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

I.I. Mazin¹ and D.J. Singh²

¹Code 6691, Naval Research Laboratory, Washington, DC 20375
²CSI, George Mason University, Fairfax, VA

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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. WDA is constructed so that it is exact in the limit of one-electron systems. We derive an expression for the linear response of the uniform gas in the WDA, and calculate it for several flavors of 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, and should be useful for practical nonlocal density functional calculations.

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 non-local functionals are practical and able to correct the deficiencies of LDA and GGA methods.

The first efforts at developing practical non-local functionals date from the 1970’s when the weighted density approximation (WDA) and average density approximation (ADA) 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 known¹² and benchmark calculations have been reported. In the cases that have been studied ground state properties are generally improved over the LDA⁵.

Both methods were proposed in 1978–1979 by Alonso et al and Gunnarsson et al⁶.⁷. Both exploit the general expression for $E_{xc}$,

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

where the function $G(r,r')$ is also a functional of the total electronic density $n(r)$. A rigorous expression for $G$ can be derived³ in terms of coupling constant averaged pair correlation function: $G(r,r') = \int \int_{0}^{\pi} g(|r-r'|; \lambda) \{n(r)-1\}d\lambda$. For the uniform gas this function, $G_0(|r-r'|, n)$, is known with high accuracy⁸, but for an arbitrary system there is no practical way to use this formula. The LDA instead of Eq. (1) uses $(e^2/2) \int d\mathbf{r}d\mathbf{r'} n^2(r) G_0(|r-r'|, n(r)/|r-r'| + \int n(r) \epsilon_{xc}[n(r)]d\mathbf{r}$, $\epsilon_{xc}$ 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 $(e^2/2) \int d\mathbf{r}d\mathbf{r'} n(r)n(r')/|r-r'|$ + $\int n(r) \epsilon_{xc}[n(r)]d\mathbf{r}$, which is widely thought⁹ 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, $K_{xc}(r-r') = \delta^2 E_{xc}/\delta n(r)\delta n(r')$, is a delta 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 $q = 0$. GGAs also give correct behavior at $q = 0$, but become even worse than the LDA at high $q$’s.

The two nonlocal expressions for $E_{xc}$, 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 $\tilde{n}$, to be defined later. In the original papers it was suggested that $G(r,r', \tilde{n}) = G_h(r,r', \tilde{n}) = \int_{0}^{\pi} g(|r-r'|; \lambda, \tilde{n}) - 1)d\lambda$, where $g$ is the pair correlation function of the homogeneous electron gas. Later it was
realized\(^{10}\) that other choices of \(G\) may be better than \(G_{h}\). In the WDA \(\bar{n}\) is a function of \(r\), and differs from \(n(r)\), and is chosen so that \(\int G[r, r', \bar{n}(r)]d\mathbf{r'} = -1\). This assures that for a one electron system \(E_{xc}\) cancels the self-interaction exactly.

In the ADA \(n(r')\) in Eq. (1) is substituted by \(n(r)\), which results in \(E_{xc}^{ADA} = \int n(r)\epsilon_{xc}[\bar{n}(r)]d\mathbf{r}\). Then \(\bar{n}(r)\) is defined as \(\bar{n}(r) = \int \omega[|r - r'|, \bar{n}(r)]n(r')d\mathbf{r}'\), and the universal function \(\omega\) is chosen so that \(E_{xc}^{ADA}/\delta n(r)\delta n(r')\) 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 Barth\(^{11}\) suggested that the WDA should give substantial improvement over the LDA in this limit, but till 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 an improved WDA method.

We start by deriving a closed expression for \(K_{xc}\) in the WDA for an arbitrary \(G\). First some notation: we denote the product \((e^2/\pi)G(r)\) as \(W(r)\), use atomic units where \(\epsilon = 1\), \(\hbar = 1\), 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:

\[
d(r' - r) = \frac{\delta \bar{n}(r')/\delta n(r)}{\delta \bar{n}(r')/\delta n(r')} = \frac{\delta d(r' - r)}{\delta \bar{n}(r')}\quad (2)
\]

Using the WDA expression for the exchange-correlation energy,

\[
E_{xc} = (1/2) \int n(r)n(r')W[|r - r'|, \bar{n}(r)]d\mathbf{r}d\mathbf{r}', \quad (4)
\]

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

\[
\int dr'n(r')g[|r - r'|, \bar{n}(r)] = -1, \quad (5)
\]

and the LDA limit condition

\[
\int dr'W[|r - r'|, n] = 2\epsilon_{xc}/n. \quad (6)
\]

We proceed in reciprocal space, which corresponds to using density perturbation of the form \(\delta n(r) = \eta_{q}e^{iq\cdot r}\). Let \(W_{q}\), \(G_{q}\), \(d_{q}\) and \(f_{p,q}\) will be the Fourier transforms of the corresponding functions. Then the above condition can be written as

\[
G_{0} = -1/n, \quad W_{0} = 2\epsilon_{xc}/n. \quad (7)
\]

For \(d_{q}\) one finds \(d_{q} = -nG_{q}\). For \(f_{p,q}\) we need only diagonal elements, \(f_{q,-q} = 2nG_{q}(nG'_{q} + G_{q})\). In terms of \(d\) and \(f\), \(K_{xc}\) is

\[
K_{xc}(q) = W_{q} + n_{0}d_{q}W'_{q} + n_{0}d_{q}W''_{q} + \frac{n_{0}^2}{2}(d_{q}^{2}W''_{q} + n_{0}^{2}f_{q,-q}W'_{q}),
\]

resulting in

\[
K_{xc}(q) = W_{q} - n^{2}G_{q}(W'_{q} + W''_{q}) + n^{2}(n^{2}G_{q}^{2}W'_{q})/2. \quad (8)
\]

FIG. 1. Exchange-correlation local field factor in the WDA of Ref. 10 (Gunnarsson-Jones), Ref. 12 (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. 13. Densities, from top to bottom, correspond to \(r_{s} = 1, 2, 5\).
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 function $G$ derived for the uniform gas by Perdew and Wang\(^8\), the Gunnarsson-Jones function $G^{GJ}(r) = C_1(n)/(1 - \exp[-(\frac{\pi}{c_2(n)})^k])$, and the Gritsenko et al\(^12\) function $G^{GRBA}(r) = C_1(n)\exp[-(\frac{\pi}{c_2(n)})^k]$, $k = 1.5$ (note that the uniform gas function\(^8\) is approximately given by the same expression with $k = 2$). We tested these functions for the densities $r_s = 1, 2, 5$ and obtained modest agreement with the Monte Carlo results\(^13\) (Cf. Fig.1, where we plotted calculated exchange-correlation local field factor $I_{xc}(q) = \frac{2}{\pi^2}K_{xc}(q)$, and compare it with Monte Carlo data\(^13\)). By construction, $K_{xc}(0)$ is correct (and in fact the LDA value). At $q \gtrsim 1.5 - 1.8k_F$ $K_{xc}$ falls below its LDA value and continues to decrease at large $q$’s. However, a closer look reveals two major disagreements: first, $I_{WDA}^{xc}(q)$ is considerably larger than the Monte-Carlo data for the wave vectors between $\approx 0.5k_F$ and $1.5k_F$. Second, $I_{xc}(q)$ in WDA tends to a constant value equal to $\lim_{q \to \infty}[W_q/(4\pi/q^2)]$. In Monte Carlo calculations it is $K_{xc}(q)$ itself that has a finite limit at $q \to \infty$, while $I_{xc}(q) \to \text{const} \cdot q^2$ at $q \to \infty$. The latter result was predicted by Holas\(^14\) 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 in fact decays slower with $q$ than the interaction part of $E_{xc}$).

Can one correct these two deficiencies without compromising the correct one-electron limit of WDA? In fact, it was noticed long ago\(^10\) that there is no particular reason to use the homogeneous electron gas pair correlation function for $G$. Since using $G_h$ in 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.(8) 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. (8). For this purpose, we write $G_q = -\varphi(p/Q)/n$, 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

$$W_p = \frac{1}{8\pi^3} \int d^3q \frac{-4\pi}{|q - p|^2} G_q = \frac{1}{\pi p} \int_0^{\infty} dq dq \log \frac{|q + p|}{|q - p|} G_q$$

$$W_0 = \frac{2}{\pi} \int_0^{\infty} dq G_q dq = -\frac{2Q}{\pi n_0} \int_0^{\infty} \varphi(x) dx = \frac{2\varepsilon_{xc}(n_0)}{n_0}.$$

If we now define $Q(n) = -\pi \varepsilon_{xc}(n)$, 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 $q/Q = -q/\pi \varepsilon_{xc}$. At high density $Q = 1.33k_F$, and only close to $r_s \gtrsim 6$ does it approach $2k_F$, 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 bump in $K_{xc}$ at too low $q$. Nonmonotonic and explicitly density-dependent functions $\varphi(x)$ may be able to shift the bump 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 wave length behavior of $K_{xc}$. Fortunately, this is easy to correct. Farid et al\(^5\) tabulated the coefficient $\gamma$ that defines the asymptotic behavior of $K_{xc}(q \to \infty)$ as $K_{xc}(q \to \infty) = -\frac{\pi}{q^2} \gamma(n)\frac{q^2}{\pi p}$. These values can be fit as

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

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

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

Since $\int G_1(r)^2 dr = 0$, 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

$$4\pi \int G_2(r) r dr = 2\varepsilon_{xc}(n)/n, \quad \varepsilon_{xc}(n) = \varepsilon_{xc}(n) - An/2.$$

Thus

$$A = -\frac{4\pi \gamma(n)}{k_F^2} = -\left(\frac{9\pi}{4}\right)^{4/3} \frac{\pi r_p^2}{15} f(\sqrt{r_s}) = -3.08565 r_p^2 f(\sqrt{r_s}),$$

$$\varepsilon_{xc}(n) = \varepsilon_{xc}(n) + \frac{0.368037}{r_s} f(\sqrt{r_s})$$

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

$$K_{xc}(q) = A + W_{2q} - n^2 G_{2q}(A' + W_{2q} + W_{2,0}') + n^2 (n^2 G_{2,0}')' = A - n_0^2 G_{2p} A' + \tilde{K}_{xc},$$

where $\tilde{K}_{xc}$ is calculated from $\varepsilon_{xc}$ in exactly the same way as $K_{xc}$ is calculated from $\varepsilon_{xc}$. The corresponding functional for the exchange-correlation energy is...
\[ E^{AWDA}_{xc} = \frac{1}{2} \int \frac{n(r)n(r')}{W(|r - r'|)} G[|r - r'|, \bar{n}(r)] dr dr' + \int \frac{0.368317}{\bar{f}_s(r)} f \left[ \sqrt{\bar{f}_s(r)} \right] dr. \] (10)

Here \( 4\pi^2/3 = \bar{n} \), and \( G(r) \) is normalized to \( \bar{\epsilon}_{xc}(\bar{n}) \). Since we do not require that \( G(r) = f_0^{-1}[g(r; \lambda, \bar{n}) - 1]d\lambda \), 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, and should, be used to yield \( K_{xc} \) according to Eq. (9) close to the linear response of the homogeneous electron gas, including correct behavior near \( q = 2k_F \). In Fig. 2, we show \( I_{xc}(q) \) calculated according to Eq. 10 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 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. 13, which is a fit to the Monte Carlo data.

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 \( q \to \infty \), and (2) the characteristic feature at \( q = 2k_F \) is displaced towards smaller \( q \)'s. The former can be easily corrected by adding a delta-function component to \( G(r) \), which results in Eq. (10). The latter is harder to fix, but there are still unused degrees of freedom in the formalism which may be used to tune the behavior near \( 2k_F \). In our opinion, this new scheme for WDA calculations (Eq. 10) is currently most promising for practical applications.

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