (2752.04)	-5.4 (-5.9)	-3.2 (-0.7)

for atoms. The validity conditions (1) and (2) play different roles, and it is only when both are well satisfied that convergence is assured for the gradient expansions of the exchange and kinetic energies.

The near equivalence of the gradient expansion to the exact exchange energy for the metal surface, demonstrated here and in Ref. 29, provides some justification for an approach recently proposed by Langreth and Mehl.[30] They suggest employing the gradient expansion for the exchange energy, but a generalization of the gradient expansion for the correlation energy, in order to go beyond the local-density approximation.

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