

Exchange density-functional gradient expansion

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The coefficient γ_x of the first term in a gradient expansion of the Hartree-Fock (HF) density functional was calculated by Sham to first order in e^2 . It is now known that γ_x^{HF} diverges if e^2 is included to all orders. It has recently been claimed that if the exchange energy is defined in terms of density-functional (DF) eigenfunctions, rather than HF eigenfunctions, not only is γ_x^{DF} first order in e^2 but also $\gamma_x^{\text{DF}} = \gamma_{\text{Sham}}^{\text{DF}}$. It is proven in this paper that, in fact, $\gamma_x^{\text{DF}} = \frac{8}{7}\gamma_{\text{Sham}}^{\text{DF}}$.

Sometime ago Sham¹ calculated the coefficient of the first term in the gradient expansion of the exchange energy density functional.^{2,3} He argued that since the exchange energy is proportional to e^2 (where e is the charge of the electron), an expansion in powers of e^2 must stop with the first term. I⁴ and others^{5,6} performed the calculation to all orders in e^2 and found the coefficient diverged. I pointed out⁴ that the exchange functional contained not only exchange energy but also the difference between the kinetic energy of the Hartree-Fock (HF) eigenfunctions and the density-functional (DF) eigenfunctions and thus was not expected to be proportional to e^2 . Perdew *et al.*⁷⁻⁹ noted that the exchange energy could be defined to be the Fock integral of eigenfunctions of a local (i.e., DF) potential which would eliminate the kinetic energy correction and result in an exchange energy proportional to e^2 . Local potentials which result in a charge density identical to the HF charge density or which minimize the total energy have been used;⁹ empirically, they are nearly identical, but only the latter seems to satisfy the variational property of the density functional theorem.² Langreth and Perdew⁷ assumed that Sham's first-order (in e^2) HF calculation is equivalent to the DF calculation and reobtained his result. In this paper I calculate γ_{DF} with no assumptions or approximations and obtain $\gamma_{\text{DF}} = \frac{8}{7}\gamma_{\text{Sham}}^{\text{DF}}$.

We consider a free-electron gas to which a weak external potential

$$V_{\text{ext}}(\vec{K})e^{i\vec{K}\cdot\vec{r}} + V_{\text{ext}}(-\vec{K})e^{-i\vec{K}\cdot\vec{r}}$$

is applied. With no loss of generality, we take $V_{\text{ext}}(-\vec{K}) = V_{\text{ext}}^*(\vec{K})$ to be real. This results in a self-

consistent DF potential $V_{\vec{K}}(e^{i\vec{K}\cdot\vec{r}} + e^{-i\vec{K}\cdot\vec{r}})$ to which the electrons respond. Thus

$$\psi_{\vec{k}} = \Omega^{-1/2}[(1 - \alpha_{\vec{k}}^2 - \beta_{\vec{k}}^2)^{1/2}e^{i\vec{k}\cdot\vec{r}} + \alpha_{\vec{k}}e^{i(\vec{k} + \vec{K})\cdot\vec{r}} + \beta_{\vec{k}}e^{i(\vec{k} - \vec{K})\cdot\vec{r}}], \quad (1)$$

where Ω is a normalization volume and

$$\alpha_{\vec{k}} = V_{\vec{K}}/\frac{1}{2}(K^2 + 2\vec{k}\cdot\vec{K}), \quad \beta_{\vec{k}} = V_{\vec{K}}/\frac{1}{2}(K^2 - 2\vec{k}\cdot\vec{K}). \quad (2)$$

The exchange energy of a pair of electrons

$$- \int \psi_{\vec{k}}(\vec{r}_1)\psi_{\vec{k}'}^*(\vec{r}_1)r_{12}^{-1}\psi_{\vec{k}}^*(\vec{r}_2)\psi_{\vec{k}'}(\vec{r}_2)d^3r_1d^3r_2$$

is easily evaluated to obtain

$$E_x(\vec{k}, \vec{k}') = -\frac{4\pi}{\Omega} \left[\frac{1 - (\alpha_{\vec{k}} - \alpha_{\vec{k}'})^2 - (\beta_{\vec{k}} - \beta_{\vec{k}'})^2}{|\vec{k} - \vec{k}'|^2} + \frac{(\alpha_{\vec{k}} + \beta_{\vec{k}'})^2}{|\vec{k} - \vec{k}' + \vec{K}|^2} + \frac{(\alpha_{\vec{k}'} + \beta_{\vec{k}})^2}{|\vec{k} - \vec{k}' - \vec{K}|^2} \right]. \quad (3)$$

The corrections to the $|\vec{k} - \vec{k}'|^{-1}$ term arise both from the renormalization of the \vec{k} and \vec{k}' plane waves and from $\vec{k} - \vec{k}'$ momentum transfers between $\vec{k} + \vec{K}$ and $\vec{k}' + \vec{K}$ plane waves. The total exchange energy per unit volume is

$$E_x = \frac{1}{\Omega} \int E_x(\vec{k}, \vec{k}')f_{\vec{k}}f_{\vec{k}'}[\Omega^2/(2\pi)^6]d^3k d^3k', \quad (4)$$

where $f_{\vec{k}}$ is the Fermi function and a factor of 2 for spin has canceled a factor of $\frac{1}{2}$ to correct for counting each $\vec{k} - \vec{k}'$ pair twice. Noting that $\beta_{\vec{k} + \vec{K}} = -\alpha_{\vec{k}}$ and substituting from (2) and (3) into (4) yields

$$E_x = \frac{-2}{(2\pi)^5} \left[\int \frac{f_{\vec{k}}f_{\vec{k}'}}{|\vec{k} - \vec{k}'|^2}d^3k d^3k' + V_{\vec{K}}^2 \int \frac{2kk'}{|\vec{k} - \vec{k}'|^2} \left[1 - \frac{K^2 + 2\vec{k}'\cdot\vec{K}}{K^2 + 2\vec{k}\cdot\vec{K}} \right] \Theta_{\vec{k}}(\vec{K})\Theta_{\vec{k}'}(\vec{K})d\Omega d\Omega' dE dE' \right]; \quad (5)$$

where

$$\Theta_{\vec{k}}(\vec{K}) = (f_{\vec{k} + \vec{K}} - f_{\vec{k}})/(\frac{1}{2}K^2 + \vec{k}\cdot\vec{K}) = f_{\vec{k}'} + \frac{1}{4}(K^2 + 2\vec{k}\cdot\vec{K})f_{\vec{k}''} + \frac{1}{24}(K^2 + 2\vec{k}\cdot\vec{K})^2f_{\vec{k}'''} \quad (6)$$

and we have used $d^3k = k d\Omega dE$. Equation (5) is exact to order $V_{\vec{K}}^2$ and in the $\vec{K} \rightarrow 0$ limit exact to order K^2 if the expansion of $\Theta_{\vec{k}}(\vec{K})$ given in (6) is used. There

$$f_{\vec{k}'} = -\delta(E - E_F), \quad f_{\vec{k}''} = -\frac{d}{dE}\delta(E - E_F)$$

and

$$f_{\vec{k}'''} = -\frac{d^2}{dE^2}\delta(E - E_F).$$

The first integral in (5) is the well-known free-electron gas exchange energy. The second we write as a sum of integrals

$I(f_{\vec{k}}^m, f_{\vec{k}'}^{n'}) = I(m, n')$. We have

$$I(1, 1') = -\frac{4V_{\vec{K}}^2}{(2\pi)^5} \int \frac{2(\vec{K} - \vec{k}') \cdot \vec{K} k k'}{|\vec{k} - \vec{k}'|^2 (K^2 + 2\vec{k} \cdot \vec{K})} d\Omega d\Omega' f_{\vec{k}}' f_{\vec{k}'}' dE dE' \quad (7)$$

Letting μ be the cos of the angle \vec{k} makes with \vec{K} and μ' the cos of the angle \vec{k}' makes with \vec{K} , we have

$$\vec{k}' \cdot \vec{K} = \mu\mu' - (1 - \mu^2)^{1/2}(1 - \mu'^2)^{1/2} \sin(\phi - \phi')$$

and

$$\begin{aligned} I(1, 1') &= -\frac{8V_{\vec{K}}^2}{(2\pi)^5} \int \frac{k_F K [\mu - \mu\mu' - (1 - \mu^2)^{1/2}(1 - \mu'^2)^{1/2} \sin(\phi - \phi')]}{2k_F^2(1 - \mu')(K^2 + 2k_F K \mu)} k_F^2 d\phi d\phi' d\mu d\mu' \\ &= -\frac{4V_{\vec{K}}^2 k_F}{(2\pi)^3} \int_{-1}^1 \frac{\mu}{K + 2k_F \mu} d\mu d\mu' = -\frac{8V_{\vec{K}}^2 k_F}{(2\pi)^3} \left[\frac{1}{k_F} - \frac{K}{4k_F^2} \ln \left(\frac{2k_F + K}{2k_F - K} \right) \right] \end{aligned} \quad (8)$$

To order K^2 this gives

$$I(1, 1') = -\frac{8V_{\vec{K}}^2}{(2\pi)^3} \left[1 - \frac{K^2}{4k_F^2} \right] \quad (9)$$

Note the cancellation of the divergent $(1 - \mu')^{-1}$ in Eq. (8). Because of the integration by parts necessitated by f'' and f''' , the remaining $I(m, n')$ have more divergent denominators whose cancellation is much less obvious. Because of the tedious nature of these integrations, we only list the results:

$$I(2, 1') = 0, \quad I(1, 2') = -4V_{\vec{K}}^2 K^2 / (2\pi)^3 k_F^2,$$

$$I(2, 2') = \frac{2}{3} V_{\vec{K}}^2 K^2 / (2\pi)^3 k_F^2, \quad I(3, 1') = \frac{4}{9} V_{\vec{K}}^2 K^2 / (2\pi)^3 k_F^2,$$

and

$$I(1, 3') = \frac{4}{3} V_{\vec{K}}^2 K^2 / (2\pi)^3 k_F^2.$$

All $I(m, n')$ with $m + n' > 4$ are of order K^4 or higher.

Squaring Eq. (1) and integrating we obtain (including a factor of 2 for spin)

$$\begin{aligned} \rho(\vec{K}) = \rho(-\vec{K}) &= \frac{4V_{\vec{K}}}{(2\pi)^3} \int_0^{k_F} \frac{2\pi k^2}{\frac{1}{2}K^2 + kK\mu} d\mu dk \\ &= \frac{V_{\vec{K}} k_F}{(2\pi)^2} \left[2 + \left(\frac{2k_F}{K} - \frac{K}{2k_F} \right) \ln \left| \frac{2k_F + K}{2k_F - K} \right| \right] \end{aligned} \quad (10)$$

or in the $K \rightarrow 0$ limit

$$\rho(\vec{K}) = \frac{4V_{\vec{K}} k_F}{(2\pi)^2} \left[1 - \frac{1}{12} \left(\frac{K}{k_F} \right)^2 \right] \quad (11)$$

Inverting this we obtain

$$V_{\vec{K}}^2 = \frac{(2\pi)^4}{32k_F^2} \left[1 - \frac{1}{6} \left(\frac{K}{k_F} \right)^2 \right] \{ [\rho(\vec{K})]^2 + [\rho(-\vec{K})]^2 \} \quad (12)$$

Inserting this in the $I(m, n')$ and using $k_F^2 = (3\pi^2 \rho_0)^{2/3}$ we obtain

$$\begin{aligned} E_x &= \left\{ \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \rho_0^{4/3} + \left[\frac{1}{6} \left(\frac{3}{\pi} \right)^{1/3} \rho_0^{-2/3} + \frac{\rho_0^{-4/3} K^2}{54\pi (3\pi^2)^{1/3}} \right] \right. \\ &\quad \left. \times \{ [\rho(\vec{K})]^2 + [\rho(-\vec{K})]^2 \} \right\} \end{aligned} \quad (13)$$

Comparing this with the local density approximation (LDA),

we find

$$\begin{aligned} E_x^{\text{LDA}} &= -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \frac{1}{\Omega} \int d^3r [\rho_0 + \rho(\vec{K}) e^{i\vec{K} \cdot \vec{r}} \\ &\quad + \rho(-\vec{K}) e^{-i\vec{K} \cdot \vec{r}}]^{4/3} \\ &= -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \left[\rho_0^{4/3} + \frac{2}{9} \rho_0^{-2/3} \{ [\rho(\vec{K})]^2 + [\rho(-\vec{K})]^2 \} \right] \end{aligned} \quad (14)$$

where we have made a second-order binomial expansion and integrated over the normalization volume Ω . Thus

$$E_x = E_x^{\text{LDA}} + \frac{1}{2} \gamma_x \rho_0^{-4/3} \int |\vec{\nabla} \rho(\vec{r})|^2 d^3r \quad (15)$$

with $\gamma_x = -1/27\pi (3\pi^2)^{1/3} = \frac{8}{7} \gamma_{\text{Sham}}$. Since we are working only to second order in $\rho(\vec{K})$, Eq. (15) is equivalent to the standard gradient term $\frac{1}{2} \gamma_x \int \rho(\vec{r})^{-4/3} |\vec{\nabla} \rho(\vec{r})|^2 d^3r$. Sham's calculation, based on the density response function, is equivalent to finding an exchange potential (and hence density functional) which produces a charge density identical to that obtained from a HF Hamiltonian with its infinities averaged out. Because by definition the DF eigenfunctions yield the correct charge density, that path was not open here and I had to calculate the exchange energy directly as a function of the charge density. In view of these basic differences, it is perhaps surprising that the integrals we evaluated differ only in that Sham used screened exchange. (I thank Professor Langreth for pointing this out to me.) The difference in our results is a consequence of the fact that the $\lambda \rightarrow 0$ limit of screened exchange is not equal to unscreened exchange.¹⁰ Presumably then, the exchange-only limit of Ref. 7, which is based on a screened interaction, is incorrect, but the exchange-correlation γ_{xc} obtained there is correct.

It is trivial to evaluate E_x in the $\vec{K} \rightarrow \infty$ limit. Working to order K^{-6} , Eq. (3) becomes

$$\begin{aligned} E_x(\vec{K}, \vec{K}') &= -\frac{4\pi}{\Omega} \left[\frac{1}{|\vec{K} - \vec{K}'|^2} \right. \\ &\quad \left. + \frac{32V_{\vec{K}}^2}{K^6} \left[1 - \frac{[\vec{K} \cdot (\vec{K} - \vec{K}')]^2}{K^2 |\vec{K} - \vec{K}'|^2} \right] \right] \end{aligned} \quad (16)$$

Since this has to be independent of the direction of \vec{k} , the last term can be averaged over that direction to yield a \vec{k} and \vec{k}' independent result which can be factored out of Eq. (4). Equation (10) becomes

$$\rho(\vec{k}) = 8V_{\vec{k}}(2\pi)^{-3}K^{-2} \int f_{\vec{k}} d^3k$$

so that

$$E_x(\vec{k} \rightarrow \infty) = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \rho_0^{4/3} - \frac{2\pi}{3K^2} \{[\rho(\vec{k})]^2 + [\rho(-\vec{k})]^2\} \quad (17)$$

Note that the last term cancels $\frac{2}{3}$ of the Coulomb self-energy of parallel spin electrons. Had we considered only the $\vec{k} - \vec{k}' \pm \vec{k}$ momentum transfer terms in Eq. (3), as is sometimes done, the cancellation would have been perfect.

Finally, note that in general one can write for $\rho(\vec{k}) \ll \rho_0$

$$E_x = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \rho_0^{-2/3} [\rho_0^2 + \sum_{\vec{k}} |\rho(\vec{k})|^2 F(\vec{k})] \quad (18)$$

where

$$F(\vec{k} \rightarrow \infty) = \frac{8}{27} \frac{k^2}{K^2}$$

and

$$F(\vec{k} \rightarrow 0) = \frac{2}{9} + \frac{2}{81} \frac{K^2}{k^2}$$

$F(\vec{k})$ can be obtained in principle for any \vec{k} by substituting (3) into (4), integrating numerically, and using (10) to eliminate $V_{\vec{k}}$ in favor of $\rho(\vec{k})$. Taking the variation of E_x with respect to ρ and noting that because the number of electrons is conserved, ρ_0 is not varied, the KS^3 exchange potential is obtained:¹¹

$$V_x^{KS} = -\frac{3}{2} \left(\frac{3}{\pi} \right)^{1/3} \rho_0^{-2/3} \sum_{\vec{k}} \rho(\vec{k}) F(\vec{k}) e^{i\vec{k} \cdot \vec{r}} \quad (19)$$

In metals and semiconductors where the valence $\rho(\vec{k})$ is small this result should be nearly exact and can be superposed with a valence-core HF potential to obtain the total exchange potential seen by valence electrons. This potential appears to be more negative than the LDA in the intermediate wave-vector region and may correct the large errors in semiconductor energy gaps calculated with the LDA.

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¹⁰In particular, we have evaluated the $\lambda \rightarrow 0$ limit of a screened $I(3, 1')$ and obtained $I_{\lambda \rightarrow 0}(3, 1') = -\frac{1}{2} I_{\lambda=0}(3, 1')$.

¹¹Because the charge density, and hence the energy, is independent of the zeroth Fourier transform of potential, the zeroth Fourier transform cannot be obtained from a variation of the energy.