Gradient expansion of the exchange-energy density functional: Effect of taking limits in the wrong order

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We show that if one uses a screened Coulomb potential $V(K)=4\pi/(K^2+K_s^2)$ to calculate γ_x, the exchange-energy density-functional gradient expansion coefficient, one obtains Sham's result if one takes $K\rightarrow 0$ before taking $K_s\rightarrow 0$. The exchange energy is by its very definition an unscreened quantity so that the correct order of the limits is $K_s\rightarrow 0$ before $K\rightarrow 0$, in which case $\gamma_x=1.42\gamma_x^{\rm Sham}$.

A few years ago one of us[1] claimed that $\gamma_x=\frac{8}{7}\gamma_x^{\rm Sham}$ where $\gamma_x^{\rm Sham}=7/[216\pi(3\pi^2)^{1/3}]$ is Sham's[2] result for the exchange-energy density-functional gradient coefficient in

$$E_x=-\int\left[\frac{3}{4}\left[\frac{3}{\pi}\right]^{1/3}\rho^{4/3}(\mathbf{r})+\tfrac{1}{2}\gamma_x\rho^{-4/3}(\mathbf{r})\,|\,\nabla\rho(\mathbf{r})\,|^2\right]d^3r\ . \tag{1}$$

The gradient expansion becomes inaccurate when $\rho(\mathbf{r})$ contains high-$\mathbf{K}$ Fourier components, $\rho(\mathbf{K})$. An expansion accurate for any $\mathbf{K}$ as long as $\rho(\mathbf{K})$ is small, is

$$E_x=-\frac{3}{4}\frac{3}{\pi}\rho_0^{-2/3}\left[\rho_0^2+\sum_{\mathbf{K}}{}'\,|\,\rho(\mathbf{K})\,|^2F_x(K/k_F)\right]\ . \tag{2}$$

One may write (letting $\kappa=K/k_F$)

$$F_x(\kappa)=F_x(0)+\kappa^2Z_x(\kappa)\ , \tag{3}$$

in which case

$$\gamma_x=3Z(0)/2\pi(3\pi^2)^{1/3} \tag{4}$$

follows, using $k_F=(3\pi^2\rho_0)^{1/3}$. Our disagreement with Sham's result was attributed[1] to Sham's use of a screened Coulomb potential

$$V(K,K_s)=4\pi/(K^2+K_s^2) \tag{5}$$

in calculating $Z_x(\kappa)$ and taking $\kappa=0$ before allowing κ_s to become zero. In fact, our result for γ_x was also incorrect because we had discarded a term whose numerator vanished by symmetry but whose denominator also vanished.[3] This we soon discovered when we[4] calculated $Z_x(\kappa)$ numerically for finite κ and found that the $\kappa\rightarrow 0$ limit yielded $\gamma\approx\frac{10}{7}\gamma_x^{\rm Sham}$. We concluded that $Z_x(\kappa\equiv 0)$ is not defined (for unscreened exchange), that γ_x must be obtained from the $\kappa\rightarrow 0$ limit, and if screened exchange is used, that κ_s must be set equal to zero before the $\kappa\rightarrow 0$ limit is taken. Note that Eq. (3) which defines $Z_x(\kappa)$ is satisfied for $Z_x(\kappa\equiv 0)$ having any noninfinite value.

This controversy remains of interest because

$$\gamma_{xc}^{\rm LP}=\gamma_x^{\rm Sham}+\gamma_c^{\rm MB}\ , \tag{6}$$

where $\gamma_{xc}^{\rm LP}$ is the Langreth-Perdew[5] exchange-correlation gradient coefficient and $\gamma_c^{\rm MB}$ the Ma-Brueckner[6] coefficient for correlation only. Langreth[7] remains unconvinced that $\gamma_x^{\rm Sham}$ suffers from $\kappa\sim 0$ Coulomb anomalies. Langreth and Vosko[8] state that one can use Sham's method to resolve any $K\sim 0$ anomalies, since such anomalies, *if they exist* (italics ours), must cancel out of the sum in Eq. (6), so that γ_x may be taken equal to $\gamma_x^{\rm Sham}$. It is not the purpose of this paper to argue that $\gamma_{xc}^{\rm LP}$ and $\gamma_c^{\rm MB}$ are incorrect, although we believe that to be the case.[9] (We believe that any calculation resulting in a part of the correlation energy being first order in the coupling constant e^2 must be in error.) Rather, it is our purpose to make absolutely convincing what we have already demonstrated, namely that $Z_x(K\rightarrow 0,K_s\equiv 0)$ results in $\gamma_x\approx\frac{10}{7}\gamma_x^{\rm Sham}$. Perdew[10,3] suggested that our numerical re-

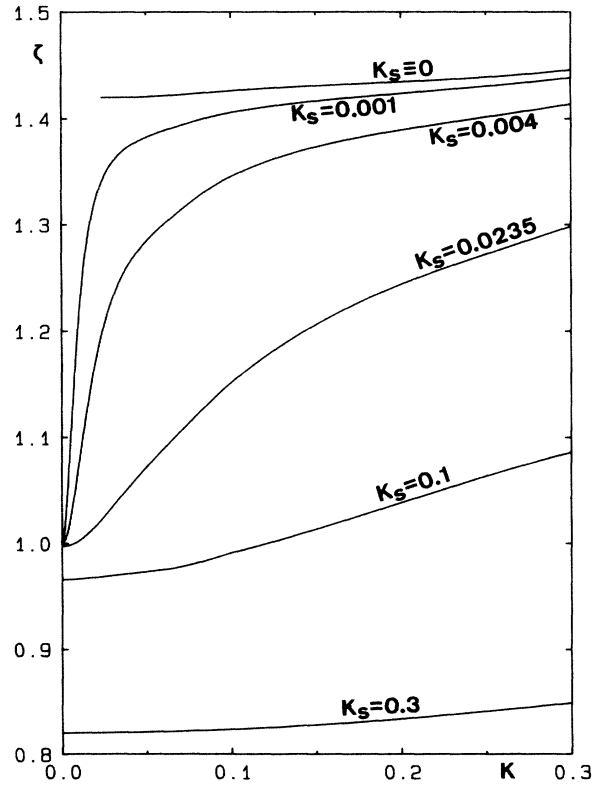

FIG. 1. Plot of $\zeta=Z_x(\kappa,\kappa_S)/Z_x^{\rm Sham}$ as a function of $\kappa=K/k_F$ for various values of κ_S.

TABLE I. $Z_x(\kappa,\kappa_s)/Z_x^{\text{Sham}}$ for values of $\kappa=K/k_F$ listed in the first column and κ_S/k_F at the head of the other columns. The results in parentheses at $\kappa=0.0235$ are of less accuracy than those at $\kappa=0.023\,75$ which were calculated using four times as many mesh points.

κ	$Z_x(0.3)$	$Z_x(0.1)$	$Z_x(0.0235)$	$Z_x(0.004)$	$Z_x(0.001)$	$Z_x(0)$
0	0.819 92	0.966 10	0.997 10	0.999 88	0.999 99	
0.0235	(0.8212)	0.9688	1.0222	1.1953	(1.3406)	(1.4116)
0.023 75	0.8204				1.3404	1.4200
0.0495	0.8211	0.9732	1.0707	1.2832	1.3821	1.4207
0.0995	0.8235	0.9907	1.1505	1.3452	1.4057	1.4264
0.1995	0.8336	1.0381	1.2436	1.3894	1.4239	1.4348
0.2995	0.8488	1.0860	1.2981	1.4142	1.4386	1.4461

sults would be unimpeachable if we calculated $Z_x(K,K_s)$ and found that $Z_x(K\to 0,K_s)$ agreed with the analytic result[11] for $Z_x(0,K_s)$, which includes $Z_x(0,K_s\to 0)=Z_x^{\text{Sham}}$.

Aside from using the screened interaction of Eq. (5) we follow Ref. 4 to obtain

$$F_x(K,K_s)=A(K)I(K,K_s)\,, \tag{7}$$

where

$$I(K,K_s)=\int d^3k\int d^3k'\frac{1}{|\mathbf{k}-\mathbf{k}'|^2+K_s^2}\left[1-\frac{1}{2}\frac{K^2+2\mathbf{k}'\cdot\mathbf{K}}{K^2+2\mathbf{k}\cdot\mathbf{K}}-\frac{1}{2}\frac{K^2+2\mathbf{k}\cdot\mathbf{K}}{K^2+2\mathbf{k}'\cdot\mathbf{K}}\right]\times\frac{f(\mathbf{k}+\mathbf{K})-f(\mathbf{k})}{\frac{1}{2}K^2+\mathbf{k}\cdot\mathbf{K}}\frac{f(\mathbf{k}'+\mathbf{K})-f(\mathbf{k}')}{\frac{1}{2}K^2+\mathbf{k}'\cdot\mathbf{K}}\,, \tag{8}$$

$$A(K)=\frac{4}{9\pi^2}\left[2+\left[\frac{2k_F}{K}-\frac{K}{2k_F}\right]\ln\left|\frac{2k_F+K}{2k_F-K}\right|\right]^{-2}\,, \tag{9}$$

and $f(\mathbf{k})$ is the Fermi function. After performing the same tedious analytic integrations as in Ref. 4 we arrive at an equation which differs only in the addition of K_s^2 to the a_i and b_i inside the curly brackets:[12]

$$I(K,K_s)=(\pi/K)^2\int_{-k_F}^{k_F}dz\int_{-|z|}^{|z|}dz'(z+\tfrac{1}{2}K)^{-2}(z'+\tfrac{1}{2}K)^{-2}\times\sum_{i=1}^{2}(-1)^i a_i\{b_i^s-a_i^s+z^2+z'^2-2k_F^2+2(k_F^2-z^2)\ln[(z^2-z'^2+a_i^s+b_i^s)/2a_i^s]+2(k_F^2-z'^2)\ln[2(k_F^2-z'^2)/(z^2-z'^2-a_i^s+b_i^s)]\}\,, \tag{10}$$

where

$$a_i^s=a_i+K_s^2\,,\qquad a_1=(z-z')^2,\quad a_2=(z'+z+K)^2\,, \tag{11}$$

and

$$b_i^s=[(a_i^s+2k_F^2-z^2-z'^2)^2-4(k_F^2-z^2)(k_F^2-z'^2)]^{1/2}\,. \tag{12}$$

To obtain the principal value of the integral we normalize to $k_F=1$ and evaluate the integrand at mesh points z_n and $z_n'=\pm n/4000$ with n even and require that $\frac{1}{2}\kappa=m/4000$ with m odd.[13] This gives better results for $\kappa_s\equiv 0$ and $\kappa\to 0$ than we obtained in Ref. 4 where we took n odd and m even. It has the disadvantage that when we improve the accuracy by taking z_n and $z_n'=\pm n/8000$, the allowed values of $\frac{1}{2}\kappa$ change slightly.

In the first row of Table I are listed values of $Z_x(0,\kappa_s)/Z_x^{\text{Sham}}$ obtained from the exact analytic expression of Mohammed and Sahni,[11]

$$Z_x(0,\kappa_s)=\frac{1}{54}\left[2-\frac{3\kappa_s^2}{4}\ln\left[1+\frac{4}{\kappa_s^2}\right]-\frac{40-6\kappa_s^2-3\kappa_s^4}{3(4+\kappa_s^2)^2}\right]\,. \tag{13}$$

Taking $\kappa_s=0$ in (13) gives $Z_x^{\text{Sham}}=\frac{7}{324}$, which when inserted in (4) yields γ_x^{Sham}. The remaining rows of Table I list

$$Z_x(\kappa,\kappa_s)/Z_x^{\text{Sham}}=\frac{F_x(\kappa,\kappa_s)-F_x(0,\kappa_s)}{\frac{7}{324}\kappa^2}\,, \tag{14}$$

where

$$F_x(0,\kappa_s)=\tfrac{2}{9}[1-(\kappa_s/2)^2\ln(1+4/\kappa_s^2)] \tag{15}$$

may be obtained by using the screened interaction in

Ref. 1.[14]

Because of the $1/K^2$ in Eq. (10) and the $1/\kappa^2$ in (14), at the smallest κ in Table I over six significant figures of numerical accuracy are lost relative to $\kappa=1$. Also, in Eq. (8) there is a singularity at $\mathbf{k}=\mathbf{k}'$ which should result in a loss of numerical accuracy for $K_s=0$. This corresponds to $z=z'$ in Eq. (10) where it does not appear obvious that a nonzero κ_s will improve the accuracy. Using four times as many mesh points[15] (i.e., z_n and $z_n'=\pm n/8000$) we have repeated the $\kappa=0.0235$ calculations[16] for $\kappa_s=0$, 0.001, and 0.3 with the results shown[17] in Table I. We note a moderate change for $\kappa_s=0$ but a much smaller one for $\kappa_s=0.001$, so that obvious or not, even a very small κ_s in Eq. (10) results in a large improvement in numerical accuracy. The results of Table I (discarding those in parentheses) are fit in Fig. 1 assuming a κ^2 dependence at small κ. From either the table or the figure we note that for nonzero κ_s the numerically evaluated $Z_x(\kappa,\kappa_s)$ join smoothly to the exact $\kappa=0$ results, that $Z_x(\kappa\equiv 0,\kappa_s\rightarrow 0)=Z_x^{\text{Sham}}$ but that $Z_x(\kappa\rightarrow 0,\kappa_s\equiv 0)=1.42Z_x^{\text{Sham}}$, QED.

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[9]By its very definition the correlation energy when added to the unscreened Hartree-Fock exchange energy is equal to the total energy. Therefore, $\gamma_{xc}\equiv\gamma_x+\gamma_c$. Since $\gamma_x\neq\gamma_x^{\text{Sham}}$ and Eq. (6) is numerically verified, either γ_{xc}^{LP} is not the correct γ_{xc} or γ_x^{Sham} and γ_c^{MB} contain compensating errors so that $\gamma_x^{\text{Sham}}+\gamma_c^{\text{MB}}=\gamma_x+\gamma_c$.

[10]J. P. Perdew (private communication).

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[12]The omission of absolute-value signs on the z's in the limits of integration in Ref. 4 was a misprint.

[13]We weight each point according to the fraction of its proximity square which lies within the integration limits. Thus $z'=z$ (including $z'=z=0$) and $z=k_F$ are weighted $\frac{1}{2}$ but $z'=z=k_F$ is weighted $\frac{1}{8}$.

[14]If one uses the screened interaction in Eq. (7) of Ref. 1, one sees that the integral in Eq. (8) becomes

$$\int_{-1}^{1}\int_{-1}^{1}\frac{\mu}{K+2k_F\mu}\frac{(1-\mu')k_F^2}{2k_F^2(1-\mu')+K_s^2}d\mu\,d\mu' .$$

The μ' integral yields the factor in square brackets in Eq. (15) of this paper.

[15]Each integration using Cray X-MP double precision requires one hour of central processor time.

[16]The closest allowed values of κ to $\kappa=0.0235$ when $z=z'=\pm n/8000$ are $\kappa=0.023\,25$ and $0.023\,75$.

[17]Because of the weak κ dependence of the $\kappa_s=0.3$ curve, the more accurate value obtained at $\kappa=0.023\,75$ may be directly compared with the value at $\kappa=0.0235$. When the curvature of the $\kappa_s=0.001$ curve is taken into account, we estimate the correction at $\kappa=0.0235$ to be about twice the -0.0008 found for $\kappa_s=0.3$.