Spin scaling of the electron-gas correlation energy in the high-density limit

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(Received 1 October 1990)

The ground-state correlation energy per particle in a uniform electron gas with spin densities $n_\uparrow$ and $n_\downarrow$ may be expressed as $\varepsilon_c(\zeta,r_s)=I(\zeta,r_s)\varepsilon_c(0,r_s)$, where $r_s=[3/4\pi(n_\uparrow+n_\downarrow)]^{1/3}$ is the density parameter and $\zeta=(n_\uparrow-n_\downarrow)/(n_\uparrow+n_\downarrow)$ is the relative spin polarization. We find an analytic expression for the spin-scaling factor (SSF) $I(\zeta,r_s)$ in the high-density limit $r_s\to 0$. It decreases from the value 1 at $\zeta=0$, approaching the value $\frac{1}{2}$ with slope $-\infty$ as ζ approaches 1. A simple approximation to this SSF which displays the correct qualitative behavior is $g^3(\zeta)$, where $g(\zeta)=[(1+\zeta)^{2/3}+(1-\zeta)^{2/3}]/2$. We find that $g(\zeta)$ is the SSF for the coefficient of the $|\nabla n|^2/n^{4/3}$ term of the spin-density gradient expansion of the exchange energy, and a good approximation to the SSF for that of correlation: $\mathcal{C}_x(\zeta)/\mathcal{C}_x(0)=g(\zeta)$ and $\mathcal{C}_c(\zeta,r_s\to 0)/\mathcal{C}_c(0,r_s\to 0)\approx g(\zeta)$. We also find that the $|\nabla\zeta|^2$ contribution to the correlation energy is always negligible.

I. UNIFORM ELECTRON GAS

Although it is possible to evaluate the random-phase-approximation (RPA) correlation energy of a uniform electron gas exactly for all densities n and spin polarizations ζ from the von Barth and Hedin (vBH) formula,[1] such a calculation would involve a two-dimensional numerical integration. In this work, we present an *analytic* form for the spin-scaling factor (SSF) which, in the high-density limit, scales the correlation energy of the paramagnetic state ($\zeta=0$) to that of an arbitrary spin-polarized state (ζ). This study is motivated by the following observations. (1) vBH have already given an approximate spin-scaling factor for correlation in a parametrization of their numerical RPA results.[1] However, their SSF is based upon the spin scaling for exchange. In the low-density limit ($r_s \gg 1$), the beyond-RPA correlation energy is proportional to $1/r_s$ like the exchange energy.[2] Hence, it is reasonable that the correlation energy might scale the same way as exchange does. But in the high-density limit $r_s\to 0$, where the relative error of the RPA vanishes asymptotically, the correlation energy diverges like[3] $\ln r_s$, much more weakly than the $1/r_s$ of the exchange energy. Therefore we cannot expect the vBH scaling to be accurate in this limit. (2) A better knowledge of the spin dependence of the correlation energy in some limits (e.g., $r_s\to 0$ and $r_s\to\infty$) can provide an insight into the construction of more accurate yet simple spin-density functionals for the correlation energy.[4]

We employ the vBH expression for the correlation energy per electron of a uniform electron gas with spin densities $n_\uparrow$ and $n_\downarrow$ (in atomic units where $\hbar=e^2=m=1$):

$$\varepsilon_c(\zeta,r_s)=-\frac{12}{\pi}\frac{1}{(cr_s)^2}\int_0^\infty dW \int_0^\infty dQ\, Q^2\{\alpha_\zeta(Q,W)-\ln[1+\alpha_\zeta(Q,W)]\}\,, \tag{1}$$

where $c=(4/9\pi)^{1/3}$ and

$$r_s=(3/4\pi n)^{1/3}\,, \tag{2}$$

$$n=n_\uparrow+n_\downarrow\,, \tag{3}$$

$$\alpha_\zeta(Q,W)=\frac{cr_s}{4\pi}[x_1\beta(x_1 Q,x_1^2 W)+x_2\beta(x_2 Q,x_2^2 W)]\,, \tag{4}$$

$$\beta(Q,W)=\frac{1}{Q^2}\left\{1+\frac{W^2+Q^2-Q^4}{4Q^3}\ln\left[\frac{W^2+Q^2(1+Q)^2}{W^2+Q^2(1-Q)^2}\right]-\frac{W}{Q}\left[\arctan\left[\frac{Q+Q^2}{W}\right]+\arctan\left[\frac{Q-Q^2}{W}\right]\right]\right\}\,, \tag{5}$$

$$x_1=(1+\zeta)^{-1/3}\,, \tag{6}$$

$$x_2=(1-\zeta)^{-1/3}\,, \tag{7}$$

$$\zeta=(n_\uparrow-n_\downarrow)/n\,. \tag{8}$$

Here $k_F=1/cr_s$ is the Fermi wave vector, while $Q=k/2k_F$ and $W=\omega/2k_F^2$ are reduced expressions for the wave vector k and frequency ω of dynamic density fluctuations.

If $\beta(Q,W)$ were bounded, we could expand $\ln[1+\alpha_\zeta(Q,W)]$ in powers of r_s and find that $\varepsilon_c(\zeta,r_s)$ tends to a value independent of r_s as $r_s\to 0$. Thus the correct $\ln r_s$ divergence of $\varepsilon_c(\zeta,r_s)$ arises from the $1/Q^2$

singularity of $\beta(Q,W)$ as $Q \to 0$. Note that for small Q ($Q \ll 1$), $\beta(Q,W)$ has the following structure:[4]

$$\beta(Q,W)= \begin{cases} \dfrac{2}{Q^2}R(u)+O(Q^0u^0), & u<1 \quad (9) \\[2mm] \dfrac{2}{Q^2}R(u)+O(Q^0u^{-2}), & u>1 \;, \quad (10) \end{cases}$$

where

$$u=\frac{W}{Q} \;, \tag{11}$$

$$R(u)=1-u\arctan(u^{-1}) \;. \tag{12}$$

[As u varies from 0 to ∞, the function $R(u)$ decreases monotonically from 1 to 0]. Keeping only the leading term in the small-wave-vector approximation $Q \ll 1$ (valid for the high-density limit), we have

$$\beta(Q,W)=\frac{2}{Q^2}R(u) \tag{13}$$

for any u. Gell-Mann and Brueckner have arrived at a similar expression.[5] However, we stress here that they did not give a spin-dependent version of their derivation.

We split the Q integration in Eq. (1) into two parts,

$$\int_0^\infty dQ=\int_0^{Q_0} dQ+\int_{Q_0}^\infty dQ \;, \tag{14}$$

where Q_0 is a critical point which is determined by

$$\alpha_\zeta(Q_0,W)=1 \;. \tag{15}$$

Explicitly

$$Q_0=\left[\frac{cr_s}{2\pi}R_\zeta(u)\right]^{1/2} \;, \tag{16}$$

with

$$R_\zeta(u)=\frac{1}{x_1}R(x_1u)+\frac{1}{x_2}R(x_2u) \;. \tag{17}$$

Hence, in the first integral of Eq. (14), Q can be considered very small everywhere. $\alpha_\zeta(Q,W)$ is thus well approximated by

$$\alpha_\zeta(Q,W)=\frac{cr_s}{2\pi}\frac{1}{Q^2}R_\zeta(u)=\frac{Q_0^2}{Q^2} \;, \tag{18}$$

according to Eq. (13).

In the second integral of Eq. (14), the integrand has a power expansion around $\alpha_\zeta(Q,W)=0$,

$$Q^2\{\alpha_\zeta(Q,W)-\ln[1+\alpha_\zeta(Q,W)]\}$$
$$=Q^2[\tfrac{1}{2}\alpha_\zeta^2(Q,W)-\tfrac{1}{3}\alpha_\zeta^3(Q,W)+\cdots] \;. \tag{19}$$

Inserting Eqs. (14), (18), and (19) into Eq. (1), we find that only the first term in the series (19) is responsible for the logarithmic divergence of the correlation energy in the high-density limit,

$$\varepsilon_c(\zeta,r_s)\approx-\frac{12}{\pi}\frac{1}{(cr_s)^2}\int_0^\infty du\int_{Q_0}^\infty dQ\,Q^3\tfrac{1}{2}\alpha_\zeta^2(Q,Qu)$$

$$=-\frac{3}{8\pi^3}\int_0^\infty du\,G_\zeta(r_s,u) \;, \tag{20}$$

where

$$G_\zeta(r_s,u)=\int_{Q_0}^\infty dQ\,Q^3[x_1\beta(x_1Q,x_1^2Qu)$$
$$+x_2\beta(x_2Q,x_2^2Qu)]^2 \;. \tag{21}$$

All other terms contribute at most a constant independent of r_s to the correlation energy in the limit $r_s \to 0$. To find the r_s dependence of $G_\zeta(r_s,u)$, we differentiate it with respect to r_s,

$$\frac{\partial G_\zeta(r_s,u)}{\partial r_s}=-Q_0^3[x_1\beta(x_1Q_0,x_1^2Q_0u)$$
$$+x_2\beta(x_2Q_0,x_2^2Q_0u)]^2\frac{\partial Q_0}{\partial r_s} \;. \tag{22}$$

Since $Q_0 \ll 1$, we have

$$\frac{\partial G_\zeta(r_s,u)}{\partial r_s}=-\frac{2}{r_s}[R_\zeta(u)]^2 \;. \tag{23}$$

Hence

$$G_\zeta(r_s,u)=-2[R_\zeta(u)]^2\ln r_s \;. \tag{24}$$

It follows that

$$\varepsilon_c(\zeta,r_s)\approx-\frac{3}{8\pi^3}\int_0^\infty du(-2)[R_\zeta(u)]^2\ln r_s$$
$$=A(\zeta)\ln r_s \;, \tag{25}$$

where

$$A(\zeta)=\frac{3}{4\pi^3}\int_0^\infty du\,[R_\zeta(u)]^2 \;. \tag{26}$$

For the paramagnetic state,

$$A(0)=\frac{3}{4\pi^3}\int_0^\infty du[2R(u)]^2$$
$$=\frac{1}{\pi^2}(1-\ln 2)\approx 0.031\,090\,7 \tag{27}$$

recovers the original result of Macke.[3]

Define the SSF for the correlation energy as

$$I(\zeta)=\frac{\varepsilon_c(\zeta,r_s)}{\varepsilon_c(0,r_s)} \;. \tag{28}$$

Then we have, in the high-density limit ($r_s \to 0$),

$$I(\zeta)=\frac{A(\zeta)}{A(0)}$$
$$=\frac{1}{2}\left[1+\frac{1}{x_1x_2}\frac{\int_0^\infty du\,R(x_1u)R(x_2u)}{\int_0^\infty du[R(u)]^2}\right] \;. \tag{29}$$

As a check on Eq. (29), recall that[6]

$$\varepsilon_c^{RPA}(\zeta = 1, r_s) = \tfrac{1}{2}\varepsilon_c^{RPA}(\zeta = 0, r_s/2^{4/3}) \ . \tag{30}$$

In the high-density limit, Eq. (30) implies that

$$I(\zeta) = \frac{1}{2}\left[1 + \frac{y_1 y_2 (y_1 + y_2) + y_1^3 \ln y_1 + y_2^3 \ln y_2 - 2\ln(y_1 + y_2)}{2(1 - \ln 2)}\right] , \tag{32}$$

where

$$y_1 = x_1^{-1} = (1 + \zeta)^{1/3} \ , \tag{33}$$

$$y_2 = x_2^{-1} = (1 - \zeta)^{1/3} \ . \tag{34}$$

As a check on Eq. (32), we evaluated the integral of Eq. (29) numerically and found that the results agreed.

In Table I we compare $I(\zeta)$ with various spin-scaling factors and with the numerical RPA for $r_s = 0.5$ and 0.01. We see that as $r_s \to 0$, the numerical RPA ratio approaches $I(\zeta)$. We also observe that as ζ approaches its fully polarized value 1, the SSF $I(\zeta)$ approaches its minimum 0.5 with infinite slope. On the other hand, the SSF is quite insensitive to the change of ζ near $\zeta = 0$. These features can be well understood if we look at the power expansion of Eq. (32) near $\zeta = 0$ and 1. For small ζ, we find

$$I(\zeta) = 1 - 0.271\,57\zeta^2 \ . \tag{35}$$

But, for ζ near 1, we find

$$I(\zeta) = \tfrac{1}{2} + 1.539\,73(1 - \zeta)^{2/3} \ . \tag{36}$$

As a direct physical consequence of these features, the ferromagnetic state ($\zeta = 1$) of a high-density uniform electron gas is extremely unstable against infinitesimal depolarization. The local correlation potential

$$\mu_c^\sigma = \frac{\partial}{\partial n_\sigma}[n\varepsilon_c(n_\uparrow, n_\downarrow)] \quad (\sigma = \downarrow \text{ or } \uparrow) \tag{37}$$

for the minority ($\downarrow$) spin diverges to $-\infty$ as $\zeta \to 1$, to lure more electrons into the $\downarrow$-spin state.

$$I(1) = \tfrac{1}{2} \ . \tag{31}$$

Equation (29) indeed satisfies this condition. We perform the necessary integrations in Eq. (29), and find (see the Appendix)

In the high-density limit, the Fourier transform of the RPA correlation hole density is accurately approximated by[4]

$$\tilde{\rho}_c(\zeta, r_s, k) \to \frac{\pi g(\zeta)^2}{k_s}\frac{\alpha_1 z + \alpha_2 z^2 + \alpha_3 z^3}{[1 + \beta_1 z + \beta_2 z^2 + O(r_s^{9/8}z^3)]^2} \ , \tag{38}$$

where $k_s = \sqrt{4/\pi c r_s}$ is the Thomas-Fermi screening wave vector and $z = k/g(\zeta)k_s$, and where

$$g(\zeta) = \tfrac{1}{2}[(1 + \zeta)^{2/3} + (1 - \zeta)^{2/3}] \ . \tag{39}$$

α_1, α_2, α_3, β_1, and β_2 are constants independent of r_s and ζ. Now

$$\varepsilon_c(\zeta, r_s) = \frac{1}{\pi}\int_0^\infty dk\, \tilde{\rho}_c(\zeta, r_s, k)$$

$$= g(\zeta)^3 \int_0^\infty dz \frac{\alpha_1 z + \alpha_2 z^2 + \alpha_3 z^3}{[1 + \beta_1 z + \beta_2 z^2 + O(r_s^{9/8}z^3)]^2} \ . \tag{40}$$

Clearly, in the approximation of Eqs. (38) and (40),

$$I(\zeta) \approx [g(\zeta)]^3 \ . \tag{41}$$

In the same approximation, the real-space correlation hole in the high-density limit is

$$\rho_c(\zeta, r_s, R) = g^3 (gk_s)^2 A_c(gk_s R) \ ,$$

a relationship which persists[4] for large R even away from the high-density limit and beyond the RPA.

In Table I, we see that $[g(\zeta)]^3$ is a much more accurate

TABLE I. Various spin-scaling factors for the correlation energy of a uniform electron gas with spin polarization ζ in the high-density limit, along with numerical RPA values for $r_s = 0.5$ and 0.01.

ζ	$\dfrac{\varepsilon_c(\zeta, 0.5)^a}{\varepsilon_c(0, 0.5)}$	$\dfrac{\varepsilon_c(\zeta, 0.01)}{\varepsilon_c(0, 0.01)}$	$I(\zeta)$	$I_{vBH}(\zeta)$	$\dfrac{1}{d^3}$	$[g(\zeta)]^3$	$I_{VWN}(\zeta)$
0.0	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.2	0.990	0.990	0.989	0.983	0.968	0.987	0.989
0.4	0.959	0.957	0.955	0.931	0.879	0.945	0.955
0.6	0.902	0.896	0.892	0.840	0.758	0.872	0.891
0.8	0.812	0.794	0.785	0.705	0.626	0.756	0.769
0.9		0.711	0.699	0.616	0.562	0.669	0.664
0.999		0.551	0.513	0.502	0.501	0.509	0.502
1.0	0.635		0.500	0.500	0.500	0.500	0.500

[a]From Ref. 8.

approximation to the SSF than d^{-3} (Ref. 7) and $I_{\mathrm{vBH}}(\zeta)$ (Ref. 1). Here

$$d = 2^{1/3}\left[\left[\frac{1+\zeta}{2}\right]^{5/3} + \left[\frac{1-\zeta}{2}\right]^{5/3}\right]^{1/2} , \qquad (42)$$

$$I_{\mathrm{vBH}}(\zeta) = 1 - \tfrac{1}{2}f(\zeta) , \qquad (43)$$

$$f(\zeta) = \frac{[(1+\zeta)^{4/3} + (1-\zeta)^{4/3} - 2]}{2(2^{1/3} - 1)} . \qquad (44)$$

The last column of Table I lists the SSF of Vosko, Wilk, and Nusair (VWN),[8]

$$I_{\mathrm{VWN}}(\zeta) = 1 - \frac{1}{2}\frac{1+\delta\zeta^4}{1+\delta}f(\zeta) , \qquad (45)$$

where

$$\delta = 3\pi^2 A(0)f''(0) - 1 \approx 0.574082 . \qquad (46)$$

By construction, Eq. (45) is exact to order ζ^2. We plot all these spin-scaling factors in the high-density limit in Fig. 1. Observe that $I_{\mathrm{VWN}}(\zeta)$ is slightly more accurate than $[g(\zeta)]^3$ for $\zeta < 0.87$. However, $I_{\mathrm{VWN}}(\zeta)$ displays incorrect behavior (i.e., finite slope) near $\zeta = 1$. $[g(\zeta)]^3$, on the other hand, behaves more correctly near $\zeta = 1$.

The total correlation energy of the uniform electron gas is $E_c = \int d^3r\, n\varepsilon_c(n,\zeta)$. Sometimes it is of interest to separate E_c into $\uparrow\uparrow$, $\downarrow\downarrow$, and $\uparrow\downarrow$ terms, where $E_c^{\uparrow\uparrow}$ arises from $n_\uparrow$ alone (with no contribution from $n_\downarrow$). From

Eqs. (17) and (25)–(27) we find, in the high-density limit,

$$E_c^{\uparrow\uparrow}/E_c = (1+\zeta)/[4I(\zeta)] . \qquad (47)$$

In conclusion, we find the spin-scaling factor for the correlation energy of a uniform electron gas in the high-density limit. As a decent approximation, $[g(\zeta)]^3$ shows the proper qualitative behavior near $\zeta = 0$ and 1. Moreover, as discussed below, $g(\zeta)$ is the SSF for the exchange coefficient (when $\nabla\zeta$ can be neglected) and a good approximation to the SSF for the correlation coefficient of the density-gradient expansion.

II. ELECTRON GAS WITH SLOWLY VARYING SPIN DENSITIES

The exchange-correlation energy $(E_{\mathrm{xc}} = E_x + E_c)$ of a many-electron system has a spin-density gradient expansion[9]

$$\begin{aligned}
E_{\mathrm{xc}} = &\int d^3r\, n\varepsilon_{\mathrm{xc}}(n,\zeta) \\
&+ \int d^3r[C_{\mathrm{xc}}^{\uparrow\uparrow}(n,\zeta)|\nabla n_\uparrow|^2/n_\uparrow^{4/3} \\
&+ C_{\mathrm{xc}}^{\downarrow\downarrow}(n,\zeta)|\nabla n_\downarrow|^2/n_\downarrow^{4/3} \\
&+ C_{\mathrm{xc}}^{\uparrow\downarrow}(n,\zeta)\nabla n_\uparrow \cdot \nabla n_\downarrow/(n_\uparrow n_\downarrow)^{2/3}] , \qquad (48)
\end{aligned}$$

valid for slowly varying spin densities. By symmetry, $C_{\mathrm{xc}}^{\downarrow\downarrow}(n,\zeta) = C_{\mathrm{xc}}^{\uparrow\uparrow}(n,-\zeta)$ and $C_{\mathrm{xc}}^{\uparrow\downarrow}(n,\zeta) = C_{\mathrm{xc}}^{\uparrow\downarrow}(n,-\zeta)$. The exchange coefficients are constants: $C_x^{\uparrow\uparrow} = C_x^{\downarrow\downarrow}$ and

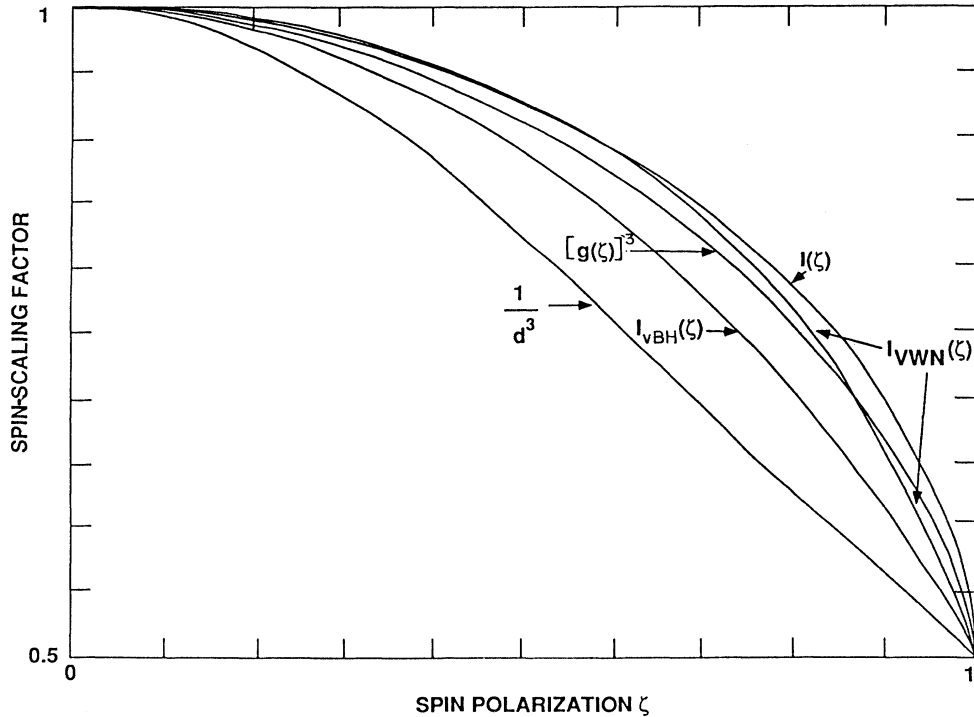FIG. 1. Various spin-scaling factors for the correlation energy of a uniform electron gas in the high-density limit vs spin polarization ζ. $I(\zeta)$ is exact. See Eqs. (32) and (41)–(46).

$C_x^{\uparrow\downarrow}=0$. In the high-density limit, the correlation coefficients $C_c^{\sigma\sigma'}$ depend only upon the local spin polarization ζ, not upon n. A parametrization of this dependence has been given by Rasolt and Davis.[10]

For $|\nabla\zeta|=0$, Eq. (48) simplifies to

$$E_{xc}=\int d^3r[n\varepsilon_{xc}(n,\zeta)+\mathcal{C}_{xc}(n,\zeta)|\nabla n|^2/n^{4/3}] , \qquad (49)$$

$$\mathcal{C}_{xc}(n,\zeta)=C_{xc}^{\uparrow\uparrow}(n,\zeta)\left[\frac{1+\zeta}{2}\right]^{2/3}+C_{xc}^{\downarrow\downarrow}(n,\zeta)\left[\frac{1-\zeta}{2}\right]^{2/3}$$

$$+C_{xc}^{\uparrow\downarrow}(n,\zeta)\left[\frac{1+\zeta}{2}\right]^{1/3}\left[\frac{1-\zeta}{2}\right]^{1/3} . \qquad (50)$$

Thus the exchange coefficient scales exactly as

$$\mathcal{C}_x(\zeta)/\mathcal{C}_x(0)=g(\zeta) , \qquad (51)$$

where $\mathcal{C}_x(0)=-0.001\,667\,21$. (For present purposes, we use Sham's exchange coefficient,[11] ignoring Kleinman's order-of-limits problem.[12]) For correlation, we use the Rasolt-Davis parametrization[10] of the high-density limit to find (see Table II)

$$\mathcal{C}_c(n,\zeta)/\mathcal{C}_c(n,0)\approx g(\zeta) , \qquad (52)$$

with an error of less than 1%. [Equation (52) is exact at $|\zeta|=0$ and 1, and the error is less than 0.5% for $|\zeta|\leq 0.6$.] In contrast, the spin-scaling factor $d^{-1}(\zeta)$ proposed by Hu and Langreth[7] for the correlation coefficient [see Eq. (42)] makes an error as great as 5.5%. Thus we propose Eq. (52) as a useful relationship for gradient expansions and generalized gradient approximations.[7,13] Because the n dependence of $\mathcal{C}_c(n,0)$ is very weak[14,15] within or beyond the RPA, Eq. (52) might well be valid over a broad range of densities.

When $|\nabla\zeta|\neq 0$, we must add to Eq. (49) the following terms derived from Eq. (48):

$$\int d^3r\{-\mathcal{D}_{xc}(n,\zeta)\nabla n\cdot\nabla\zeta/[n^{1/3}(1-\zeta^2)^{2/3}]$$

$$+\mathcal{E}_{xc}(n,\zeta)|\nabla\zeta|^2 n^{2/3}/(1-\zeta^2)^{4/3}\} , \qquad (53)$$

where $\mathcal{D}(-\zeta)=-\mathcal{D}(\zeta)$ and $\mathcal{E}(-\zeta)=\mathcal{E}(\zeta)$. Table II shows the exchange (x) and correlation (c) contributions to the coefficients $\mathcal{D}$ and $\mathcal{E}$ in the high-density limit.

Note that $\mathcal{E}_c$ is so small that the $|\nabla\zeta|^2$ contribution to the correlation energy is never important. In a spin-density wave of a uniform-density electron gas, and in some atoms (e.g., H and He), the $\nabla n\cdot\nabla\zeta$ contribution to the correlation energy is zero. In some other atoms (e.g., Li), this contribution is positive like the $|\nabla n|^2$ contribution, but much smaller than the latter. Thus, like Hu and Langreth,[7] we drop the $\nabla n\cdot\nabla\zeta$ and $|\nabla\zeta|^2$ contributions to the correlation energy.

APPENDIX A: ANALYTIC INTEGRATION OF EQ. (29) FOR THE SPIN-SCALING FACTOR

Denote

$$F(y_1,y_2)=\int_0^\infty du\, R\left[\frac{u}{y_1}\right]R\left[\frac{u}{y_2}\right]$$

$$=\int_0^\infty du\left[1-\frac{u}{y_1}\arctan\left[\frac{y_1}{u}\right]\right]$$

$$\times\left[1-\frac{u}{y_2}\arctan\left[\frac{y_2}{u}\right]\right] . \qquad (A1)$$

It follows that

$$\frac{\partial F(y_1,y_2)}{\partial y_2}=\frac{1}{y_2}G(y_1,y_2) , \qquad (A2)$$

where

$$G(y_1,y_2)=\int_0^\infty du\left[1-\frac{u}{y_1}\arctan\left[\frac{y_1}{u}\right]\right]$$

$$\times\left[\frac{u}{y_2}\arctan\left[\frac{y_2}{u}\right]-\frac{u^2}{u^2+y_2^2}\right] . \qquad (A3)$$

Now

TABLE II. Exchange (x) and correlation (c) coefficients for the spin-density gradient expansion, Eqs. (49) and (53), in the high-density limit. Here $\mathcal{C}_x(0)=-0.001\,667\,21$ (Ref. 11) [or $-0.002\,381\,73$ (Ref. 12)], and $\mathcal{C}_c(0)=0.004\,231\,5$ (Ref. 10).

ζ	$\dfrac{\mathcal{C}_x(\zeta)}{\mathcal{C}_x(0)}$	$\dfrac{\mathcal{D}_x(\zeta)}{\mathcal{C}_x(0)}$	$\dfrac{\mathcal{E}_x(\zeta)}{\mathcal{C}_x(0)}$	$\dfrac{\mathcal{C}_c(\zeta)}{\mathcal{C}_c(0)}$	$\dfrac{\mathcal{D}_c(\zeta)}{\mathcal{C}_c(0)}$	$\dfrac{\mathcal{E}_c(\zeta)}{\mathcal{C}_c(0)}$
0.0	1.000	0.000	1.000	1.000	0.000	-0.037
0.2	0.996	0.133	1.009	0.995	0.090	-0.033
0.4	0.981	0.260	1.036	0.979	0.173	-0.020
0.6	0.955	0.373	1.083	0.951	0.241	-0.001
0.8	0.911	0.449	1.153	0.903	0.272	0.021
0.9	0.875	0.445	1.200	0.866	0.251	0.029
0.999	0.798	0.146	1.259	0.797	0.055	0.009
1.0	0.794	0.000	1.260	0.794	0.000	0.000

$$\frac{\partial G(y_1,y_2)}{\partial y_2} = -\frac{1}{y_2}G(y_1,y_2)$$

$$+2y_2\int_0^\infty du\left[1-\frac{u}{y_1}\arctan\left[\frac{y_1}{u}\right]\right]$$

$$\times\left[\frac{1}{u^2+y_2^2}-\frac{y_2^2}{(u^2+y_2^2)^2}\right].$$

$$(A4)$$

With the help of the following results:[16]

$$\int_0^\infty du\frac{1}{u^2+y_2^2}=\frac{\pi}{2y_2},$$

$$(A5)$$

$$\int_0^\infty du\frac{u\arctan\left[\frac{y_1}{u}\right]}{u^2+y_2^2}=\frac{\pi}{2}\ln\left[\frac{y_1+y_2}{y_2}\right],$$

$$(A6)$$

$$\int_0^\infty du\frac{1}{(u^2+y_2^2)^2}=\frac{\pi}{4y_2^3},$$

$$(A7)$$

$$\int_0^\infty du\frac{u\arctan\left[\frac{y_1}{u}\right]}{(u^2+y_2^2)^2}=\frac{\pi y_1}{4y_2^2(y_1+y_2)},$$

$$(A8)$$

we perform the integrations in Eq. (A4) and find after reorganization

$$y_2\frac{\partial G}{\partial y_2}+G=\pi y_2-\frac{\pi}{2}y_1+\frac{\pi}{2}y_1^2\frac{1}{y_1+y_2}$$

$$-\frac{\pi}{y_1}y_2^2\ln(y_1+y_2)+\frac{\pi}{y_1}y_2^2\ln y_2.$$

$$(A9)$$

Integrating this equation results in

$$y_2G(y_1,y_2)=\frac{\pi}{3}y_2^2-\frac{\pi}{6}y_1y_2+\frac{\pi}{6}y_1^2\ln(y_1+y_2)$$

$$-\frac{\pi}{3y_1}y_2^3\ln(y_1+y_2)$$

$$+\frac{\pi}{3y_1}y_2^3\ln y_2+A(y_1),$$

$$(A10)$$

where $A(y_1)$ is an undetermined function of y_1 alone.

Inserting Eqs. (A10) into Eq. (A2) and integrating the resultant equation, we get

$$F(y_1,y_2)=\frac{\pi}{6}y_2-\frac{\pi}{6}\left[\frac{y_1^2}{y_2}+\frac{y_2^2}{y_1}\right]\ln(y_1+y_2)$$

$$+\frac{\pi}{6y_1}y_2^2\ln y_2-\frac{A(y_1)}{y_2}+B(y_1),$$

$$(A11)$$

where $B(y_1)$ is another undetermined function of y_1.

Because Eq. (A1) is symmetric in y_1 and y_2, we must have

$$A(y_1)=-\frac{\pi}{6}y_1^2\ln y_1,$$

$$(A12)$$

$$B(y_1)=\frac{\pi}{6}y_1.$$

$$(A13)$$

Hence Eq. (A11) becomes

$$F(y_1,y_2)=F(y_2,y_1)$$

$$=\frac{\pi}{6}(y_1+y_2)+\frac{\pi}{6}\left[\frac{y_2^2}{y_1}\ln y_2+\frac{y_1^2}{y_2}\ln y_1\right]$$

$$-\frac{\pi}{6}\left[\frac{y_1^2}{y_2}+\frac{y_2^2}{y_1}\right]\ln(y_1+y_2).$$

$$(A14)$$

Finally Eq. (32) is obtained after the substitution of Eq. (A14) into Eq. (29).

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