

Density Functionals and Small Interparticle Separations in Electronic Systems

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We review some recent results concerning the probability that two electrons will be found close together in any interacting electronic system, and why this probability is usually well-approximated by local (LSD) and semi-local spin density functional theories. The success of these approximations for the energy in “normal” systems is explained by the usual sum-rule arguments on the system- and spherically-averaged exchange-correlation hole density  $\langle n_{\text{XC}}(u) \rangle$ , coupled with the nearly correct, but not exact, behavior of these approximations as the interelectronic separation  $u \rightarrow 0$ . We argue that the accuracy of the LSD on-top hole density in “normal” systems is due to its accuracy in the non-interacting, weakly-interacting, and strongly-interacting limits.

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The problem of solving for the ground-state energy of a system of  $N$  electrons in a given external potential occurs in many branches of science: atomic physics, quantum chemistry, solid state physics, and materials science. The local spin density (LSD) approximation [1] of density functional theory provides a practical, first principles, moderate-accuracy method for solving this problem in all these fields [2]. Recent gradient-corrected functionals, such as PW91 [3], typically significantly improve the accuracy of LSD [4], but do not yet yield chemical accuracy.

These schemes approximate the exchange-correlation energy of the system, a contribution to the total ground state energy which is defined (in atomic units,  $e^2=m=\hbar=1$ ) as [5]

$$E_{\text{XC}} = \int d^3r \int d^3r' \frac{n(\mathbf{r})n_{\text{XC}}(\mathbf{r}, \mathbf{r}')}{2|\mathbf{r} - \mathbf{r}'|}, \quad (1)$$

where  $n(\mathbf{r})$  is the density at point  $\mathbf{r}$ , and  $n_{\text{XC}}(\mathbf{r}, \mathbf{r}')$  is the density at  $\mathbf{r}'$  of the exchange-correlation hole about an electron at  $\mathbf{r}$ , given by

$$n_{\text{XC}}(\mathbf{r}, \mathbf{r}') = \int_0^1 d\lambda P_\lambda(\mathbf{r}, \mathbf{r}')/n(\mathbf{r}) - n(\mathbf{r}'). \quad (2)$$

Here  $P_\lambda(\mathbf{r}, \mathbf{r}')$  is the pair density, i.e.,  $P_\lambda(\mathbf{r}, \mathbf{r}')$   $d^3r d^3r'$  is the probability of finding one electron in  $d^3r$  surrounding  $\mathbf{r}$ , and another in  $d^3r'$  surrounding  $\mathbf{r}'$ , while  $\lambda$  is the strength of the interelectronic Coulomb repulsion,  $\lambda/|\mathbf{r} - \mathbf{r}'|$ , which is varied from 0 (non-interacting) to 1 (full interaction), keeping the density fixed [6]. Once an approximation to  $E_{\text{XC}}$  in terms of the density is given, the local external potential of the effective non-interacting equations of density functional theory (the Kohn-Sham equations [1]) may be found, and the self-consistent solution of these equations yields the ground state density and energy of the given system (within that approximation).

LSD may be generated by the ansatz

$$n_{\text{XC}}(\mathbf{r}, \mathbf{r}') = n_{\text{XC}}^{\text{LSD}}(n(\mathbf{r}), \zeta(\mathbf{r}); |\mathbf{r} - \mathbf{r}'|), \quad (3)$$

where  $n_{\text{XC}}^{\text{LSD}}(n, \zeta; u)$  is the exchange-correlation hole in a uniform electron gas of density  $n$  and relative spin polarization  $\zeta = (n_\uparrow - n_\downarrow)/n$  at separation  $u$  from the electron [7]. In fact, the complete hole carries more information than is needed to perform an LSD calculation, which requires only the energy density. One way to define the exact energy density is in terms of the exchange-correlation energy per electron at the point  $\mathbf{r}$ ,

$$\epsilon_{\text{XC}}(\mathbf{r}) = \int d^3r' \frac{n_{\text{XC}}(\mathbf{r}, \mathbf{r}')}{2|\mathbf{r} - \mathbf{r}'|}, \quad (4)$$

and within LSD,  $\int d^3u n_{\text{XC}}^{\text{LSD}}(n(\mathbf{r}), \zeta(\mathbf{r}); u)/2u$ .

LSD, which is exact for a uniform system, is also a good approximation for slowly-varying densities, but not necessarily for any other system. However, in practice, it produces a moderate accuracy energy for many systems with rapidly-varying densities. In an attempt to understand this moderate accuracy, we might study  $\epsilon_{\text{XC}}(\mathbf{r})$ , which is plotted in Fig. 1 for the hydrogen atom, in which  $n_{\text{XC}}(\mathbf{r}, \mathbf{r}') = -n(\mathbf{r})$ . (Compare Fig. 8 of Ref. [8].) We see that LSD yields the wrong value and slope as  $r \rightarrow 0$  and an incorrect asymptotic form at large  $r$ . Despite this, the LSD energy is correct to within a few percent ( $E_{\text{XC}} = -0.3125$  hartree,  $E_{\text{XC}}^{\text{LSD}} = -0.290$  hartree). Another point-wise property, the exchange-correlation potential, is similarly poorly approximated by LSD [9,10].

To understand why LSD works in such a case, we consider instead the real-space decomposition of the hole into contributions from different interelectronic separations. We define the system- and spherically-averaged hole by

$$\langle n_{\text{XC}}(u) \rangle = \frac{1}{N} \int \frac{d\Omega_u}{4\pi} \int d^3r n(\mathbf{r}) n_{\text{XC}}(\mathbf{r}, \mathbf{r} + \mathbf{u}), \quad (5)$$

where  $N = \int d^3r n(\mathbf{r})$  is the total number of electrons, so that, from Eq. (1), the average exchange-correlation energy per particle is simply given by

$$E_{\text{XC}}/N = \int_0^\infty du 4\pi u^2 \frac{\langle n_{\text{XC}}(u) \rangle}{2u}. \quad (6)$$

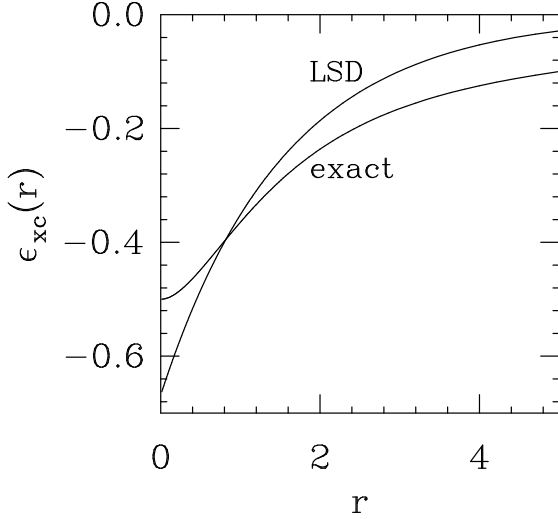


FIG. 1. Exchange-correlation energy per particle in the hydrogen atom, evaluated exactly and in LSD, as a function of distance from the nucleus (atomic units).

The averaged hole satisfies several important conditions, which may be proven from its definition, Eq. (2), namely

$$\langle n_x(u) \rangle \leq 0, \quad (7)$$

$$\int_0^\infty du 4\pi u^2 \langle n_x(u) \rangle = -1, \quad (8)$$

$$\int_0^\infty du 4\pi u^2 \langle n_c(u) \rangle = 0, \quad (9)$$

where  $\langle n_x(u) \rangle$  is the exchange (i.e.,  $\lambda = 0$ ) hole, which is practically [11] that hole found in a Hartree-Fock calculation, while  $\langle n_c(u) \rangle$  is the correlation hole. We intuitively expect LSD to work well for the hole at small separations, because the density at the hole point  $\mathbf{r}'$  has not changed much from the input density at the electron point  $\mathbf{r}$ . Then, since LSD replaces the system-averaged hole by that of another physical system,  $\langle n_{xc}^{\text{LSD}}(u) \rangle$  also satisfies the above conditions, which constrain the hole to be reasonably good even at large separations, for *any* system [12]. In Fig. 2, we plot  $\langle n_{xc}(u) \rangle$  for hydrogen, and see just how good LSD is. This accuracy is then reflected in the energy, through the integral in Eq. (6).

An obvious way to improve accuracy in LSD is to treat the LSD hole as the zero-order term of an expansion in gradients of the density at  $\mathbf{r}$ . In principle, the next order terms, which can be arranged to behave as  $|\nabla n|^2$ , are straightforward to calculate [13,14], producing the gradient expansion approximation (GEA). However, GEA proves less accurate than LSD for most systems where the density is not slowly-varying. We can understand this result in

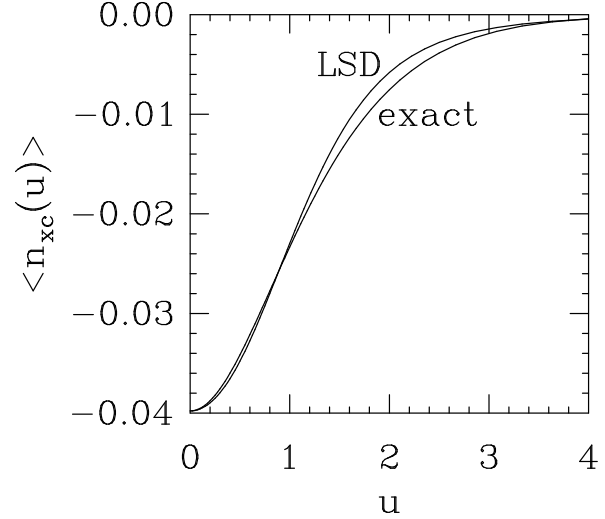


FIG. 2. System- and spherically-averaged exchange-correlation hole for the hydrogen atom, evaluated exactly and in LSD, as a function of the separation between the electron and the hole observation point (atomic units).

terms of the real-space decomposition: Since GEA produces a hole which is *not* the hole of any real system, this hole violates the exact conditions, Eqs. (7)- (9). This failure can be “fixed” by cutting off the GEA hole in real space, and choosing the cutoff so as to restore those exact conditions. The numerically-defined functional which results from this procedure has been fit analytically, and is called PW91 [3,15]. The on-top exchange-correlation hole in PW91 was designed to recover its LSD value as  $u \rightarrow 0$ .

However, this justification for the accuracy of LSD, and the improved accuracy of PW91, relies on the hole being well-approximated at small separations. In fact, we only need LSD to be accurate at  $u = 0$ , to make LSD accurate for small  $u$ . This is because of the electron-electron cusp condition [16,17], a universal property of all electronic systems, arising from the dominance of Coulomb repulsion between the electrons at small separations. The cusp condition relates the derivative of the pair density with respect to the interelectronic separation to the on-top pair density itself, for each value of  $\lambda$ , and yields

$$\langle n'_{xc,\lambda}(0) \rangle = \lambda [\langle n_{xc,\lambda}(0) \rangle + \langle n(0) \rangle], \quad (10)$$

where  $f'(0) \equiv \partial/\partial u|_{u=0} \int d\Omega_u f(\mathbf{u})/(4\pi)$ , and

$$\langle n(u) \rangle = \frac{1}{N} \int \frac{d\Omega_u}{4\pi} \int d^3r n(\mathbf{r}) n(\mathbf{r} + \mathbf{u}). \quad (11)$$

Since  $\langle n'_{xc,\lambda}(0) \rangle$  is determined by  $\langle n_{xc,\lambda}(0) \rangle$  and by  $\langle n(0) \rangle$ , which is a local functional of the density, if the on-top hole is well-approximated in LSD, so will the derivative be, and likewise the value of the hole for any small  $u$ . Note that

this cusp in the hole as  $u \rightarrow 0$  is entirely in the correlation contribution, as the exchange hole is evaluated on a non-interacting wavefunction. These results are illustrated by Fig. 2, where the LSD hole becomes exact at  $u = 0$ . This is so for any fully spin-polarized system, where the probability of finding two electrons at the same spot is identically zero by the exclusion principle, and where from Eq. (2), the remaining contribution to the on-top hole is a local functional of the density. For such a system, the cusp at  $u = 0$  vanishes, both exactly and in LSD.

This leads us directly to the central question of this work: Just how well is  $\langle n_{\text{XC}}(0) \rangle$  approximated in LSD, and why?

First we consider the exchange contribution. If the exchange wavefunction is a single Slater determinant, as is often the case, then

$$P_{\lambda=0}(\mathbf{r}, \mathbf{r}) = 2 n_{\uparrow}(\mathbf{r}) n_{\downarrow}(\mathbf{r}), \quad (12)$$

and the exchange hole is given simply by [18–20]

$$\langle n_{\text{X}}(0) \rangle = -\frac{1}{N} \int d^3r [n_{\uparrow}^2(\mathbf{r}) + n_{\downarrow}^2(\mathbf{r})]. \quad (13)$$

Since this is a local functional of the spin densities, LSD is exact for this quantity. We now define a “normal” system as one in which the on-top pair density  $P_{\lambda}(\mathbf{r}, \mathbf{r})$  for  $\lambda \ll 1$  is given rather accurately by LSD, applied to the exact physical spin densities,  $n_{\uparrow}(\mathbf{r})$  and  $n_{\downarrow}(\mathbf{r})$ . In such a system, the  $\lambda = 0$  wavefunction is always a single Slater determinant. Examples of normal systems include hydrogen, helium, Hooke’s atom (see below), and the uniform electron gas. However, some systems are abnormal. A simple example of such a system is the  $\text{H}_2$  molecule, with its bond length stretched to a large distance. The ground-state wavefunction for all  $\lambda$  is a spin singlet of Heitler-London type, a linear combination of two Slater determinants. If the exact ground state spin densities are fed into the LSD expression for the on-top exchange hole, i.e., Eq. (13), a very incorrect value is found. Other examples of such abnormal systems include the molecule  $\text{Cr}_2$ , at its equilibrium bond length, and anti-ferromagnetic solids. With Andreas Savin [21], we have shown that nevertheless the energies and on-top pair densities of these abnormal systems can be well-approximated in self-consistent LSD, but that the self-consistent  $n_{\uparrow}(\mathbf{r})$  and  $n_{\downarrow}(\mathbf{r})$  must be re-interpreted as intermediate quantities, and not as physical spin densities. In the rest of this article, we restrict our attention to normal systems, as we have done before [22].

For any normal system, the exchange contribution dominates at high density, so  $\langle n_{\text{XC}}^{\text{LSD}}(0) \rangle$  becomes exact in this limit. In the opposite limit of low density,  $P(\mathbf{r}, \mathbf{r}) = 0$ , and again the on-top hole is exact in LSD. Also, two arguments had been given in the literature in support of the idea that  $\langle n_{\text{XC}}^{\text{LSD}}(0) \rangle$  is exact for *all* densities. Both of these arguments were based on approximate calculations made in wave vector space, which simply means analyzing the Fourier transform of  $\langle n_{\text{XC}}(u) \rangle$ . In the first [6,23], a perturbation calculation in

the Coulomb repulsion was performed for a spin-unpolarized surface. Since such an analysis is only valid for high densities, this result is just a special case of Eq. (13) above. In the second [24,25], it was shown that, within the random phase approximation (RPA) to the density fluctuations in  $n_{\text{XC}}(\mathbf{r}, \mathbf{r}')$ , the leading gradient correction to  $\langle n_{\text{XC}}^{\text{LSD}}(0) \rangle$  vanishes. However, as is well-known, RPA is a very poor approximation at *short* distances. In fact, we recently showed that [22,26]

$$\langle n_{\text{XC},\lambda}^{\text{RPA}}(0) \rangle = \lambda \langle n(0) \rangle. \quad (14)$$

Thus, the RPA on-top hole derivative is a local functional of the density (for all densities), so that *all* gradient corrections to this quantity are zero. However, even in the high density limit, comparison with Eqs. (10) and (13) shows that RPA yields the *wrong* local functional. Simple attempts to improve on RPA by using a local field correction, while retaining the local nature of the on-top hole derivative, proved unpromising [22].

Thus, early arguments for the exactness of  $\langle n_{\text{XC}}^{\text{LSD}}(0) \rangle$  turn out to be special cases, and leave open the question of exactness in general [27]. We therefore tested this hypothesis on an interacting electronic system which allows exact solutions. This was provided by Hooke’s atom, in which two electrons are bound to a center via an external oscillator potential,  $k(r_1^2 + r_2^2)/2$ , while repelling each other via the Coulomb repulsion [28]. Analytic solutions for the ground state are known for certain discrete values of the force constant  $k$  [29] but, due to imprecision in our knowledge of the uniform gas on-top hole, such solutions do not provide a definitive counter-example.

However, as  $k \rightarrow \infty$  and the Coulomb repulsion becomes negligible, since Hooke’s atom is a normal system, the exchange-correlation hole reduces to the exchange hole, and is given by Eq. (13). The leading correction in powers of  $\lambda$ , where  $\lambda$  is the strength of the Coulomb repulsion, is therefore the leading contribution to the correlation hole in this high density limit, and may be written in the suggestive form

$$\langle n_{\text{C},\lambda}(0) \rangle = -\frac{\alpha\lambda}{2} \int d^3r n^2(\mathbf{r}) r_s(\mathbf{r}) + O(\lambda^2), \quad (15)$$

where  $n = 3/4\pi r_s^3$ . Treating the Coulomb repulsion as a perturbation, this constant  $\alpha$  was already known *analytically* for the uniform gas ( $= 0.7317$ ) [30,31] and we calculated it analytically for Hooke’s atom ( $= 0.7713$ ) [22,32]. Thus  $\langle n_{\text{XC}}^{\text{LSD}}(0) \rangle$  is not exact in general.

Hooke’s atom, which has no continuous energy spectrum, might be regarded as an unnatural example. But, with Andreas Savin [33], we have found very similar behavior from a more physical example of a normal system, the two-electron ion of nuclear charge  $Z$ . Starting from accurate correlated wavefunctions [34], we evaluated  $\langle n_{\text{X}}(0) \rangle = -\langle n(0) \rangle/2$ ,  $\langle n_{\text{XC},\lambda=1}(0) \rangle$ , and  $\langle n_{\text{XC},\lambda=1}^{\text{LSD}}(0) \rangle$ , for  $Z = 1, 2, 3, 4, 10, 20$ , and  $\infty$ , and fitted the results to a  $Z^{-1}$  expansion of the

form  $aZ^3 + bZ^2 + \dots$ , from which we found that  $\alpha = 0.799$ , proving that LSD is not exact for this case either.

Nevertheless, for all normal cases studied so far,  $\langle n_{\text{xc}}(0) \rangle$  is very well-approximated by LSD. We can understand why this is so by undoing the coupling-constant integral in  $n_{\text{xc}}$ , and taking advantage of the limits in which LSD is exact. We first define the pair distribution function

$$g_\lambda(\mathbf{r}, \mathbf{r}') = \frac{P_\lambda(\mathbf{r}, \mathbf{r}')}{n(\mathbf{r}) n(\mathbf{r}')}, \quad (16)$$

and its system- and spherical-average

$$\langle g_\lambda(u) \rangle = \frac{\int d\Omega_u \int d^3r P_\lambda(\mathbf{r}, \mathbf{r} + \mathbf{u})}{4\pi N \langle n(u) \rangle}, \quad (17)$$

chosen so that  $\langle n_{\text{xc},\lambda}(u) \rangle = \langle n(u) \rangle [\langle g_\lambda(u) \rangle - 1]$ . We also define a system-averaged Wigner-Seitz radius,

$$\langle r_s \rangle_x = \frac{\int d^3r P_{\lambda=0}(\mathbf{r}, \mathbf{r}) r_s(\mathbf{r})}{\int d^3r P_{\lambda=0}(\mathbf{r}, \mathbf{r})}. \quad (18)$$

Note that both  $\langle r_s \rangle_x$  and  $\langle g_x(0) \rangle (\equiv \langle g_{\lambda=0}(0) \rangle)$  are local functionals of the spin densities for normal systems. In fact, from Eq. (12),

$$\langle g_x(0) \rangle = (1 - \langle \zeta^2 \rangle)/2, \quad (19)$$

where

$$\langle \zeta^2 \rangle = \frac{\int d^3r \zeta^2(\mathbf{r}) n^2(\mathbf{r})}{\int d^3r n^2(\mathbf{r})}. \quad (20)$$

The limits  $\zeta = 0$  (unpolarized) and  $\zeta = 1$  (fully polarized) are commonly encountered. Finally we define the (slightly) non-local functional

$$\alpha = - \frac{\int d^3r \frac{dP}{d\lambda} \Big|_{\lambda=0}(\mathbf{r}, \mathbf{r})}{\int d^3r P_{\lambda=0}(\mathbf{r}, \mathbf{r}) r_s(\mathbf{r})}, \quad (21)$$

which determines how the non-interacting limit is approached. For the uniform electron gas,  $\alpha$  is expected to be approximately independent of polarization [7].

We may use these quantities, and the regimes where the LSD on-top hole is known to be exact, to describe how the on-top exchange-correlation hole varies as a function of coupling-constant. In the strongly-interacting (i.e.,  $\lambda \rightarrow \infty$ ) limit,  $P_\lambda(\mathbf{r}, \mathbf{r}) \rightarrow 0$ , and  $\langle n_{\text{xc},\lambda}(0) \rangle / \langle n(0) \rangle \rightarrow -1$ . In the non-interacting (i.e.,  $\lambda = 0$ ) limit, exchange dominates, and  $\langle n_x(0) \rangle / \langle n(0) \rangle = \langle g_x(0) \rangle - 1$ . Finally, in the weakly-interacting limit (i.e., as  $\lambda \rightarrow 0$ ),

$$\frac{\langle n_{\text{xc},\lambda}(0) \rangle}{\langle n(0) \rangle} = -\alpha \lambda \langle r_s \rangle_x \langle g_x(0) \rangle + O(\lambda^2). \quad (22)$$

(Eq. (15) is a specific example of Eq. (22)). Any approximation which reproduces these limits, as LSD does (although not exactly for  $\alpha$ ), should be very accurate for all values of

$\lambda$ . To illustrate this point, we construct a simple interpolation formula for the coupling-constant dependence of the on-top hole,

$$\frac{\langle n_{\text{xc},\lambda}(0) \rangle}{\langle n(0) \rangle} = \langle g_\lambda(0) \rangle - 1 = \langle g_x(0) \rangle e^{-0.7317\lambda \langle r_s \rangle_x} - 1, \quad (23)$$

which reproduces these limits correctly. Moreover, as a function of  $\lambda \langle r_s \rangle_x$ , Eq. (23) displays the correct Levy scaling [35]. Under a uniform wavefunction scaling  $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \rightarrow \gamma^{3N/2} \Psi(\gamma\mathbf{r}_1, \dots, \gamma\mathbf{r}_N)$ , which implies a density scaling  $n(\mathbf{r}) \rightarrow \gamma^3 n(\gamma\mathbf{r})$  and hence  $\langle r_s \rangle_x \rightarrow \gamma^{-1} \langle r_s \rangle_x$ ,  $\langle g_\lambda(0) \rangle$  is invariant. Since this scaling is achieved by simultaneously scaling the external potential,  $v(\mathbf{r}) \rightarrow \gamma^2 v(\gamma\mathbf{r})$ , and the electron-electron interaction,  $\lambda \rightarrow \gamma\lambda$ , we find that  $\lambda \langle r_s \rangle_x \rightarrow \lambda \langle r_s \rangle_x$ , and thus Eq. (23) satisfies this condition.

The result of the interpolation Eq. (23), applied to the first analytic solution of Hooke's atom, at  $k = 1/4$ , is plotted in Fig. 3. Clearly our interpolated result is very accurate.

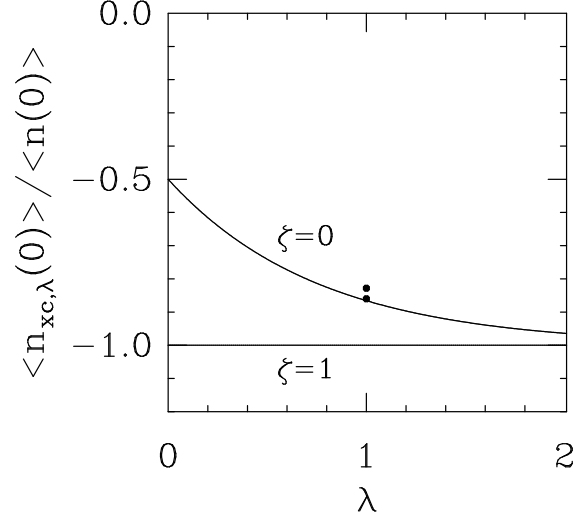


FIG. 3. On-top exchange-correlation hole of the  $k = 1/4$  Hooke's atom, scaled by  $\langle n(0) \rangle$ , as a function of coupling-constant  $\lambda$ . The  $\zeta = 0$  curve is the value interpolated from the high density limit, using Eq. (23). The upper dot marks the LSD value at full coupling constant, while the lower dot marks the exact value at  $\lambda = 1$ . The  $\zeta = 1$  curve is also gotten from the interpolation formula, but is exact in this case. Note that  $\lambda \rightarrow 0$  corresponds to the weakly-interacting or high-density limit, and  $\lambda \rightarrow \infty$  to the strongly-interacting or low-density limit.

The fractional errors may be even smaller in the coupling-constant averaged quantities, which go directly into the exchange-correlation energy integral, Eq. (6). (Eq. (23) makes the evaluation of the coupling-constant integral trivial, but exact values for comparison are not available.) The

TABLE I. Values for  $\langle n_{\text{XC},\lambda=1}(0) \rangle / \langle n(0) \rangle$  calculated several different ways, using numerically exact densities. Interpolated values are based on Eq. (23). Systems denoted by a force constant  $k$  are Hooke's atoms. (Atomic units.)

system	$\langle r_s \rangle_x$	interpolated	LSD <sup>a</sup>	exact
$k = 1/100$	4.441	-0.981	-0.953	-0.971
$k = 1/4$	1.796	-0.866	-0.828	-0.860
H <sup>-b</sup>	1.668	-0.852	-0.809	-0.898
He <sup>b</sup>	0.726	-0.706	-0.682	-0.724

<sup>a</sup>Using the electron gas on-top hole of Ref. [36].

<sup>b</sup>Using the wavefunction of Ref. [34].

horizontal line in Fig. 3 shows the result for the fully spin-polarized system, where our interpolation becomes exact, as  $\langle g_x(0) \rangle = 0$ .

Numerical results for several small systems are listed in Table I. Note that the interpolation result is always more negative than the LSD result, in part because the exponential decay with  $r_s$  of the interpolation formula is faster than the actual decay in the uniform gas [36]. This flaw is, however, relatively unimportant for the exchange-correlation energy, as the fractional error in  $\langle n_{\text{XC},\lambda}(0) \rangle$  becomes very small in the large- $\lambda$  or large- $r_s$  regime.

To summarize, the LSD on-top system-averaged exchange-correlation hole is exact under uniform scaling in the limits of high density ( $\langle r_s \rangle_x \rightarrow 0$ ) (if a single Slater determinant suffices), low density ( $\langle r_s \rangle_x \rightarrow \infty$ ), and full spin-polarization ( $\zeta = 1$ ). Earlier arguments claiming exactness in general have been shown to be special cases of these limits, or artifacts of other approximations. LSD is also typically a very good approximation to the leading correction in the high density limit (as given by first-order perturbation theory around a single-determinant wavefunction), i.e.,  $\alpha \approx 0.7317$ . We are currently trying to understand precisely why this is so. (Relevant to this question is the fact that for the uniform electron gas  $\langle n_{\text{C},\lambda}(u) \rangle$  is of order  $\lambda^1$  for any finite  $u$ , even though it is of order  $\lambda^0$  as  $u \rightarrow \infty$ , leading to the familiar  $\lambda^2 \ln \lambda$  behavior of its correlation energy in the  $\lambda \rightarrow 0$  limit.) But, given these constraints, we have argued here that LSD should therefore be a good approximation for the on-top hole for all normal systems. Together with the exact conditions Eqs. (7)-(9), this explains why LSD achieves moderate accuracy for  $E_{\text{XC}}$ , even in systems of rapidly-varying density.

## ACKNOWLEDGMENTS

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