

## Real Space Analysis of the Exchange-Correlation Energy

Kieron Burke and John P. Perdew

*Department of Physics and Quantum Theory Group, Tulane University, New Orleans, LA 70118*

Presented at *Thirty Years of Density Functional Theory, 13-16 June, 1994, Cracow*  
to appear in the *International Journal of Quantum Chemistry*

**Synopsis:** The exchange-correlation energy of a many-electron system may be written as the electrostatic interaction between the electron density at position  $\mathbf{r}$  and the density of the exchange-correlation hole at position  $\mathbf{r} + \mathbf{u}$ . If we average the hole over the entire system, we find that the energy is uniquely decomposed into contributions from various electronic separations  $\mathbf{u}$ . We may also decompose the hole into contributions from parallel and anti-parallel spins. We give several exact conditions which this system-averaged, spin-decomposed exchange-correlation hole satisfies. Local spin density (LSD) and generalized gradient approximations (GGA's) are more appropriate for  $u \rightarrow 0$  than for large  $u$ , and more trustworthy for antiparallel spins than for parallel spins. We illustrate how good LSD is as  $u \rightarrow 0$  with explicit examples, but also note that, contrary to expectation, LSD is *not* exact for  $u = 0$ , except in certain limiting cases. We show that the dramatic failure of the second-order gradient expansion for large  $u$  can be cured by a real-space cutoff procedure which generates a nonempirical GGA, the PW91 functional. We conclude with some thoughts about the search for greater accuracy in the next thirty years of density functional theory.

**Keywords:** density functional theory, local spin density, generalized gradient approximation, exchange energy, correlation energy.

### I. INTRODUCTION

The problem of finding the ground-state properties of a system of  $N(> 1)$  electrons is important in the study of atoms, molecules, clusters, surfaces, and solids. Since no exact solution exists in general, many approximate methods have been developed for approaching this problem. Each successful method has its own advantages and disadvantages.

Wave function methods [1] have proved very successful in the study of small molecules. They have the important merit that their accuracy can be systematically improved by enlarging the size of the calculation. Unfortunately, since their implementation implies finding the wave function, which depends on  $3N$  coordinates, for large  $N$  they become prohibitively expensive in terms of computer time/memory. Hence their success for molecules, and inapplicability to solids.

The density, on the other hand, is a function of only 3 spatial variables,  $\mathbf{r} = x, y, z$ , so it is a much easier quantity to work with in practice. Furthermore, the ground-breaking work of Hohenberg and Kohn [2] and its subsequent extension in the constrained search formulation [3–5], proved that all quantities of interest could, in principle, be determined from knowledge of the density alone. The Hohenberg-Kohn theorem inaugurated the modern era of density functional theory, and is honored in the title of this conference.

All the key elements for practical calculations were pre-

sented in a paper of Kohn and Sham which appeared the following year [6]. The essential idea is to replace the Schrödinger equation for the interacting electronic system with a set of single-particle equations whose density is the same as that of the original system. These equations are the Kohn-Sham equations [6], and may be written (in atomic units, with  $e = \hbar = m = 1$ )

$$\left[ -\frac{1}{2}\nabla^2 + v_\sigma(\mathbf{r}) + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc,\sigma}([n_\uparrow, n_\downarrow]; \mathbf{r}) \right] \psi_{\alpha,\sigma}(\mathbf{r}) = \epsilon_{\alpha,\sigma} \psi_{\alpha,\sigma}(\mathbf{r}). \quad (1)$$

where  $\sigma = \uparrow$  or  $\downarrow$  is the spin index,  $\alpha$  labels the Kohn-Sham orbitals,  $v_\sigma(\mathbf{r})$  is the (spin-dependent) external potential, and  $v_{xc,\sigma}([n_\uparrow, n_\downarrow]; \mathbf{r})$  is the exchange-correlation potential, defined below, which is a functional of the spin densities. The total density of the system is then

$$n(\mathbf{r}) = n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r}), \quad (2)$$

where

$$n_\sigma(\mathbf{r}) = \sum_\alpha |\psi_{\alpha,\sigma}(\mathbf{r})|^2 \theta(\mu - \epsilon_{\alpha,\sigma}). \quad (3)$$

The sum in Eq. (3) is over all Kohn-Sham orbitals, and  $\mu$  is the chemical potential. The total ground state energy is

$$E = -\frac{1}{2} \sum_{\alpha,\sigma} \langle \psi_{\alpha,\sigma} | \nabla^2 | \psi_{\alpha,\sigma} \rangle \theta(\mu - \epsilon_{\alpha,\sigma})$$

$$\begin{aligned}
& + \sum_{\sigma} \int d^3r n_{\sigma}(\mathbf{r}) v_{\sigma}(\mathbf{r}) \\
& + \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n_{\uparrow}, n_{\downarrow}] \quad (4)
\end{aligned}$$

where  $E_{xc}[n_{\uparrow}, n_{\downarrow}]$  is the exchange-correlation energy of the system, in terms of which  $v_{xc,\sigma}(\mathbf{r}) = \delta E_{xc} / \delta n_{\sigma}(\mathbf{r})$ . These equations are, in principle, exact for any electronic system, if the *exact* functional  $E_{xc}[n_{\uparrow}, n_{\downarrow}]$  is used. In practice, with an explicit (approximate) functional, the Kohn-Sham equations are straightforward to solve, being a set of self-consistent equations for the orbitals  $\psi_{\alpha,\sigma}(\mathbf{r})$ . Because density functional theory deals directly with the density, and never produces an interacting wave function, it has no particular difficulties with large periodic systems. Thus it is the method of choice for solid systems, which contain  $O(10^{23})$  electrons.

The functional  $E_{xc}[n_{\uparrow}, n_{\downarrow}]$  is an extremely sophisticated many-body object, whose functional dependence cannot be written down explicitly for most systems. However, Kohn and Sham also proposed a remarkably simple and robust approximation for this functional, the local spin density (LSD) approximation, which is still the most-used approximate functional today in solid state physics.

The aim of this paper is to show how a study of the real space decomposition of  $E_{xc}$  helps explain why LSD works well for so many systems, and suggests how to construct more accurate approximations. This decomposition is given by [7]

$$E_{xc} = \int d^3\mathbf{u} E_{xc}(\mathbf{u}), \quad (5)$$

where  $\mathbf{u}$  is the interelectronic spacing, and

$$E_{xc}(\mathbf{u}) = \frac{e^2}{2u} \int d^3r n(\mathbf{r}) \bar{n}_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{u}), \quad (6)$$

where  $\bar{n}_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{u})$  is the exchange-correlation hole at separation  $\mathbf{u}$  about an electron at  $\mathbf{r}$ . Note that  $E_{xc}(\mathbf{u})$  depends only on the angle- and system-average of the exchange-correlation hole, not on its value in a given direction, nor at each point in the system. The LSD approximation may then be derived by replacing the exact hole at  $\mathbf{r}$  with that of a uniform gas with spin densities  $n_{\uparrow}(\mathbf{r})$  and  $n_{\downarrow}(\mathbf{r})$ , and inserting the resulting expression for  $E_{xc}(\mathbf{u})$  into Eq. (5).

In section II, we discuss several exact conditions satisfied by the system-averaged exchange-correlation hole, and its spin decomposition. We illustrate these conditions using an exact solution of Hooke's atom. Because LSD replaces the exact hole by the exact hole of another physical system, LSD respects these conditions. We show, in section III, how this forces LSD to be a moderately-accurate approximation even for systems with rapidly varying densities, which is a tribute to the insight of Kohn and Sham. We also point out how further study suggests difficulties for the weighted density approximation (WDA). In section IV, we discuss an approximate condition on the exchange-correlation hole, namely

that LSD is approximately correct at  $u = 0$ . We give some examples showing how good this approximate condition is, and old arguments for why this condition *ought* to be exact, but also demonstrate that this condition is *not* exact. In section V, we discuss the character of the gradient expansion for the hole, and suggest why a real space cutoff procedure is necessary to make it converge.

## II. EXACT CONDITIONS SATISFIED BY THE EXCHANGE-CORRELATION HOLE

We begin this section with some precise definitions which explain the origin of the real space decomposition. We define the second order density matrix in terms of the wave function

$$\begin{aligned}
\rho_2(\mathbf{r}\sigma, \mathbf{r}'\sigma') &= N(N-1) \sum_{\sigma_3, \dots, \sigma_N} \int d^3r_3 \dots \int d^3r_N \\
&\times \left| \Psi(\mathbf{r}\sigma, \mathbf{r}'\sigma', \dots, \mathbf{r}_N\sigma_N) \right|^2, \quad (7)
\end{aligned}$$

where  $\Psi$  is the many-body wave function. (Note that this definition differs from that of Ref. [7] by a factor of 2.) This function has the probability interpretation that  $\rho_2(\mathbf{r}\sigma, \mathbf{r}'\sigma') d^3r d^3r'$  is the probability of finding an electron of spin  $\sigma$  in volume element  $d^3r$  at  $\mathbf{r}$  and another electron of spin  $\sigma'$  in volume element  $d^3r'$  at  $\mathbf{r}'$ . We may define a conditional probability density by

$$\rho_2(\mathbf{r}\sigma, \mathbf{r}'\sigma') \equiv n_{\sigma}(\mathbf{r}) n_2(\mathbf{r}\sigma, \mathbf{r}'\sigma'), \quad (8)$$

so that  $n_2(\mathbf{r}\sigma, \mathbf{r}'\sigma') d^3r'$  is the probability of finding an electron of spin  $\sigma'$  in volume element  $d^3r'$  at  $\mathbf{r}'$ , given that there is an electron of spin  $\sigma$  in volume element  $d^3r$  at  $\mathbf{r}$ . The (unaveraged) spin-decomposed exchange-correlation hole around an electron of spin  $\sigma$  at  $\mathbf{r}$  is then defined by the relation

$$n_2(\mathbf{r}\sigma, \mathbf{r}'\sigma') \equiv n_{\sigma'}(\mathbf{r}') + n_{xc}(\mathbf{r}\sigma, \mathbf{r}'\sigma'), \quad (9)$$

while the non-spin decomposed hole is defined as

$$n_{xc}(\mathbf{r}, \mathbf{r}') = \sum_{\sigma, \sigma'} \frac{n_{\sigma}(\mathbf{r})}{n(\mathbf{r})} n_{xc}(\mathbf{r}\sigma, \mathbf{r}'\sigma'), \quad (10)$$

so that it is related to the spin-summed second order density matrix by

$$\begin{aligned}
\rho_2(\mathbf{r}, \mathbf{r}') &\equiv \sum_{\sigma, \sigma'} \rho_2(\mathbf{r}\sigma, \mathbf{r}'\sigma') = n(\mathbf{r}) [n(\mathbf{r}') + n_{xc}(\mathbf{r}, \mathbf{r}')]. \\
&\hspace{15em} (11)
\end{aligned}$$

Figure 1 is a plot of the exact hole of Eq. (10) (and its LSD approximation) for Hooke's atom, which consists of two electrons bound to a nuclear center with springs of force

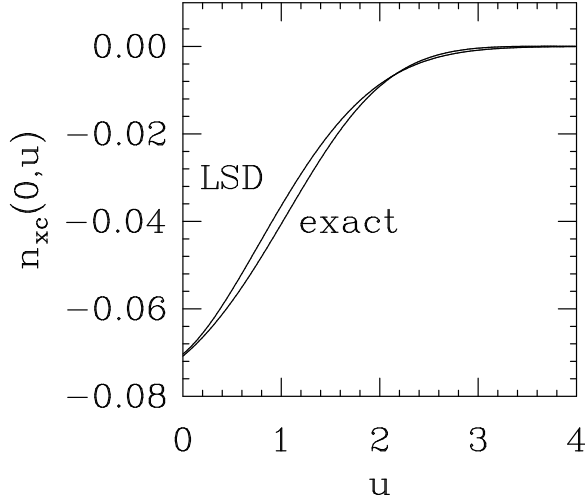


FIG. 1. Exchange-correlation hole around an electron at the origin of Hooke's atom.

constant  $k$ . The figure is plotted for  $k = 1/4$ ,  $\lambda = 1$ , and  $\mathbf{r} = 0$ .

Another useful concept is the pair distribution function, defined as [8]

$$g(\mathbf{r}\sigma, \mathbf{r}'\sigma') = \rho_2(\mathbf{r}\sigma, \mathbf{r}'\sigma') / [n_\sigma(\mathbf{r})n_{\sigma'}(\mathbf{r}')]. \quad (12)$$

The exchange-correlation hole may be written in terms of the pair distribution as

$$n_{xc}(\mathbf{r}\sigma, \mathbf{r}'\sigma') = n_{\sigma'}(\mathbf{r}') [g(\mathbf{r}\sigma, \mathbf{r}'\sigma') - 1]. \quad (13)$$

By use of the Hellmann-Feynman theorem, we may now write the exchange-correlation energy as the electrostatic interaction between the density and the hole, averaged over coupling constant [7], i.e.,

$$E_{xc} = \frac{1}{2} \int d^3r n(\mathbf{r}) \int d^3u \frac{\bar{n}_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{u})}{u}, \quad (14)$$

where

$$\bar{n}_{xc}(\mathbf{r}, \mathbf{r}') = \int_0^1 d\lambda n_{xc,\lambda}(\mathbf{r}, \mathbf{r}'), \quad (15)$$

and  $n_{xc,\lambda}(\mathbf{r}, \mathbf{r}')$  is the exchange-correlation hole for a system with a Coulomb repulsion of strength  $\lambda e^2$  and external potential  $v_{\sigma,\lambda}(\mathbf{r})$ , chosen to keep the density equal to the exact density [9]. Thus, if  $\langle \dots \rangle$  denotes a system-average, i.e.,

$$\langle \bar{n}_{xc}(\mathbf{u}) \rangle \equiv \frac{1}{N} \int d^3r n(\mathbf{r}) \bar{n}_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{u}). \quad (16)$$

then the real space decomposition of  $E_{xc}$  of Eq. (5) is given by

$$E_{xc}(\mathbf{u}) = \frac{N}{2} \langle \bar{n}_{xc}(\mathbf{u}) \rangle \frac{1}{u}. \quad (17)$$

This real space analysis is complemented by a Fourier transform decomposition [10] of Eq. (5). If we write

$$n_{xc}(\mathbf{r}, \mathbf{k}) = \int d^3u n_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{u}) \exp(-i\mathbf{k} \cdot \mathbf{u}), \quad (18)$$

then, from Eq. (5), we have

$$E_{xc} = \int \frac{d^3k}{(2\pi)^3} E_{xc}(\mathbf{k}), \quad (19)$$

with

$$E_{xc}(\mathbf{k}) = \frac{N}{2} \frac{4\pi}{k^2} \langle \bar{n}_{xc}(\mathbf{k}) \rangle. \quad (20)$$

where  $\langle \bar{n}_{xc}(\mathbf{k}) \rangle$  is the Fourier transform of the real space system-averaged hole  $\langle \bar{n}_{xc}(\mathbf{u}) \rangle$ . This momentum space hole is simply related to the static structure factor of the system, as [10]

$$\bar{S}(\mathbf{k}) = 1 + \langle \bar{n}_{xc}(\mathbf{k}) \rangle, \quad (21)$$

which can be easily related to quantities more common in many-body diagrammatic treatments, such as the dynamic susceptibility [10].

Equations (18)-(20) decompose  $E_{xc}$  into contributions from density fluctuations of various wave vectors  $\mathbf{k}$  with wavelengths  $2\pi/|\mathbf{k}|$ . The relation between this Fourier decomposition and the real space analysis is straightforward. The large distance behavior of the hole is determined by the small wave vector behavior of the structure factor. For the uniform gas, the structure factor is quadratic in  $k$  for small values of  $k$ , which means that the total hole decays as  $1/u^5$ . Note that both the exchange and correlation holes each separately decay only as  $1/u^4$ , but that these long tails cancel, yielding a more rapid decay of the total. This cancellation probably also occurs in finite inhomogeneous systems. Similarly, the short distance behavior in real space, especially the cusp at zero separation in Fig. 1, determines the large wave vector behavior of  $\bar{S}(\mathbf{k})$  [11].

We can further decompose the hole into exchange and correlation contributions:

$$n_{xc}(\mathbf{r}\sigma, \mathbf{r}'\sigma') = n_x(\mathbf{r}\sigma, \mathbf{r}'\sigma') + n_c(\mathbf{r}\sigma, \mathbf{r}'\sigma'). \quad (22)$$

By exchange, we mean the density functional definition of exchange, in which the wave function is a Slater determinant whose density is the exact density of the interacting system, and which minimizes the energy of the non-interacting system in the Kohn-Sham external potential,  $v_{\sigma,\lambda=0}$ . We also write

$$g(\mathbf{r}\sigma, \mathbf{r}'\sigma') = g_x(\mathbf{r}\sigma, \mathbf{r}'\sigma') + g_c(\mathbf{r}\sigma, \mathbf{r}'\sigma'), \quad (23)$$

where

$$n_x(\mathbf{r}\sigma, \mathbf{r}'\sigma') = n_{\sigma'}(\mathbf{r}') [g_x(\mathbf{r}\sigma, \mathbf{r}'\sigma') - 1], \quad (24)$$

and

$$n_c(\mathbf{r}\sigma, \mathbf{r}'\sigma') = n_{\sigma'}(\mathbf{r}') g_c(\mathbf{r}\sigma, \mathbf{r}'\sigma'). \quad (25)$$

We may now list some of the simple physical conditions that the exact exchange-correlation hole satisfies. The exchange (or Fermi) hole is the hole due to the Pauli exclusion principle, and obeys the exact conditions:

$$n_x(\mathbf{r}\sigma, \mathbf{r}'\sigma') \leq 0, \quad (26)$$

and

$$\int d^3r' n_x(\mathbf{r}\sigma, \mathbf{r}'\sigma') = -\delta_{\sigma\sigma'} \quad (27)$$

The correlation hole obeys

$$\int d^3r' n_c(\mathbf{r}\sigma, \mathbf{r}'\sigma') = 0, \quad (28)$$

so that electrons of both spins are Coulombically repelled from the electron of spin  $\sigma$  at  $\mathbf{r}$ , but accumulate in a bump at a finite distance away. The exchange conditions may be deduced from the fact that the non-interacting wave function is a Slater determinant, while the integral condition on the correlation hole comes from the normalization of the second order density matrix. The symmetry in the definition of the second order density matrix, Eq. (11), also implies symmetry conditions on the contributions to the hole:

$$n_\sigma(\mathbf{r}) n_x(\mathbf{r}\sigma, \mathbf{r}'\sigma') = n_{\sigma'}(\mathbf{r}') n_x(\mathbf{r}'\sigma', \mathbf{r}\sigma) \quad (29)$$

and

$$n_\sigma(\mathbf{r}) n_c(\mathbf{r}\sigma, \mathbf{r}'\sigma') = n_{\sigma'}(\mathbf{r}') n_c(\mathbf{r}'\sigma', \mathbf{r}\sigma). \quad (30)$$

The spin decomposition of the hole of Fig. 1 is shown in Figs. 3-5 of Ref. [12].

Another more subtle condition is the electron-electron cusp condition. As two electrons approach each other, their Coulomb interaction dominates, and this leads to a cusp in the exchange-correlation hole at zero separation [13]. It is most simply expressed in terms of the pair distribution function. We define its spherically-averaged derivative at zero separation as

$$g'(\mathbf{r}, \mathbf{r}) = \left. \frac{\partial}{\partial u} \right|_{u=0} \int \frac{d\Omega_u}{4\pi} g(\mathbf{r}, \mathbf{r} + \mathbf{u}), \quad (31)$$

where

$$g(\mathbf{r}, \mathbf{r}') = \sum_{\sigma, \sigma'} \frac{n_\sigma(\mathbf{r}) n'_\sigma(\mathbf{r}')}{n(\mathbf{r}) n(\mathbf{r}')} g(\mathbf{r}\sigma, \mathbf{r}'\sigma'), \quad (32)$$

and the cusp condition is then [14]

$$g'(\mathbf{r}, \mathbf{r}) = g(\mathbf{r}, \mathbf{r}). \quad (33)$$

One can clearly see the cusp in the exchange-correlation hole of Fig. 1. However, we may decompose this relation further. In fact, the cusp only occurs for antiparallel spins, as, by the exclusion principle, two parallel spins cannot have zero separation. Furthermore, the non-vanishing derivative is a pure correlation effect, as the exchange hole is the hole of a non-interacting system, which has no cusp. Thus we can write

$$g'_x(\mathbf{r}\sigma, \mathbf{r}\sigma') = 0, \quad (34)$$

and

$$g'_c(\mathbf{r}\sigma, \mathbf{r}\sigma') = (1 - \delta_{\sigma\sigma'}) g(\mathbf{r}\sigma, \mathbf{r}\sigma'). \quad (35)$$

The electron-electron cusp condition is *not* obeyed by some popular approximations, e.g., the random phase approximation [15,11]. We have recently shown, with Juan Carlos Angulo, that a possible extension of Eq. 33 in the form of an inequality applying to all interelectronic separations is *not* a universal condition [16].

What is the point of decomposing the exchange-correlation energy in all these different ways? We will show how these decompositions guide our intuition in the construction of approximate functionals. Clearly, any approximation which works well for both the exchange and correlation contributions to  $n_{xc}(\mathbf{r}\sigma, \mathbf{r}'\sigma')$  at all points  $\mathbf{r}$  and  $\mathbf{r}'$  for all spin combinations  $\sigma$  and  $\sigma'$  will yield a good approximation to  $E_{xc}$ . However, such an approximation is still far beyond our present capabilities, and, moreover, is not *necessary*. We only require a good approximation to  $E_{xc}$  itself, in order to do calculations. On the other hand, by applying these decompositions to our approximations, we discover their limitations, i.e., which exact conditions they fail to satisfy, and so we can, occasionally, fix them.

Historically, the most common decomposition has been

$$E_{xc}[n] = E_x[n] + E_c[n]. \quad (36)$$

By studying how the separate exchange and correlation contributions scale when the density is scaled, Levy, Perdew, and co-workers [17-19] have found many important exact conditions which each contribution must satisfy.

The next decomposition in the hierarchy is the real space analysis discussed in the introduction, which is based on the system averaged exchange-correlation hole. We may perform the spin- and system-average of Eqs. (26) - (30). For Eqs. (26)-(28), this involves performing the spin average of Eq. (10), and then taking an integral over all  $\mathbf{r}$ , keeping  $\mathbf{u} = \mathbf{r}' - \mathbf{r}$  fixed, to yield

$$\langle n_x(\mathbf{u}) \rangle \leq 0, \quad (37)$$

$$\int d^3u \langle n_x(\mathbf{u}) \rangle = -1, \quad (38)$$

$$\int d^3u \langle n_c(\mathbf{u}) \rangle = 0, \quad (39)$$

To do this for the symmetry conditions of Eqs. (29)-(30), we simply perform a spin sum over both indices, perform the integral over all  $\mathbf{r}$ , keeping  $\mathbf{u} = \mathbf{r}' - \mathbf{r}$  fixed, and, on the right-hand side, make a change of variables from  $\mathbf{r}$  to  $\mathbf{r} - \mathbf{u}$ , to find

$$\langle n_x(\mathbf{u}) \rangle = \langle n_x(-\mathbf{u}) \rangle \quad (40)$$

and

$$\langle n_c(\mathbf{u}) \rangle = \langle n_c(-\mathbf{u}) \rangle \quad (41)$$

Equations (37)-(39) are very important conditions on the system-averaged hole, which we use throughout the rest of this paper. The symmetry conditions of Eqs. (40)-(41) become tautologies when spherically-averaged, indicating that the symmetry conditions on the second order matrix lead to no restrictions on the system- and spherically-averaged holes. The cusp condition on the pair distribution function of Eq. (33) may also be system-averaged, to yield the cusp condition on the system-averaged hole at zero separation

$$\langle n'_{xc}(0) \rangle = \langle n_{xc}(0) \rangle + \frac{1}{N} \int d^3r n^2(\mathbf{r}). \quad (42)$$

Again, the exchange contribution has no cusp, so that we find

$$\langle n'_c(0) \rangle = \langle n_c(0) \rangle + \frac{1}{2N} \int d^3r n^2(\mathbf{r}), \quad (43)$$

for the cusp condition on the system-averaged correlation hole.

At the next level down, we may go back and study the spin decomposition of these conditions. Equations (37)-(39) become simply the system-average of Eqs. (26)-(28). The symmetry conditions now becomes slightly less trivial, and imply

$$\langle n_x(\sigma\sigma', \mathbf{u}) \rangle = \langle n_x(\sigma'\sigma, -\mathbf{u}) \rangle \quad (44)$$

and

$$\langle n_c(\sigma\sigma', \mathbf{u}) \rangle = \langle n_c(\sigma'\sigma, -\mathbf{u}) \rangle. \quad (45)$$

These conditions are satisfied by any approximation that retains the symmetry of the pair distribution function under interchange of spins in the antiparallel contribution, i.e.,

$$g(\mathbf{r}\sigma, \mathbf{r}'\sigma') = g(\mathbf{r}'\sigma', \mathbf{r}\sigma), \quad (46)$$

a condition which is trivially obeyed by LSD. Also, the cusp at zero separation in  $\langle n_c(\mathbf{u}) \rangle$  contains only contributions from antiparallel spins.

Lastly, we mention the coupling-constant average. With the generalization, given later, of Eq. (33) to arbitrary  $\lambda$ , each of the above conditions applies for every value of  $\lambda$  separately, and so to all quantities averaged over  $\lambda$ . We will show in section IV that some quantities may be simply related only after undoing the  $\lambda$  integration.

In the next section, we discuss how LSD satisfies all conditions mentioned in this hierarchy, while in section V, we show how use of the hierarchy has led to systematic improvement on LSD.

### III. LOCAL SPIN DENSITY APPROXIMATION

The LSD approximation to  $E_{xc}$  is defined as

$$E_{xc}^{\text{LSD}}[n_\uparrow, n_\downarrow] = \int d^3r n(\mathbf{r}) \epsilon_{xc}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})), \quad (47)$$

where  $\epsilon_{xc}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r}))$  is the exchange-correlation energy per particle of a uniform electron gas (jellium). This function is now well-known from Monte Carlo data [20,21], and has been accurately fitted to analytic forms [22,23]. LSD is thus a first-principles approximation, in the sense that no parameter is fitted empirically to better solutions or experimental values for other systems. It is exact for a uniform system, and a good approximation for slowly-varying systems. Furthermore, it has also been found to provide moderate accuracy for a large variety of systems in which the density varies rapidly, and which are therefore beyond the obvious range of validity.

In terms of the exchange-correlation hole, we may write the LSD approximation as

$$n_{xc}^{\text{LSD}}(\mathbf{r}\sigma, \mathbf{r} + \mathbf{u}\sigma') = n_{xc}^{\text{jell}}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r}); \sigma\sigma', u), \quad (48)$$

where  $n_{xc}^{\text{jell}}(n_\uparrow, n_\downarrow; \sigma\sigma', u)$  is the spin-decomposed hole of the uniform electron gas (jellium) with spin densities  $n_\uparrow$  and  $n_\downarrow$  at separation  $u$  from the electron. Eq. (48) is expected to be most accurate for small  $u$ ; see Fig. 1 and subsection IV. If this approximation for the hole is inserted in Eqs. (5) and (17), one recovers Eq. (47) above.

We have also calculated the LSD approximation to the exchange-correlation hole in Hooke's atom, as shown in Fig. 1. These plots were made using a parameterization of the Monte Carlo data [24] for the electron gas hole. We point out that LSD works atypically well here, because the density has zero gradient at  $r = 0$  in Hooke's atom. Furthermore, it has been shown (at least for the exchange piece) that the off-center (i.e.  $r \neq 0$ ) hole at a given point in space, can be very poorly approximated by the LSD expression above [25]. However, since, as discussed in section II, the exchange-correlation energy depends only on the system-averaged, spherically-averaged, and spin-summed hole, LSD can and does still work well for the complete exchange-correlation energy. LSD has also been criticized for not satisfying the symmetry requirement

$$g(\mathbf{r}, \mathbf{r}') = g(\mathbf{r}', \mathbf{r}) \quad (49)$$

on a point-by-point basis (pg. 191 of Ref. [7]). However, as noted in section II, the system-average of this condition, even spin-decomposed, as in Eqs. (44) and (45), is obeyed by LSD.

We believe that much of the huge success of the LSD approximation may be attributed [26] to the fact that it obeys many of the exact relations known to be obeyed in non-uniform systems. It obeys these relations because the

LSD approximation to the hole given in Eq. (48) above represents the hole of a physical system, the spin-polarized uniform gas, and therefore obeys all exact universal relations as they apply to that system. For example, LSD satisfies all the system-averaged relations discussed in section II. Clearly, any improvement on LSD should at least satisfy these same conditions.

We note a very important point in density functional theory and the construction of approximate functionals. It is the hole itself which can be well-approximated by, e.g., a local approximation. This is because it is the hole which obeys the exact conditions we have been discussing. To illustrate this point, Fig. 2 is a plot of the pair distribution function around the origin in Hooke's atom, both exactly and within LSD. We see that the two functions are quite different. In

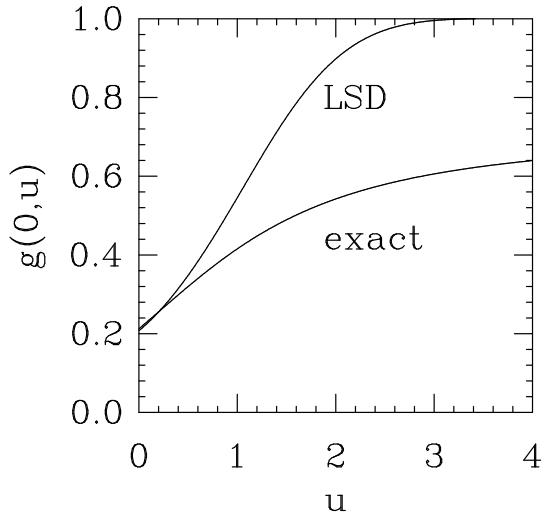


FIG. 2. Pair distribution function around an electron at the origin of Hooke's atom.

particular, the exact pair distribution function has not saturated even far from the center. The corresponding holes of Fig. 1, on the other hand, are much more similar.

This result illustrates a difficulty inherent in the weighted density approximation (WDA) [27, 28]. That approximation, extended to include both exchange and correlation, may be written, for the unpolarized case, as

$$n_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{u}) = n(\mathbf{r} + \mathbf{u}) [g^{\text{jell}}(\tilde{n}(\mathbf{r}); u) - 1] \quad (50)$$

where  $g^{\text{jell}}(n; u)$  is the unpolarized pair distribution function of jellium of density  $n$ , and  $\tilde{n}(\mathbf{r})$  is the weighted density, chosen to satisfy the spin sum of the integral conditions, Eqs. (27) and (28). The difficulty posed by Fig. 2 for this approximation is that it demonstrates that the exact pair distribution function is not similar to  $g^{\text{jell}}(n; u)$  for *any* value of  $n$ . Thus no prescription for the choice of  $\tilde{n}(\mathbf{r})$  is likely to produce a very realistic approximation. Furthermore, any

$\tilde{n}(\mathbf{r})$  significantly different from  $n(\mathbf{r})$  is apt to give a poor result for  $n_{xc}(\mathbf{r}, \mathbf{r})$ , as discussed further in section IV.

To be fair, there are several well-known exact conditions that LSD does *not* get right: unlike WDA, it is not self-interaction free [29],  $v_{xc, \sigma}^{LSD}(\mathbf{r})$  does not have the correct  $-1/r$  behavior at large  $r$  for finite systems [30], it does not contain the integer discontinuity [31–33], etc. These shortcomings may be overcome by other improvements [34], but not by the gradient corrections discussed in section V.

#### IV. IS LSD EXACT “LOCALLY”?

LSD treats the exchange-correlation hole around a point  $\mathbf{r}$ ,  $n_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{u})$ , as if the surrounding electronic distribution were uniform, as expressed by Eq. (48). The gradient expansion adds corrections to this based on the gradient of the density at the point  $\mathbf{r}$ . Clearly such a procedure will be worst for large values of  $u$ , where the density can be very different from that at  $\mathbf{r}$ , and work best for small values of  $u$ . Close inspection of Fig. 1 shows that indeed the LSD hole is either identical or very close to the exact hole as  $u \rightarrow 0$ . Furthermore, this is not an artifact of the fact that the  $\nabla n(\mathbf{r})$  vanishes at  $r = 0$  in Hooke's atom. Figure 3 shows that this is the case throughout the entire Hooke's atom with  $k = 1/4$ , which includes regions of large density gradients. We also show results for these quantities in the He

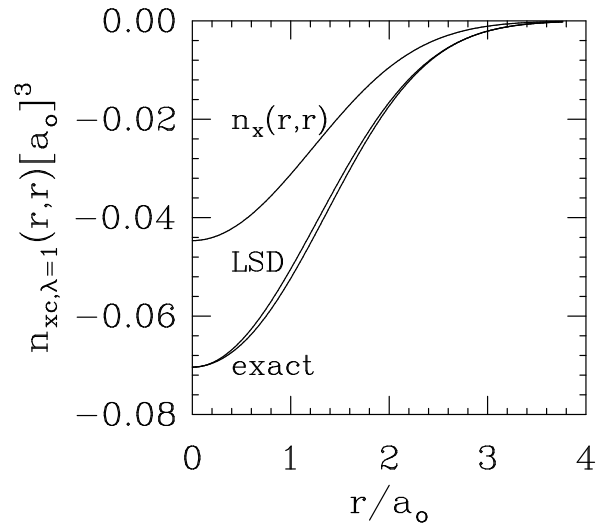


FIG. 3. Zero separation exchange and exchange-correlation holes at full coupling constant  $\lambda = 1$  throughout the  $k = 1/4$  Hooke's atom.

atom, from Slamet and Sahní [35], in Table I, which show a similar agreement, except near the origin, where the density itself has a cusp. In this section, we explore just how good LSD is for the system-averaged exchange-correlation hole as  $u \rightarrow 0$ , i.e., “locally”, in the neighborhood of the electron

TABLE I. Zero separation exchange-correlation hole density  $n_{xc}(\mathbf{r}, \mathbf{r})$  at the position  $\mathbf{r}$  of an electron in the He atom, at full coupling constant  $\lambda = 1$ , from the 39 parameter correlated wave function of Kinoshita.

$r$	$r_s(r)$	$n_x(r, r)$	$n_{xc}(r, r)$	$n_{xc}^{\text{LSD}}(r, r)$
0	0.404	-1.8104	-2.6035	-2.2319
0.2	0.525	-0.8263	-1.1682	-1.0600
0.5662	0.823	-0.2145	-0.3099	-0.3033
0.8	1.076	-0.0957	-0.1442	-0.1436
1.5	2.275	-0.0101	-0.0175	-0.0177

at  $u = 0$ . (Because the on-top hole density  $n_{xc}(\mathbf{r}, \mathbf{r})$  is not precisely known for the uniform electron gas, Fig. 3 by itself does not rule out the possibility that LSD is exact locally.)

Almost twenty years ago, this question was addressed from a different perspective in a series of papers by Langreth and Perdew [10,9,36–38]. In these papers, Langreth and Perdew studied the Fourier decomposition of the exchange-correlation hole, as given in Eq. (20). They gave two arguments in favor of what we call the short wavelength hypothesis, namely that LSD is exact for short wavelengths (i.e., large  $k$ ) for all inhomogeneous electronic systems. This idea has considerable intuitive appeal, as, by Fourier transforming back to real space, it implies that LSD is exact “locally” [11]. In fact, this hypothesis has since passed into the literature as one of the reasons for the success of LSD [7,8], and the LSD behavior for large wave vectors (or small interelectronic distances) has been incorporated in the LM, PW86, and PW91 GGA’s.

The first argument was based on the result of a second order (in  $e^2$ ) calculation of  $E_{xc}(\mathbf{k})$  for a spin-unpolarized surface. Langreth and Perdew found that, for large  $k$ ,  $E_{xc}^{(2)}(\mathbf{k})$  is explicitly a local functional of the density, where the superscript indicates the number of powers of  $e^2$  retained. Then, since the Coulomb interaction is  $4\pi e^2/k^2$  in momentum space, they argued that all higher powers would be vanishingly small for large  $k$ , and so the short wavelength hypothesis would be valid in general. Rasolt also proved the short wavelength hypothesis through second order in  $e^2$  for an electron gas in the presence of a small inhomogeneity, but asserted that higher order terms in  $e^2$  should also contribute in this limit, which might invalidate the hypothesis [39]. The second argument of Langreth and Perdew came from the density functional version of the random phase approximation [36,37]. Within that scheme, they found that for any spin-unpolarized system, the leading gradient corrections to  $E_{xc}^{\text{LSD}}(\mathbf{k})$  became vanishingly small as  $k \rightarrow \infty$ .

With David Langreth, we have recently studied this short wavelength hypothesis in considerable detail [11]. While the short wavelength hypothesis *is* correct for several limiting regimes and for certain approximate treatments of the inhomogeneous gas, the short wavelength hypothesis is *not* exact in general. A definitive counter-example is provided by the high-density limit of Hooke’s atom, where the spring

constant  $k \rightarrow \infty$ , and where

$$\langle \bar{n}_{xc}(u=0) \rangle = -\frac{1}{2N} \int d^3r n^2(\mathbf{r}) \left[ 1 + \frac{\alpha e^2}{2} r_s(\mathbf{r}) + O(e^4) \right], \quad (51)$$

with

$$r_s(\mathbf{r}) = [4\pi n(\mathbf{r})/3]^{-1/3}. \quad (52)$$

The exact value of  $\alpha$  is about 5% bigger than the precisely-known LSD value. (Of course, Hooke’s atom, with its large reduced density gradients and its lack of a continuous spectrum, represents a severe test for LSD.)

Even if the short wavelength hypothesis were correct, it would not provide a strong explanation for the success of LSD, because the  $k^{-6}$  tail of the exchange-correlation energy is a small part of the total. However, specific examples all suggest that the short wavelength hypothesis is approximately true numerically [11]. 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 approximations which revert to LSD for short wavelengths or small interelectronic separations. This justification might best proceed via an extension [40] of the real-space argument of Harris [41], who also used the fact that the LSD exchange hole is exact at zero separation to explain the success of LSD for exchange.

## V. GENERALIZED GRADIENT APPROXIMATIONS

An obvious way to improve on LSD is to allow the exchange-correlation energy per particle to depend not only on the (spin) density at the point  $\mathbf{r}$ , but also on the (spin) density gradients. This generalizes Eq. (47) to the form

$$E_{xc}^{\text{GGA}}[n_{\uparrow}, n_{\downarrow}] = \int d^3r f(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}), \nabla n_{\uparrow}, \nabla n_{\downarrow}) \quad (53)$$

where the function  $f$  is chosen by some set of criteria. Such approximations are called generalized gradient approximations (GGA’s) and a variety of different forms for the function  $f$  have been suggested and applied in the literature. In this section, we show that there is a well-defined nonempirical procedure for producing a (more or less) unique GGA, and higher order refinements.

A simple and appealing suggestion for improving on LSD was given by Kohn and Sham [6], and is called the gradient expansion approximation (GEA). Consider LSD as the first term in a Taylor series for  $E_{xc}[n_{\uparrow}, n_{\downarrow}]$  about the uniform density, and add in the next corrections. The first corrections to LSD are in principle straightforward to calculate, and the addition of these leading corrections to the exchange-correlation energy functional produces the GEA:

$$E_{xc}^{\text{GEA}}[n_{\uparrow}, n_{\downarrow}] = \int d^3r \left[ n(\mathbf{r}) \epsilon_{xc}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})) + \sum_{\sigma, \sigma'} C_{\sigma, \sigma'}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})) \frac{\nabla n_{\sigma}}{n_{\sigma}^{2/3}} \cdot \frac{\nabla n_{\sigma'}}{n_{\sigma'}^{2/3}} \right] \quad (54)$$

where the coefficients  $C_{\sigma, \sigma'}(n_{\uparrow}, n_{\downarrow})$ , which are slowly-varying functions of the density, have been calculated by Rasolt and collaborators [42,43]. Unfortunately, while the gradient correction is an improvement over LSD for slowly-varying systems, it typically worsens results on real electronic systems, which contain regions of rapidly varying density. We claim that a principal reason for this failure is the fact that the exchange-correlation hole associated with the GEA above is *not* the hole of *any* physical system, and so it disobeys many of the exact conditions discussed in the previous section. In particular, it violates [37,44] even the negativity constraint of Eq. (26), and the sum rules Eqs. (27-28).

To understand why this occurs, we must look at the nature of the gradient expansion more closely. The first principles density-gradient expansion of the system-averaged exchange-correlation hole,

$$\langle n_{xc}(\mathbf{u}) \rangle = \frac{1}{N} \int d^3r n(\mathbf{r}) n_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{u}), \quad (55)$$

is known [45,46] only to second order in  $\nabla$ , and constitutes an input into PW91. The exchange hole  $n_x(\mathbf{r}, \mathbf{r} + \mathbf{u})$  is known [47] to third order in  $\nabla$ . The non-interacting kinetic energy, constructed [48] from the Taylor expansion of  $n_x(\mathbf{r}, \mathbf{r} + \mathbf{u})$  to second order in  $\mathbf{u}$ , is known [49] to sixth order in  $\nabla$ . Based on this limited knowledge, the gradient expansion seems to have the following character [47]: In a system of slowly-varying electron density  $n(\mathbf{r})$ , the addition of each successive term of higher order in  $\nabla$  improves the description of the hole close to its electron (small  $u$ ), but worsens the description of the hole far away (large  $u$ ). In such a system, the kinetic energy has a rapidly-convergent gradient expansion. The exchange-correlation energy of Eq. (17) would also have a rapidly convergent gradient expansion *if* the electron-electron interaction were short ranged, but the Coulomb interaction,  $1/u$ , foils this expectation.

An example where the gradient expansion appears to converge because of the short range character of a functional is provided by the noninteracting kinetic energy  $T_s[n_{\uparrow}, n_{\downarrow}]$ , the first term on the right of Eq. (4). Because of the great importance and simplicity of this term, it is treated exactly in the Kohn-Sham scheme of section I. However, if one approximates this term by a semilocal functional, one finds that its GEA is its own GGA [50].

If we define a set of reduced density derivatives, such as

$$s = |\nabla n|/(2k_F n), \quad (56)$$

or

$$t = |\nabla n|/(2k_s n), \quad (57)$$

where  $k_s = (4k_F/\pi)^{1/2}$  is the Thomas screening length, or  $\nabla^2 n/[(2k_F)^2 n]$ , etc., we may imagine a system in which all such reduced derivatives are well bounded. A bulk solid is a realistic example of such a system, apart from the cusps in the electron density, which may be removed by pseudopotential theory. Even in such a system, we should not expect that the gradient expansion for  $E_{xc}$  converges as terms of higher order in  $\nabla$  are added, although we know it gives the right asymptotic expansion in the limit where all reduced density derivatives are small. However, in each order we may construct a *generalized* gradient expansion by cutting off the spurious large  $u$  contributions to  $n_{xc}$  in a way that respects Eqs. (26)-(28). We have no reason to doubt that *this* sequence will converge.

The construction of such a GGA has a long history, spanning much of the first thirty years of density functional theory. Early work going beyond the GEA was already initiated by Ma and Brueckner [51] in 1968, and was later further pursued by Langreth and co-workers [52,53]. The most popular functional to come out of this work is the Langreth-Mehl (LM) [52]. This functional was constructed from a wave vector analysis [37] of  $E_{xc}(\mathbf{k})$  within the random phase approximation (RPA). Essentially, the full GEA for exchange was retained, while the spurious small  $k$  contribution to the gradient term in the correlation energy was replaced by zero for  $k < f|\nabla n|/n$ , where the cutoff parameter  $f = 0.15$  was adjusted to provide an overall fit to the correlation energies of atoms and metal surfaces;  $f \approx 1/6$  had been expected on theoretical grounds. Thus LM uses a cutoff in wave vector space, as opposed to real space. Unfortunately, since this functional was constructed using RPA inputs, it does not even recover the uniform gas limit correctly. The Perdew 86 correlation energy functional [54] was constructed similarly, although using beyond-RPA inputs.

The PW86 exchange energy functional [55] may be considered as the construction for the second term in the cut-off expansion for exchange. One starts from the second-order gradient expansion for the exchange hole, then eliminates spurious large  $u$  contributions via sharp real-space cutoffs designed to restore the exact conditions, Eqs. (26-27). The result is a numerically defined GGA which is then fitted to an analytic form; this real-space cutoff procedure is free from semi-empirical parameters. A later modification of PW86 was based on the introduction of the Becke functional for exchange [56]. This functional was designed to recover the correct asymptotic behavior of the exchange energy density as  $r \rightarrow \infty$  in finite systems. It contained a single adjustable parameter, which was fitted to achieve minimum error for a large number of atoms. Both qualitatively and quantitatively, B88 and PW86 are very similar, although B88 does not reduce to the correct GEA for slowly-varying densities. The real-space cutoff of the gradient expansion for the exchange hole thus justifies Becke's exchange functional. The PW91 exchange functional makes some further refinements, ensuring the satisfaction of several more known exact conditions [12].



The PW91 correlation functional is the result of the real space cutoff procedure applied to the GEA correlation hole. Although the cutoff procedure is simpler for the correlation hole, as there is no equivalent of Eq. (26) for correlation, the GEA inputs are only approximately known, and more difficult to model. Once again, this produces a numerically defined functional, which was subsequently fit to the PW91 analytic form [45,46]. This functional satisfies several scaling conditions that it was not designed to satisfy, producing further evidence for the correctness of the real space cutoff procedure. Numerous tests [12] and formal considerations [57] suggest that PW91 represents the best systematic improvement on LSD currently available.

## VI. CONCLUSIONS AND PROSPECTS

We have shown how the decomposition of  $E_{xc}$  in a series of different ways (exchange and correlation, real space analysis, spin decomposition, undoing the coupling constant average) leads to further insight into the nature of approximate functionals and, ultimately, how to improve them. This process demonstrates how robust LSD is. It also highlights the failures of GEA, and, finally, shows how to cure those failures by a simple real space cutoff procedure. This produces a uniquely-defined nonempirical GGA, the PW91 functional.

This process also suggests where to look for improvements beyond PW91. We have seen how these local and semilocal approximations work best (but not perfectly) for the part of the hole close to the electron, and do worst far away. Their worst excesses at large distances are cured by the cutoff procedure, but probably the resulting functional is least accurate at large distances. This will be more important for parallel spins, whose net contribution to the energy is greater at these larger distances. The next step toward greater accuracy in density functional theory may well therefore come from the construction of "hybrid" functionals [58]: functionals which employ a local or semilocal approximation at small separations, but some more accurate form (e.g., the random phase approximation) at large distances.

We are currently pursuing several projects along these lines. He and Perdew [59] are improving the spin decomposition of the jellium hole, to include both the higher order cusps at zero separation exactly, and the recent Monte Carlo results. We are also writing an article with Wang [46] which shows the detailed construction of PW91 using the real space cutoff procedure, including the most up-to-date model for the exchange-correlation hole of the uniform electron gas, while with Taut [60], we are studying the Hooke's atom in further detail, and will calculate the system-averaged holes discussed in this paper exactly, in LSD, and using the GGA hole of PW91. In such a finite system, the exact exchange-correlation hole cannot be long-ranged, since it is cut off by the exponential decay of the

electron density into the vacuum in all three dimensions, so GGA is almost-always superior to LSD. But in large systems (bulk solids, surfaces), the exact hole can have a long-range tail. For example, the hole falls off like  $u^{-5}$  in the bulk of jellium, and like  $u^{-4}$  around an electron at the jellium surface. By missing this tail, GGA may underestimate the positive exchange-correlation contribution  $\sigma_{xc}$  to the surface energy. Since this tail can be calculated exactly, we are currently working on just such a "hybrid" [61], which should improve the GGA for this special case. The results of this work currently in progress should make clear where, in real space, the next improvements are needed.

## ACKNOWLEDGMENTS

We thank Virah Sahni for sending us the numbers in Table I prior to publication. This work has been supported by NSF grant No. DMR92-13755.

- 
- [1] Peter Fulde, *Electron Correlations in Molecules and Solids* (Springer-Verlag, Berlin, 1991).
  - [2] P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B 864 (1964).
  - [3] M. Levy, *Proc. Natl. Acad. Sci. (U.S.A.)* **76**, 6062 (1979).
  - [4] M. Levy, *Phys. Rev. A* **26**, 1200 (1982).
  - [5] E. H. Lieb, *Int. J. Quantum Chem.* **24**, 224 (1983).
  - [6] W. Kohn and L.J. Sham, *Phys. Rev.* **140**, A 1133 (1965).
  - [7] R.G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford, New York, 1989).
  - [8] R.M. Dreizler and E.K.U. Gross, *Density Functional Theory* (Springer-Verlag, Berlin, 1990).
  - [9] D.C. Langreth and J.P. Perdew, *Solid State Commun.* **17**, 1425 (1975).
  - [10] D.C. Langreth and J.P. Perdew, *Phys. Rev. B* **15**, 2884 (1977).
  - [11] K. Burke, J. P. Perdew, D. C. Langreth, *Phys. Rev. Lett.* **73**, 1283 (1994).
  - [12] K. Burke, J. P. Perdew, and M. Levy, in *Modern Density Functional Theory: A Tool for Chemistry*, edited by J. M. Seminario and P. Politzer (Elsevier, Amsterdam, 1995).
  - [13] J. C. Kimball, *Phys. Rev. A* **7**, 1648 (1973).
  - [14] E. R. Davidson, *Reduced Density Matrices in Quantum Chemistry* (Academic Press, New York, 1976).
  - [15] H. K. Schweng, H. M. Böhm, A. Schinner, and W. Macke, *Phys. Rev. B* **44**, 13291 (1991).
  - [16] K. Burke, J. C. Angulo, and J. P. Perdew, *Phys. Rev. A* **50**, 297 (1994).
  - [17] M. Levy and J.P. Perdew, *Phys. Rev. A* **32**, 2010 (1985).
  - [18] M. Levy and J. P. Perdew, *Phys. Rev. B* **48**, 11638 (1993).
  - [19] M. Levy, *Bull. Amer. Phys. Soc.* **39**, 671 (1994).

- [20] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
- [21] W. E. Pickett and J. Q. Broughton, Phys. Rev. B **48**, 14859 (1993).
- [22] S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).
- [23] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
- [24] J. P. Perdew and Y. Wang, Phys. Rev. B **46**, 12947 (1992).
- [25] O. Gunnarsson, M. Jonson, and B. I. Lundqvist, Phys. Rev. B **20**, 3136 (1979).
- [26] O. Gunnarsson and B.I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).
- [27] J. A. Alonso and L. A. Girifalco, Solid State Commun. **24**, 135 (1977).
- [28] O. Gunnarsson, M. Jonson, and B. I. Lundqvist, Solid State Commun. **24**, 765 (1977).
- [29] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
- [30] J. P. Perdew and M. Levy, in *Many-Body Phenomena at Surfaces*, eds. D. C. Langreth and H. Suhl (Academic, New York, 1984).
- [31] J.P. Perdew, R.G. Parr, M. Levy, and J.L. Balduz, Jr., Phys. Rev. Lett. **49**, 1691 (1982).
- [32] J. P. Perdew and M. Levy, Phys. Rev. Lett. **51**, 1884 (1983).
- [33] L. J. Sham and M. Schlüter, Phys. Rev. Lett. **51**, 1888 (1983).
- [34] J. B. Krieger, Y. Li, and G. J. Iafrate, in *Density Functional Theory*, eds. R. Dreizler and E. K. U. Gross, NATO ASI Series (Plenum, New York, 1994), to appear.
- [35] M. Slamet and V. Sahni, Bull. Am. Phys. Soc. **39**, 394 (1994).
- [36] D. C. Langreth and J. P. Perdew, Solid State Commun. **31**, 567 (1979).
- [37] D.C. Langreth and J.P. Perdew, Phys. Rev. B **21**, 5469 (1980).
- [38] D.C. Langreth and J.P. Perdew, Phys. Lett. A **92**, 451 (1982).
- [39] M. Rasolt, Phys. Rev. B **29**, 3703 (1984).
- [40] J. P. Perdew, A. Savin, and K. Burke, unpublished.
- [41] J. Harris, Phys. Rev. A **29**, 1648 (1984).
- [42] M. Rasolt and H.L. Davis, Phys. Lett. A **86**, 45 (1981).
- [43] M. Rasolt and D.J.W. Geldart, Phys. Rev. B **34**, 1325 (1986).
- [44] J.P. Perdew, Phys. Rev. Lett. **55**, 1665 (1985); **55**, 2370 (1985) (E).
- [45] J.P. Perdew, in *Electronic Structure of Solids '91*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991).
- [46] J. P. Perdew, K. Burke, and Y. Wang, unpublished.
- [47] Y. Wang, J. P. Perdew, J. A. Chevary, L. D. MacDonald, and S. H. Vosko, Phys. Rev. A **41**, 78 (1990).
- [48] A. D. Becke, Int. J. Quantum Chem. **23**, 1915 (1983).
- [49] D. R. Murphy, Phys. Rev. A **24**, 1682 (1981).
- [50] J.P. Perdew, Phys. Lett. A **165**, 79 (1992).
- [51] S.-K. Ma and K.A. Brueckner, Phys. Rev. **165**, 18 (1968).
- [52] D.C. Langreth and M.J. Mehl, Phys. Rev. B **28**, 1809 (1983).
- [53] C.D. Hu and D.C. Langreth, Phys. Scr. **32**, 391 (1985).
- [54] J.P. Perdew, Phys. Rev. B **33**, 8822 (1986); **34**, 7406 (1986) (E).
- [55] J.P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986); **40**, 3399 (1989) (E).
- [56] A.D. Becke, Phys. Rev. A **38**, 3098 (1988).
- [57] J. P. Perdew and K. Burke, in *Proceedings of the 8th International Congress of Quantum Chemistry, 19-24 June, 1994, Prague*, to appear in Int. J. Quantum Chem.
- [58] J.P. Perdew, Int. J. Quantum Chem. S **27**, 93 (1993).
- [59] J. He and J. P. Perdew, unpublished.
- [60] K. Burke, J. P. Perdew, and M. Taut, unpublished.
- [61] K. Burke and J.P. Perdew, unpublished.