Is the Local Density Approximation Exact for Short Wavelength Fluctuations?

Kieron Burke and John P. Perdew
Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118

David C. Langreth
Department of Physics and Astronomy, Rutgers University, P.O. Box 849, Piscataway, New Jersey 08855-0849

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A commonly cited reason for the success of the local spin density (LSD) approximation is that it correctly accounts for short wavelength contributions to the exchange-correlation energy. We show that this result, while true in several limits and for several approximations to these fluctuations, is *not* exact in general, with an analytic demonstration on a specific system (Hooke's atom). Nevertheless, we find that LSD is rather accurate for small separations.

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Density functional theory has enjoyed remarkable success as a moderate-accuracy calculational technique over the past three decades [1]. Much of this success has depended on the use of the local spin density (LSD) approximation [2]. Recently, systematic improvements on LSD have become possible with the advent of generalized gradient approximations (GGA's) [3,4]. With these new functionals, the ground state energies of atoms, molecules, clusters, surfaces, and bulk solids can be calculated with near-chemical accuracy [5].

Key ingredients in the successful construction of a GGA are those properties of the physical system which LSD treats correctly. For example, the total electron number of the exchange-correlation hole is -1 both exactly and in LSD. Another such property can be stated in terms of the wave vector decomposition for the exchange-correlation energy [6]:

$$E_{\mathrm{xc}} = \int \frac{d^3k}{(2\pi)^3} E_{\mathrm{xc}}(\mathbf{k}), \tag{1}$$

where

$$E_{\mathrm{xc}}(\mathbf{k}) = 2\pi e^2 N \langle n_{\mathrm{xc}}(\mathbf{k})\rangle / k^2, \tag{2}$$

and $\langle n_{\mathrm{xc}}(\mathbf{k})\rangle$ is the Fourier transform of the system-averaged exchange-correlation hole, i.e., $\langle n_{\mathrm{xc}}(\mathbf{k})\rangle = \int d^3u \exp(-i\mathbf{k}\cdot\mathbf{u})\langle n_{\mathrm{xc}}(\mathbf{u})\rangle$, where

$$\langle n_{\mathrm{xc}}(\mathbf{u})\rangle = \frac{1}{N}\int d^3r\, n(\mathbf{r}) n_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}+\mathbf{u}), \tag{3}$$

and $n_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}+\mathbf{u})$ is the exchange-correlation hole at $\mathbf{r}+\mathbf{u}$ around an electron at $\mathbf{r}$. These equations decompose E_{xc} into contributions from density fluctuations of various wave vectors $\mathbf{k}$ with wavelengths $2\pi/k$, where $k = |\mathbf{k}|$. Langreth and Perdew [6] (hereafter LPI) showed that LSD is exact to second order in e^2 for $E_{\mathrm{xc}}(\mathbf{k})$ at large k for surfaces, and also that, within a density-functional version of the random phase approximation (RPA), the leading gradient correction vanishes in this limit for all systems [7] (hereafter LPII). This has led to what we call the short wavelength hypothesis, namely that LSD is exact for short wavelengths (i.e., large k) for all inhomogeneous systems. This idea has considerable intuitive appeal, as the LSD is supposed to account for local behavior correctly. In fact, this hypothesis has since passed into the literature as one of the reasons for the success of LSD [8] and LSD behavior for large wave vectors (or small interelectronic distances) has been incorporated in several GGA's [3,4].

The chief purpose of this paper is to show that the short wavelength hypothesis is correct for several limiting regimes and for certain approximate treatments of the inhomogeneous electron gas, but that the short wavelength hypothesis is *not* exact in general. The first result is achieved by proving that the short wavelength hypothesis is correct within RPA plus second-order exchange (RPA2X), an approximation for E_{xc} which becomes exact in the high density limit. However, we also show that, at least for the homogeneous gas at typical valence-electron densities, RPA2X yields a poor approximation to the exact short wavelength fluctuations. The second result is demonstrated on a specific system, where we can calculate the *exact* short wavelength behavior analytically, and see that it differs from LSD behavior. However, for this and several other examples, the error made by the short wavelength hypothesis is small, suggesting that the hypothesis is approximately true numerically.

Our proof includes, as special cases, both the earlier results of Langreth and Perdew. For large k, RPA2X is equivalent to second order perturbation theory. Thus our proof generalizes the result of LPI from surfaces to all inhomogeneous electronic systems. (LPI also claim their result is valid to *all* orders in e^2, which is not true in general.) Furthermore, our proof shows that *all* gradient corrections at short wavelengths (not just those that are second order in ∇n) vanish within RPA (and RPA2X), thereby generalizing the result of LPII considerably. However, we also show that the RPA itself never predicts short wavelength behavior correctly.

We begin with an exact analysis of the large wave vector behavior of an inhomogeneous system. To get a quantity which depends only on k, we define the angle-averaged decomposition $E_{\mathrm{xc}}(k) = \int d\Omega_k\, E_{\mathrm{xc}}(\mathbf{k})/4\pi$. Performing such an angle average on Eq. (2), we find

$$E_{\mathrm{xc}}(k) = \frac{8\pi^2 e^2 N}{k^3} \int_0^\infty du\, u \sin(ku) \langle n_{\mathrm{xc}}(u) \rangle_{\mathrm{sph.av.}}, \tag{4}$$

where the subscript sph. av. denotes a spherical average. For large k, the integral in Eq. (4) vanishes rapidly, as the sine function averages to zero. Repeated integration by parts yields its asymptotic behavior as a power series in inverse powers of k. We find

$$E_{\mathrm{xc}}(k)/N \approx -C/k^6 + O(k^{-8}), \tag{5}$$

where

$$C = 16\pi^2 e^2 \langle n'_{\mathrm{xc}}(u=0) \rangle_{\mathrm{sph.av.}}, \tag{6}$$

where the prime indicates the derivative with respect to u. Thus C is proportional to the system average of the derivative in the exchange-correlation hole at zero separation. Equations (1)–(6) are exact and apply to any inhomogeneous system. They reveal an intimate connection between the wave vector analysis [3,6,7] of E_{xc} for $k \to \infty$ and the real-space analysis [4] at $\mathbf{u} = 0$.

If $\langle n_{\mathrm{xc}}(u) \rangle$ were a smooth function of $\mathbf{u}$ as $u \to 0$, then C would vanish, as it does at the exchange-only level (i.e., to first order in e^2). However, the singular nature of the Coulomb interaction between the electrons leads to the well-known cusp in the hole density at zero separation, and a non-zero value for C. To take advantage of this, we must first undo the coupling-constant average implicit in C, by writing $C = \int_0^1 d\lambda\, C_\lambda$, where the Coulomb potential has strength λe^2 and the external potential is adjusted to keep the density fixed [6]. For each λ, the electron-coalescence cusp condition [9] is

$$g'_\lambda(\mathbf{r},\mathbf{r}) = \lambda g_\lambda(\mathbf{r},\mathbf{r})/a_0, \tag{7}$$

where $a_0 = \hbar^2/me^2$ is the Bohr radius, $g_\lambda(\mathbf{r},\mathbf{r}')$ is the pair distribution function, which is related to the hole via

$$n_{\mathrm{xc},\lambda}(\mathbf{r},\mathbf{r}) = n(\mathbf{r}')[g_\lambda(\mathbf{r},\mathbf{r}') - 1], \tag{8}$$

and $g'_\lambda(\mathbf{r},\mathbf{r}) = \partial/\partial u|_{u=0} \int d\Omega_u\, g_\lambda(\mathbf{r},\mathbf{r}+\mathbf{u})/4\pi$. Inserting this into Eq. (6) and performing both the system and coupling constant averages yields

$$C = \frac{16\pi^2 me^4}{\hbar^2 N} \int d^3r\, n^2(\mathbf{r}) \int_0^1 d\lambda\, \lambda g_\lambda(\mathbf{r},\mathbf{r}). \tag{9}$$

Note that cusps in the density $n(\mathbf{r})$, such as at a nucleus, do not contribute to C, as they occur only for discrete values of $\mathbf{r}$, while the cusp in $n_{\mathrm{xc},\lambda}(\mathbf{r},\mathbf{r}+\mathbf{u})$ occurs as $u \to 0$ for *all* values of $\mathbf{r}$. Equations (7)–(9) are exact and apply to any inhomogeneous Coulomb-interacting system.

In terms of Eq. (5), the short wavelength hypothesis is that C_{LSD}, the value of C found in an LSD calculation, is equal to the exact value of C. C_{LSD} is found from Eq. (9) by replacing $g_\lambda(\mathbf{r},\mathbf{r})$ by its value for a uniform electron gas with spin densities equal to those at $\mathbf{r}$. If this hypothesis were correct for each value of λ, Eqs. (8) and (9) imply that LSD would be exact for the system-averaged hole at zero separation. To illustrate this point, in Fig. 1 we plot the exact zero separation hole and its LSD approximation as a function of $\mathbf{r}$ throughout Hooke's atom, which consists of two electrons interacting by a Coulomb repulsion, in an external harmonic potential. This is easily calculated for oscillator frequencies at which exact analytic solutions exist [10–13]. We see that, point by point, LSD gives a very good approximation to the on-top hole density. [Because $n_{\mathrm{xc},\lambda}(\mathbf{r},\mathbf{r})$ is not precisely known for the uniform electron gas, Fig. 1 itself cannot be used to rule out the short wavelength hypothesis.] However, we show later that C is nevertheless a *nonlocal* functional of the density, invalidating the short wavelength hypothesis.

On the other hand, for high densities, exchange dominates, and $g_\lambda(\mathbf{r},\mathbf{r}) = [1 - \zeta^2(\mathbf{r})]/2$, where $\zeta(\mathbf{r}) = [n_\uparrow(\mathbf{r}) - n_\downarrow(\mathbf{r})]/n(\mathbf{r})$ is the relative spin polarization at $\mathbf{r}$. Inserting this result into Eq. (9) yields

$$C^{(2)} = \frac{4\pi^2 me^4}{\hbar^2 N} \int d^3r\, n^2(\mathbf{r})[1 - \zeta^2(\mathbf{r})], \tag{10}$$

where the superscript indicates the number of powers of e^2 retained, as for high densities and large wave vectors the Coulomb potential may be treated perturbatively. [Note that the cusp condition of Eq. (7) has bought us an extra factor of e^2 in Eq. (10).] Thus $C^{(2)}$ is explicitly

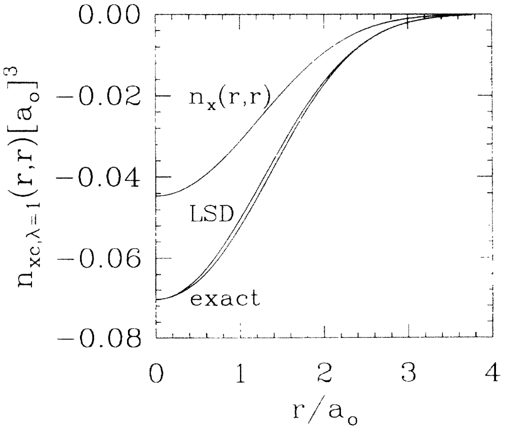

FIG. 1. Zero separation exchange and exchange-correlation hole density at full coupling constant $\lambda = 1$ throughout the $\hbar\omega = e^2/2a_0$ Hooke's atom, in which $r_s(\mathbf{r}) \geq 1.39a_0$, where $r_s(\mathbf{r}) = [4\pi n(\mathbf{r})/3]^{-1/3}$.

a local functional of the density and spin polarization, and the short wavelength hypothesis is true in the high-density limit. In their Appendix D, LPI prove this result for the special case of a spin-unpolarized surface.

We note that the short wavelength hypothesis is also absolutely (if not relatively) exact in two other limits. For either fully spin-polarized systems, or in the low-density limit, $g_\lambda(\mathbf{r},\mathbf{r}) = 0$, both exactly and in LSD.

We may also write the wave vector decomposition in terms of the dynamic susceptibility [6], which, from Eq. (5), yields

$$C_\lambda = 2\pi e^2 \lim_{k\to\infty} k^4 \left\{ 1 + \frac{1}{N}\int_0^\infty \frac{d\omega}{\pi} \operatorname{Im}[\chi_\lambda(\mathbf{k},\mathbf{k},\omega)] \right\}. \tag{11}$$

This allows an alternative derivation of Eq. (10). The first-order expansion of $e^2\chi$ produces the exchange contribution, which simply cancels the 1 on the right in Eq. (11), while the second-order terms in $e^2\chi$, which consists of a direct and a second-order exchange contibution [14], combine to yield Eq. (10).

We next examine the short wavelength behavior of $E_{\mathrm{xc}}(k)$ within the RPA. Throughout this paper, the RPA for the inhomogeneous case is the density-functional version of the RPA [7], in which the noninteracting susceptibility, from which the interacting susceptibility is calculated, is taken to be the λ-independent, single-particle response of the electrons in the Kohn-Sham potential. To second order in e^2, the RPA includes only the direct contribution [14], yielding

$$C_{\mathrm{RPA}} = \frac{8\pi^2 m e^4}{\hbar^2 N} \int d^3r\, n^2(\mathbf{r}). \tag{12}$$

Furthermore, just as for the uniform gas [15], one may show [16] that, for any system whose Kohn-Sham potential is bounded from above, because higher order (in e^2) contributions in RPA include only higher powers of $(4\pi e^2/k^2)\chi^{(0)}$, these higher order contributions all vanish more rapidly than k^{-4}, and so do not contribute to C_{RPA}. Thus Eq. (12) gives the RPA value of C for *all* densities, and the short wavelength hypothesis is exact within RPA, generalizing the result of LPII to all gradient corrections.

Comparing Eqs. (10) and (12), it is clear that the RPA is a poor approximation to C, even in the high density spin-unpolarized limit. This reflects the fact that RPA is a poor approximation at small separations [see Eq. (6)]. In fact, using Eqs. (6), (8), and (12), and undoing the system average, yields the RPA cusp condition

$$g_\lambda'(\mathbf{r},\mathbf{r}) = \lambda/a_0. \tag{13}$$

This is to be contrasted with Eq. (7). We also note that Eq. (9) does *not* hold in RPA.

Clearly, by adding second-order exchange to the RPA, we find $C_{\mathrm{RPA2X}} = C^{(2)}$, as given by Eq. (10), for which the short wavelength hypothesis is exact. If this produced a good approximation to C for all systems, then we would have a strong justification for the approximate validity of the short wavelength hypothesis. However, we can see that this is not the case, even in the spin-unpolarized uniform electron gas. Figure 2 is a plot of $Ca_0/4\pi^2e^2n$ as a function of r_s for the uniform gas. It was made using Yasuhara's ladder-diagram expression [17] for $g(\mathbf{r},\mathbf{r})$ as a function of r_s, as parametrized by Perdew and Wang [18], and confirmed by recent quantum Monte Carlo calculations [19]. Only at high densities does the RPA2X result agree well with the exact value.

An alternative way to improve an RPA calculation is to introduce an effective static local field factor. In a Hubbard-like approximation [14,20], in which this factor tends to $[1 - \zeta^2(\mathbf{r})]/2$ as $k \to \infty$, the short wavelength hypothesis remains true, but C takes the value it has in the RPA2X approximation, and so is still poorly approximated away from high densities.

Although we have pointed out the limitations of earlier arguments in favor of the short wavelength hypothesis, we have not yet explicitly shown how it fails. Consider corrections to the high density limit of Hooke's atom, i.e., for large spring constant. Elementary perturbation theory, treating the Coulomb repulsion as weak, yields the next order correction to the integrated on-top pair distribution function [16]

$$\int d^3r\, n^2(\mathbf{r}) g_\lambda(\mathbf{r},\mathbf{r}) = \frac{1}{2}\int d^3r\, n^2(\mathbf{r}) - \alpha \frac{m\lambda e^2}{2\hbar^2} \times \int d^3r\, n^2(\mathbf{r}) r_s(\mathbf{r}) + O(\lambda^2 e^4), \tag{14}$$

where $\alpha = 2\ln[(2+\sqrt{3})/8(2-\sqrt{3})]5^{3/2}/3^{11/6}\pi^{2/3} \approx 0.7713$. LSD yields the same form as Eq. (14), but with

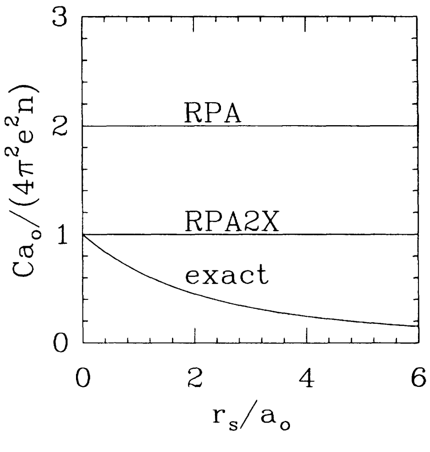

FIG. 2. Density dependence of C for the unpolarized uniform electron gas.

the precisely known value of α for the uniform electron gas [21], which is $(4/9\pi)^{1/3}2(\pi^2 + 6\ln 2 - 3)/5\pi \approx 0.7317$. Via Eq. (9), these results give the value of C through third order in e^2, the former exactly, the latter in LSD, thereby providing a definitive counterexample to the short wavelength hypothesis.

However, these values for α are not very much different numerically, suggesting that the short wavelength hypothesis may not be too bad in practice. Furthermore, Fig. 1 shows that, even subtracting out the exchange hole density, LSD is a remarkably good approximation for the on-top correlation hole density. Integrating over all space, we find an LSD error in $\langle n_{\mathrm{xc},\lambda=1}(u = 0)\rangle$ of only -4%. Using Eq. (9), we find $C_1 = 1.4904$ and $C_1^{\mathrm{LSD}} = 1.83$ in atomic units ($e^2 = \hbar = m = 1$), making a 23% error. For comparison, the LSD errors [12,13] in the total exchange, correlation, and exchange-correlation energies are –14%, +124%, and –5%, respectively, and the corresponding GGA [4] errors[12] are –4%, +36%, and –1%. The relative LSD error in C_1, which is purely correlation, is much smaller than that of the total correlation energy, as expected. LSD *is* almost exact for $n_{\mathrm{xc},\lambda=1}(\mathbf{r},\mathbf{r})$ at $r = 0$, where $\nabla n(\mathbf{r}) = 0$.

In this paper we have shown that the short wavelength hypothesis is not exact in general. Even if it were, it would not provide a strong explanation for the success of the local spin density approximation, because the k^{-6} tail of the exchange-correlation energy is a small part of the total. We have also shown that earlier arguments for the validity of the short wavelength hypothesis do not extend beyond the high density regime. However, the specific cases studied all suggest that the short wavelength hypothesis is approximately true numerically. Away from the high-density, low-density, and fully spin-polarized limits, the reasons for the approximate validity of the short wavelength hypothesis remain, at best, intuitive, but this limited validity does help to justify generalized gradient (or other) approximations which revert to LSD for short wavelengths [3] or small interelectronic separations [4]. We have found that LSD is rather accurate for both $\langle n_{\mathrm{xc}}(u = 0)\rangle_{\mathrm{sph.av.}}$ and $\langle n'_{\mathrm{xc}}(u = 0)\rangle_{\mathrm{sph.av.}}$, a result which should prove useful for the construction of approximate density functionals in the future.

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