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Nonlocal density functionals and the linear response of the homogeneous electron gas

I. I. Mazin

*Code 6691, Naval Research Laboratory, Washington, DC 20375**and CSI, George Mason University, Fairfax, Virginia 22030*

D. J. Singh

Code 6691, Naval Research Laboratory, Washington, DC 20375

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The known and usable truly nonlocal functionals for exchange-correlation energy of the inhomogeneous electron gas are the ADA (average density approximation) and the WDA (weighted density approximation). ADA, by design, yields the correct linear response function of the uniform electron gas. The WDA is constructed so that it is exact in the opposite limit of one-electron systems, and it was conjectured that the WDA is also accurate in the uniform gas limit. To test this conjecture, we derive an expression for the linear response of the uniform gas in the WDA, and calculate it for several flavors of the WDA. We then compare the results with the Monte Carlo data on the exchange-correlation local-field correction, and identify the weak points of conventional WDA in the homogeneous limit. We suggest how the WDA can be modified to improve the response function. The resulting approximation is a good one in both opposite limits. Future testing should show whether it will also be better than conventional WDA and ADA for practical nonlocal density-functional calculations. [S0163-1829(98)06512-6]

Calculations based on the Kohn-Sham formulation of density-functional theory¹ have become a prominent tool in condensed-matter physics. Current work is dominated by local-density approximation (LDA) studies, in which the exchange-correlation functional is a local function of the density. However, as the number and accuracy of calculations has increased, so has the number of well-documented cases where the LDA is inadequate and with this interest in beyond LDA approaches, e.g., the generalized gradient approximation (GGA), which depends locally on both the density and its gradient.

Modern GGA functionals do improve upon LDA results for a wide range of problems. However, several studies have pointed out deficiencies in GGA functionals, e.g., difficulties in describing ferroelectric materials, and cases of overcorrection of LDA errors particularly in materials containing heavy atoms. Both the LDA and GGA fail to provide a correct description of the static short-range linear response of the homogeneous electron gas. All this leads to the question of the extent to which truly nonlocal functionals are practical and able to correct the deficiencies of LDA and GGA methods.

The first efforts at developing practical nonlocal functionals date from the 1970's when the average density approximation² (ADA) and weighted density approximation³⁻⁵ (WDA) were proposed. However, over most of the intervening period the field has been relatively dormant, in part because of the success of the simpler LDA and GGA schemes and in part because it was widely thought that such schemes could not be implemented in a computationally tractable fashion. However, at least for the WDA, computationally

efficient algorithms are now known⁶⁻⁸ and benchmark calculations have been reported. In the cases that have been studied ground-state properties are generally improved over the LDA.⁹

Both methods exploit the general expression for E_{xc} ,

$$E_{xc} = \frac{e^2}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} G(\mathbf{r},\mathbf{r}') \{n(\mathbf{r})\} d\mathbf{r}d\mathbf{r}', \quad (1)$$

where the function $G(\mathbf{r},\mathbf{r}')$ is also a functional of the total electronic density $n(\mathbf{r})$. A rigorous expression for G can be derived¹ in terms of coupling constant averaged pair-correlation function:

$$G(\mathbf{r},\mathbf{r}') = \int_0^1 [g(\mathbf{r},\mathbf{r}';\lambda)\{n(\mathbf{r})\} - 1] d\lambda. \quad (2)$$

For the uniform gas this function, $G_0(|\mathbf{r}-\mathbf{r}'|,n)$, is known with high accuracy,¹⁰ but for an arbitrary system there is no practical way to use this formula. The LDA instead of Eq. (1) uses $(e^2/2) \int d\mathbf{r}d\mathbf{r}' n(\mathbf{r})n(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'| + \int n(\mathbf{r}) \epsilon_{xc}[n(\mathbf{r})] d\mathbf{r}$, so that E_{xc} becomes $E_{xc}^{LDA} = \int n(\mathbf{r}) \epsilon_{xc}[n(\mathbf{r})] d\mathbf{r}$, ϵ_{xc} being the density of exchange-correlation energy of the uniform gas. The LDA is incorrect in the two important limits: the fully localized, i.e., a one electron system, and the fully delocalized limit, i.e., homogeneous electron gas. In the former case the LDA gives a spurious self-interaction with energy $(e^2/2) \int d\mathbf{r}d\mathbf{r}' n(\mathbf{r})n(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'| + \int n(\mathbf{r}) \epsilon_{xc}[n(\mathbf{r})] d\mathbf{r}$, which is widely thought¹¹ to be a key problem with the LDA. In the homogeneous limit, the LDA gives the correct exchange-correlation energy, but the *changes* of this energy upon small

perturbations are not properly described; the second variation of E_{xc} with density, i.e., the exchange-correlation part of the dielectric response, $K_{xc}(\mathbf{r}-\mathbf{r}') = \delta^2 E_{xc} / \delta n(\mathbf{r}) \delta n(\mathbf{r}')$, is a δ function, which is incorrect. The Fourier transform of $K_{xc}(r)$ in LDA is independent of the wave vector. Since LDA is exact for the uniform gas, K_{xc}^{LDA} corresponds to the correct K_{xc} at $q=0$. GGA's also give correct behavior at $q=0$, but become even worse than the LDA at high q 's.

The two nonlocal expressions for E_{xc} , the WDA and ADA, aimed at correcting one or the other of these two limits. The former uses the general expression (1), but instead of the actual function G uses a model function, defined so that the one-electron limit is honored. This begins by choosing a generic expression for G , which depends on one parameter \bar{n} , to be defined later. In the original papers it was suggested that $G(\mathbf{r}, \mathbf{r}', \bar{n}) = G_h(\mathbf{r}, \mathbf{r}', \bar{n}) = \int_0^1 [g(\mathbf{r}, \mathbf{r}'; \lambda, \bar{n}) - 1] d\lambda$, where g is the pair-correlation function of the homogeneous electron gas. Later it was realized¹² that other choices of G may be better than G_h . In the WDA \bar{n} is a function of \mathbf{r} , but differs from $n(\mathbf{r})$, and is chosen so that $\int G[\mathbf{r}, \mathbf{r}', \bar{n}(\mathbf{r})] n(\mathbf{r}') d\mathbf{r}' = -1$. This assures that for a one-electron system E_{xc} cancels the self-interaction exactly. Moreover, in fact G need not be related to the actual pair correlation function of the system: although Eq. (1) has the same functional form as the WDA energy, the fact that G^{WDA} is a function of an averaged density \bar{n} , not a functional of the true density $n(\mathbf{r})$, tells us that the best approximations for G^{WDA} may be rather different from the physical function G defined in Eq. (2).

In the ADA $n(\mathbf{r}')$ in Eq. (1) is substituted by $n(\mathbf{r})$, which results in $E_{xc}^{\text{ADA}} = \int n(\mathbf{r}) \epsilon_{xc}[\bar{n}(\mathbf{r})] d\mathbf{r}$. Then $\bar{n}(\mathbf{r})$ is defined as $\bar{n}(\mathbf{r}) = \int w[|\mathbf{r}-\mathbf{r}'|, \bar{n}(\mathbf{r})] n(\mathbf{r}') d\mathbf{r}'$, and the universal function w is chosen so that $\delta^2 E_{xc}^{\text{ADA}} / \delta n(\mathbf{r}) \delta n(\mathbf{r}')$ gives the correct K_{xc} for the uniform gas. Contrary to the WDA, the ADA is not self-interaction free in one electron systems.

From the beginning there was substantial interest in the behavior of WDA in the delocalized limit.¹ Williams and von Barth¹³ suggested that the WDA should give substantial improvement over the LDA in this limit, but until now no systematic study has been reported. If this conjecture is true, the WDA has a great advantage over any other known approximation to the DFT in the sense that it accurately reproduces two key physical limits. Furthermore, even if it is not entirely correct, the next question is, whether or not an approximation based on the WDA exists that does provide proper limiting behavior. In this paper we derive an expression for K_{xc} in the WDA, calculate K_{xc} for popular flavors of WDA, and discuss construction of a WDA method with improved K_{xc} .

We start by deriving a closed expression for K_{xc} in the WDA for arbitrary G . First some notation: denote the product $(e^2/r)G(r)$ as $W(r)$, use atomic units ($e=1, \hbar=1$), and use primes for the derivative with respect to the density argument, e.g., $G' = dG/dn$. We also introduce two functions, reflecting implicit dependence of the weighted density \bar{n} on variations of the real density, and explicitly satisfying the translational symmetry constraints:

$$d(\mathbf{r}' - \mathbf{r}) = \delta \bar{n}(\mathbf{r}') / \delta n(\mathbf{r}) \quad (3)$$

$$f(\mathbf{r}' - \mathbf{r}, \mathbf{r}' - \mathbf{r}'') = \frac{\delta^2 \bar{n}(\mathbf{r}')}{\delta n(\mathbf{r}) \delta n(\mathbf{r}'')} = \frac{\delta d(\mathbf{r}' - \mathbf{r})}{\delta n(\mathbf{r}'')} \quad (4)$$

Using the WDA expression for the exchange-correlation energy,

$$E_{xc} = (1/2) \int n(\mathbf{r}) n(\mathbf{r}') W[|\mathbf{r}-\mathbf{r}'|, \bar{n}(\mathbf{r})] d\mathbf{r} d\mathbf{r}', \quad (5)$$

we can express K_{xc} in terms of functions d and f , and we can find these functions using the normalization condition,

$$\int d\mathbf{r}' n(\mathbf{r}') G[|\mathbf{r}-\mathbf{r}'|, \bar{n}(\mathbf{r})] = -1. \quad (6)$$

For instance, by taking the functional derivative of Eq. (6) we find that

$$G_0(r-r') + n \int G'_0(r-r'') d(r-r') = 0, \quad (7)$$

where subscript 0 corresponds to the homogeneous (unperturbed) system. We proceed then in reciprocal space, which corresponds to using density perturbation of the form $\delta n(\mathbf{r}) = n_q e^{i\mathbf{q}\cdot\mathbf{r}}$. Let W_q , G_q , d_q , and $f_{p,q}$ will be the Fourier transforms of the corresponding functions. Then the above equation can be written as

$$\begin{aligned} G_q + n G'_0 d_q &= 0 \\ d_q &= -G_q / n g'_0. \end{aligned} \quad (8)$$

Since at $q \rightarrow 0$ the LDA should be restored,

$$\int d\mathbf{r}' W[|\mathbf{r}-\mathbf{r}'|, n] = 2\epsilon_{xc}/n. \quad (9)$$

From this it immediately follows that

$$G_0 = -1/n, \quad W_0 = 2\epsilon_{xc}/n. \quad (10)$$

Thus $d_q = -n G_q$. An analogous procedure, applied to Eq. (7) instead of Eq. (6) gives us $f_{p,q}$. In fact, we need only diagonal elements, $f_{q,-q}$, for which we find $f_{q,-q} = 2n G_q (n G'_q + G_q)$. The second variation of Eq. (5) in terms of d and f is

$$K_{xc}(q) = W_q + n d_q W'_q + n d_q W'_0 + \frac{n^2}{2} (d_q^2 W''_0 + n^2 f_{q,-q} W'_0),$$

resulting in

$$K_{xc}(q) = W_q - n^2 G_q (W'_q + W'_0) + n^2 (n^2 G_q^2 W'_0)' / 2. \quad (11)$$

The original formulation of the WDA used the corresponding homogeneous electron gas function for G . Since then, three forms of G have been used in the calculations, all of which result in improvement over LDA (in the admittedly limited number of tests performed to date). These are the following: the function G derived for the uniform gas by Perdew and Wang,¹⁰ the Gunnarsson-Jones function $G^{\text{GJ}}(r) = C_1(n) \{1 - \exp(-[r/C_2(n)]^{-5})\}$, and the Gritsenko *et al.*¹⁴ function $G^{\text{GRBA}}(r) = C_1(n) (\exp\{-[r/C_2(n)]^k\})$, $k=1.5$ (note that the uniform gas function¹⁰ is approximately given by the same expression with $k=2$). We

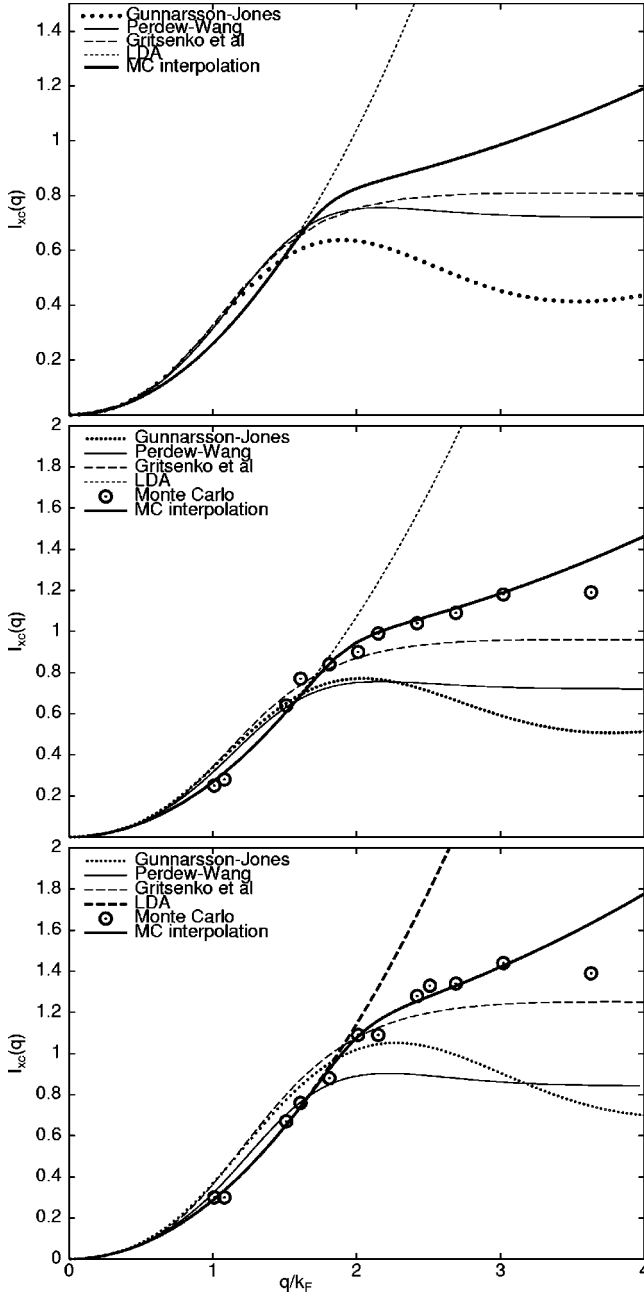


FIG. 1. Exchange-correlation local-field factor in the WDA of Ref. 12 (Gunnarsson-Jones), Ref. 14 (Gritsenko *et al.*), and derived from the homogeneous electron gas pair-correlation function (Perdew-Wang), as compared with the Monte Carlo results (Monte Carlo), and the interpolating formula thereof (MC interpolation), as given in Ref. 15. Densities, from top to bottom, correspond to $r_s = 1, 2, 5$.

tested these functions for the densities $r_s = 1, 2$, and 5 and obtained modest agreement with the Monte Carlo results¹⁵ (Cf. Fig. 1, where we plotted calculated exchange-correlation local-field factor $I_{xc}(q) = (q^2/4\pi)K_{xc}(q)$, and compare it with Monte Carlo data¹⁵). By construction, $K_{xc}(0)$ is correct (and is in fact the LDA value). At $q \geq 1.5 - 1.8k_F$ K_{xc} falls below its LDA value and continues to decrease at large q 's. However, a closer look reveals two major disagreements: first, $I_{xc}^{WDA}(q)$ is considerably larger than the Monte Carlo data for the wave vectors between $\approx 0.5k_F$ and $1.5k_F$. Sec-

ond, $I_{xc}(q)$ in the WDA tends to a constant value, while in Monte Carlo calculations it is $K_{xc}(q)$ itself that has a finite limit at $q \rightarrow \infty$, and $I_{xc}(q) \rightarrow \text{const} \times q^2$ at $q \rightarrow \infty$.

Can one correct these two deficiencies without compromising the correct one-electron limit of the WDA? In fact, it was noticed long ago¹² that there is no particular reason to use the homogeneous electron gas pair-correlation function for G (nor, as discussed above, the exact pair correlation function for the inhomogeneous system, even if it had been known). Since using G_h in the WDA does not guarantee any improvement in describing properties of the homogeneous gas itself, one may use the freedom in $G(r)$ to adjust the WDA so that the calculated local field factor (and thus linear response function) is as accurate as possible. Inversion of Eq. (11) yields $G(q)$ for a given $K_{xc}(q)$. It does not guarantee, however, that the result will be physical. So, as a first step, let us analyze Eq. (11). For this purpose, we write $G_q = -\varphi(q/Q)/n$, with the condition $\varphi(0) = 1$, where Q is some constant (both the Gunnarsson-Jones and the Gritsenko *et al.* functions are of this form). Then

$$W_p = \frac{1}{8\pi^3} \int d^3q \frac{4\pi}{|\mathbf{q}-\mathbf{p}|^2} G_q = \frac{1}{\pi p} \int_0^\infty q dq \ln \left| \frac{q+p}{q-p} \right| G_q, \quad (12)$$

$$W_0 = \frac{2}{\pi} \int_0^\infty G_q dq = -\frac{2Q}{\pi n} \int_0^\infty \varphi(x) dx = \frac{2\epsilon_{xc}(n)}{n}.$$

If we now define $Q(n) = -\pi\epsilon_{xc}(n)$, then the second condition on $\varphi(x)$ becomes $\int_0^\infty \varphi(x) dx = 1$. These two conditions reduce our freedom to adjust G_q : since the characteristic size of $\varphi(x)$ is of order of 1, the wave-vector dependence of G_q is defined by the ratio $q/Q = -q/\pi\epsilon_{xc}$. This characteristic wave vector Q is substantially smaller than $2k_F$, the number at which real local-field factor changes its behavior from low- q to the high- q limit. A monotonic function $\varphi(x)$ does not reproduce this feature, which explains why existing WDA parametrizations put the hump in K_{xc} at too low q . Nonmonotonic and explicitly density-dependent functions $\varphi(x)$ may be able to shift the hump to its correct position at $q = 2k_F$. It is still an open question whether or not a physically sound function can be found with this property.

However, even if the “ $2k_F$ ” problem is fixed, another, probably even more important problem remains: the short-wavelength behavior of K_{xc} . As one can see from Eq. (12), if $G(q) \rightarrow 0$ at $q \rightarrow \infty$, then $W_p \rightarrow \text{const}/p^2$ at $p \rightarrow \infty$, and so does, according to Eq. (11), K_{xc} . On the other hand, as mentioned above, the correct $I_{xc}(q)$ diverges at $q \rightarrow \infty$ as q^2 , much in the same manner as I_{xc}^{LDA} , but with a smaller coefficient. This result was predicted by Holas¹⁶ and is physically important: it reflects the fact that E_{xc} is not solely an interaction energy, but also includes the exchange-correlation contribution to kinetic energy (which is essentially local and decays slower with q than the interaction part of E_{xc}). The present WDA misses the corresponding physics. Fortunately, this is easy to correct. Farid *et al.*¹⁷ tabulated the coefficient γ that defines the asymptotic behavior of $K_{xc}(q \rightarrow \infty)$ as $K_{xc}(q \rightarrow \infty) = -(4\pi/q^2)\gamma(n)(q^2/k_F^2)$. These values can be fit as

$$\gamma(n) = \left(\frac{9\pi}{4}\right)^{4/3} \frac{f(\sqrt{r_s})}{15} \quad f(x) = \frac{x(a+bx)}{(1+cx+dx^2)},$$

where $a = 0.026319$, $b = 0.00823859$, $c = -0.173199$, and $d = 0.233081$. Let us now modify the function $G(r)$:

$$G(r) = G_1(r) + G_2(r) = A \delta(r)/4\pi r + G_2(r). \quad (13)$$

Since $\int G_1(r)r^2 dr = 0$, the normalization condition for G_2 is the same as for G itself. Since $4\pi \int G_1(r)r dr = A$, the LDA limit condition for G_2 becomes

$$4\pi \int G_2(r)r dr = 2\tilde{\epsilon}_{xc}(n)/n, \quad (14)$$

$$\tilde{\epsilon}_{xc}(n) = \epsilon_{xc}(n) - An/2.$$

Thus

$$A = -4\pi\gamma(n)/k_F^2 = -\left(\frac{9\pi}{4}\right)^{2/3} \frac{4\pi r_s^2}{15} f(\sqrt{r_s})$$

$$= -3.0856r_s^2 f(\sqrt{r_s}),$$

$$\tilde{\epsilon}_{xc}(n) = \epsilon_{xc}(n) + \frac{0.368317}{r_s} f(\sqrt{r_s}). \quad (15)$$

Now $G_p = G_{2p}$, $W_p = A + W_{2p}$, and $W'_p = A' + W'_{2p}$,

$$K_{xc}(q) = A + W_{2q} - n^2 G_{2q}(A' + W'_{2q} + W'_{2,0})$$

$$+ n^2(n^2 G'_q W'_{2,0})' = A - n_0^2 G_{2p} A' + \tilde{K}_{xc}, \quad (16)$$

where \tilde{K}_{xc} is calculated from $\tilde{\epsilon}_{xc}$ in exactly the same way as K_{xc} is calculated from ϵ_{xc} . The corresponding functional for the exchange-correlation energy is

$$E_{xc}^{AWDA} = \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{(|\mathbf{r}-\mathbf{r}'|)} G[|\mathbf{r}-\mathbf{r}'|, \bar{n}(\mathbf{r})] d\mathbf{r} d\mathbf{r}'$$

$$+ \int n(\mathbf{r}) \frac{0.368317}{\bar{r}_s(\mathbf{r})} f[\sqrt{\bar{r}_s(\mathbf{r})}] d\mathbf{r}. \quad (17)$$

Here $4\pi\bar{r}_s^3/3 = \bar{n}$, and $G(r)$ is normalized to $\tilde{\epsilon}_{xc}(\bar{n})$ instead of $\epsilon_{xc}(\bar{n})$. In practice, the first term gives rise to the standard expression for the WDA potential,^{5,4} and the second yields two additional terms, one from the variation of $n(\mathbf{r})$, and the other arising from $\delta\bar{n}(\mathbf{r}')/\delta n(\mathbf{r})$. Since we do *not* require that $G(r) = \int_0^1 [g(r; \lambda, \bar{n}) - 1] d\lambda$, where g corresponds to the uniform gas, but rather consider it to be a flexible function satisfying two normalization conditions, further improvement of the method should be possible along the line described in the previous paragraph, namely, the freedom in choosing $G(r)$ can, be used to yield K_{xc} according to Eq. (16) close to the linear response of the homogeneous electron gas, including correct behavior near $q = 2k_F$. In Fig. 2, we show I_{xc} calculated according to Eq. (17) with the different functional form of $G(r)$. Clearly, the results are much better than either the LDA or ‘‘conventional’’ WDA. Interestingly, when the nearly exact Perdew-Wang function, or exponential function with $k=2$, are used, the resulting $I_{xc}(q)$ is close to

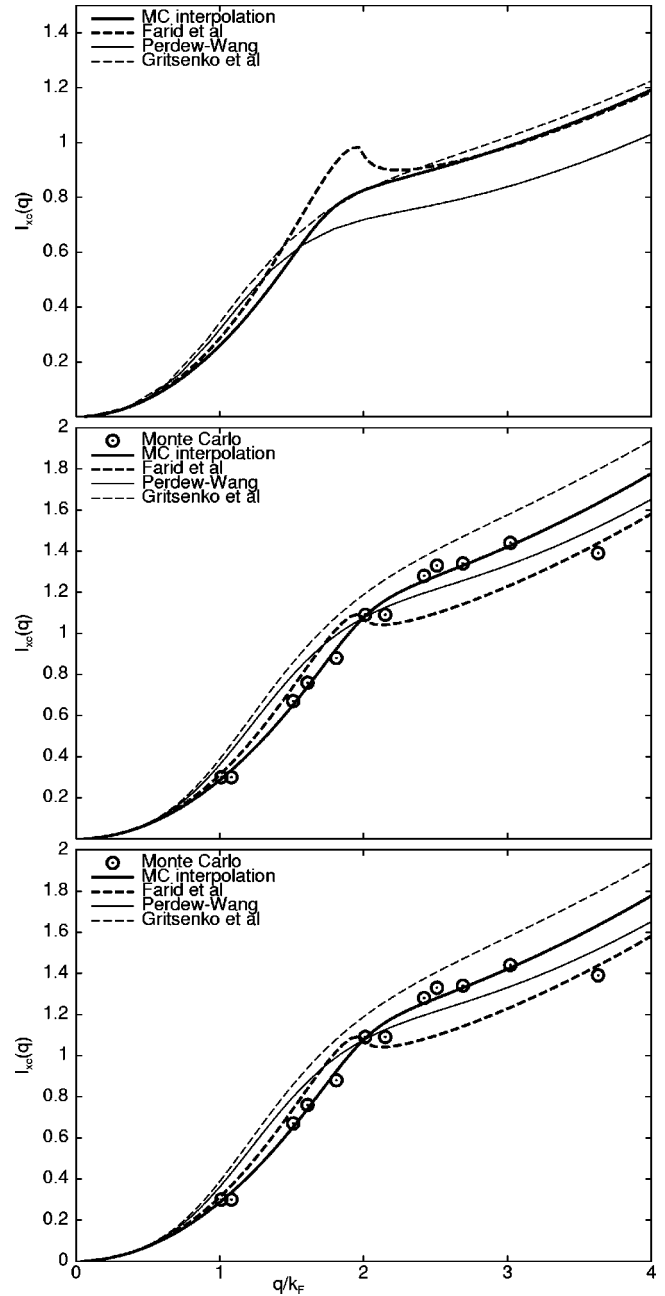


FIG. 2. $I_{xc}(q)$ as in Fig. 1, but for the modified WDA of Eq. (17). Also the analytical formula of Farid *et al.* (Ref. 17) is shown.

the analytical function derived by Farid *et al.* (arguably the best *analytically derived* $I_{xc}(q)$ available), while an exponential function with $k=1.5$ is close to the formula of Ref. 15, which is a fit to the Monte Carlo data. It is also worth mentioning that the correction of the form (13–15) is somewhat *ad hoc* and not unique in the sense that other mathematical forms exist that would yield correct asymptotic behavior of K_{xc} . However, any such form should include a δ -function component to ensure divergence of $K_{xc}(q)$ at $q \rightarrow \infty$.

To summarize, we have calculated the exchange-correlation local-field function K_{xc} in the WDA, and found that besides the expected improvement over the LDA it has two major deficiencies: (1) it does not have correct asymptotic behavior at $q \rightarrow \infty$, and (2) the characteristic fea-

ture at $q \approx 2k_F$ is displaced towards smaller q 's. The former can be easily corrected by adding a δ -function component to $G(r)$, which results in Eq. (17). The latter is harder to fix, but there are still unused degrees of freedom in the formalism that may be used to tune the behavior near $2k_F$. Intuitively (cf. Ref. 13), a method that retains the exact one-electron limit of WDA, and at the same time is accurate in

the opposite limit of the nearly uniform electron gas, seems promising for practical applications. However, tests on real materials will be needed to determine whether or not this modification of the WDA is advantageous in practice.

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¹*Theory of the Inhomogeneous Electron Gas*, edited by S. Lundqvist and N. H. March (Plenum, New York, 1983).

²O. Gunnarsson, M. Jonson, and B. I. Lundqvist, Phys. Lett. **59A**, 177 (1976).

³O. Gunnarsson, M. Jonson, and B. I. Lundqvist, Solid State Commun. **24**, 765 (1977).

⁴J. A. Alonso and L. A. Girifalco, Phys. Rev. B **17**, 3735 (1978).

⁵O. Gunnarsson, M. Jonson, and B. I. Lundqvist, Phys. Rev. B **20**, 3136 (1979).

⁶D. J. Singh, Phys. Rev. B **48**, 14 099 (1993); Ferroelectrics **194**, 299 (1997).

⁷M. Sadd and M. P. Teter, Phys. Rev. B **54**, 13 643 (1996).

⁸J. P. A. Charlesworth, Phys. Rev. B **53**, 12 666 (1996).

⁹Reference 8 is an exception, but note that the LDA results of this

work differ from most previous calculation.

¹⁰J. P. Perdew and Y. Wang, Phys. Rev. B **46**, 12 947 (1992).

¹¹See, e.g., S. Goedecker and C. J. Umrigar, Phys. Rev. A **55**, 1765 (1997) and references therein.

¹²O. Gunnarsson and R. O. Jones, Phys. Scr. **21**, 394 (1980).

¹³A. R. Williams and U. von Barth, in Ref. 1.

¹⁴O. V. Gritsenko, A. Rubio, L. C. Balbás, and J. A. Alonso, Chem. Phys. Lett. **205**, 348 (1993).

¹⁵S. Moroni, D. M. Ceperley, and G. Senatore, Phys. Rev. Lett. **75**, 689 (1995).

¹⁶A. Holas, in *Strongly Coupled Plasma Physics*, edited by F. J. Rogers and H. E. De Witt (Plenum, New York, 1987).

¹⁷B. Farid, V. Heine, G. E. Engel, and I. J. Robertson, Phys. Rev. B **48**, 11 602 (1993).